Best Available Techniques (BAT) Reference Document for the

Refining of mineral oil and gas

Industrial Emissions Directive 2010/75/EU
(Integrated Pollution Prevention and Control)

Draft 2 (March 2012)
This document is one from the series of foreseen documents listed below (at the time of writing, not all documents have been drafted):

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Economics and Cross-media Effects

General Principles of Monitoring

Electronic versions of draft and finalised documents are publicly available and can be downloaded from http://eippcb.jrc.es
EXECUTIVE SUMMARY

The executive summary is no longer a part of the BREF document.
PREFACE

Note to TWG: New text from standard redaction

1. Status of this document


This document is a working draft of the European IPPC Bureau (of the Commission’s Joint Research Centre). It is not an official publication of the European Union and does not necessarily reflect the position of the European Commission.

It should be noted that the techniques listed and described in this BREF are neither prescriptive nor exhaustive.

2. Participants in the information exchange

As required in Article 13(3) of the Directive, the Commission has established a forum to assist the work, which is composed of representatives from Member States, the industries concerned and non-governmental organisations promoting environmental protection (Commission Decision of 16 May 2011 establishing a forum for the exchange of information pursuant to Article 13 of the Directive 2010/75/EU on industrial emissions (2011/C 146/03), OJ C 146, 17.05.2011, p. 3).

Forum members have nominated technical experts constituting the technical working group (TWG) that was the main source of information for drafting this document. The work of the TWG was led by the European IPPC Bureau (of the Commission’s Joint Research Centre).

3. Structure and contents of this document

Chapters 1 and 2 provide general information on the refining of mineral oil and gas and on the industrial processes and techniques used within this sector.

Chapter 3 provides data and information concerning the environmental performance of installations within the sector in terms of current emissions, consumption and nature of raw materials, water consumption, use of energy and the generation of waste reflecting the situation in installations in operation at the time of writing.

Chapter 4 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of operating installations in this sector that were considered in reaching the BAT conclusions. This information includes, where relevant, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques.

Chapter 5 presents the BAT conclusions as defined in Article 3(12) of the Directive.

Chapter 6 presents information on 'emerging techniques’ as defined in Article 3(14) of the Directive.

Concluding remarks and recommendations for future work are presented in chapter 7.

4. Information sources and the derivation of BAT

This document is based on information collected from a number of sources, in particular through the TWG that was established specifically for this task in order to participate in the
Preface

exchange of information under Article 13 of the Directive. The information has been collated and assessed by the European IPPC Bureau (of the Commission’s Joint Research Centre) who led the work on determining BAT, guided by the principles of technical expertise, transparency and neutrality. The work of the TWG and all other contributors is gratefully acknowledged.

The BAT conclusions have been established through an iterative process involving the following steps:

- identification of the key environmental issues for the sector;
- examination of the techniques most relevant to address these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these environmental performance levels were achieved, such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT) their associated emission levels (and other environmental performance levels) and the associated monitoring for this sector according to Article 3(10) of and Annex III to the Directive.

Expert judgement by the European IPPC Bureau and the TWG has played a key role in each of these steps and in the way in which the information is presented here.

Where available, economic data have been given together with the descriptions of the techniques presented in Chapter 4. These data give a rough indication of the magnitude of the costs and benefits. However, the actual costs and benefits of applying a technique may depend strongly on the specific situation of the installation concerned, which cannot be evaluated fully in this document. In the absence of data concerning costs, conclusions on the economic viability of techniques are drawn from observations on existing installations.

5. Review of BAT reference documents (BREFs)

BAT is a dynamic concept and so, the review of BREFs is a continuing process. For example, new measures and techniques may emerge, science and technologies are continuously developing and new or emerging processes are being successfully introduced into the industries. In order to reflect such changes and their consequences for BAT, this document will be periodically reviewed and, if necessary, updated accordingly.

6. Contact information

All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

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Reference Document on Best Available Techniques on the Refining of mineral oil and gas

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SCOPE

This BREF covers the following activities within the scope of Annex I of Directive 2010/75/EU: Energy industries 1.2. Refining of mineral oil and gas.

This document, together with other BREFs in the series, are intended to cover the activity described in point 1.2 described in Annex I to Directive 96/61/EC, namely refineries.

This document only addresses the refining industry from both sectors (mineral oil refineries and natural gas plants), and more especially the activities and processes set out in the following table.

The mineral oil and gas industry is organised into four broad sectors: the exploration and production of crude oil and natural gas; transportation; refining; and marketing and distribution.

This document addresses only the refining industry from both sectors (mineral oil refineries and natural gas plants), and more especially the activities and processes set out in the following table. As shown, this table also indicates, when appropriate, other BREF reference documents dealing with related issues.

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<th>Subactivities or processes included in each category of activity</th>
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<td>Base oil production</td>
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This document does not address the following activities:

- the exploration and production of crude oil and natural gas;
- the transportation of crude oil and natural gas;
- the marketing and distribution of products.

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<td>23</td>
<td>Elimination and valorisation of external wastes as secondary materials</td>
<td>Note to the TWG: New sections 2.23, 3.23 and 4.23 will be included depending on available information</td>
<td>WT BREF</td>
</tr>
<tr>
<td>24</td>
<td>Waste gas minimisation and treatment</td>
<td>In Chapter 2, the contents related to waste gas, waste water and solid waste are merged in Section 2.25</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Waste water treatment</td>
<td>Waste gas, waste water and solid waste are merged in Section 2.25</td>
<td>WT BREF</td>
</tr>
<tr>
<td>26</td>
<td>Waste water treatment</td>
<td>Waste treatment, waste disposal and maintenance</td>
<td>Waste gas and waste water CWW BREF</td>
</tr>
<tr>
<td>27</td>
<td>Waste management</td>
<td>Waste treatment, waste disposal and maintenance</td>
<td>WT BREF</td>
</tr>
<tr>
<td>28</td>
<td>Monitoring of emissions</td>
<td>This activity is only addressed in Chapter 3</td>
<td>Monitoring MON BREF</td>
</tr>
</tbody>
</table>

As can be seen in the above table, most of the processes and activities under analysis are specifically dedicated to mineral oil refineries. The only exception is Section 17, which deals with the processes that can be found in inland natural gas plants (name used in this document to identify this industrial sector). These plants also use some of the end-of-pipe techniques (in
Scope

Sections 25 to 27) used in mineral oil refineries and, for this reason, no distinction is made between the two types of industry.

As far as agrofuels (or biofuels are concerned, the present document covers their handling, storage and process in conventional refining units within the mineral oil refinery site, usually as a mixture with mineral products but it does not cover specific biological or biochemical processes used for their production.

Finally, the TWG has considered that soil remediation techniques are not included within this BREF. The reason given is that these techniques are not techniques to prevent nor to control emissions. They are techniques used to clean up the soil when it has already been contaminated.

Some processes or activities that may be present in refineries are not included or are only partially included in this document, because they are covered in other BREFs. Some examples are:

- The present document is designed to be as comprehensive as possible, taking into consideration the need to avoid duplication with other BREFs. It contains priority information specific to the refinery sector. This means, in particular, that:
  - generally applicable information on storage, cooling systems, energy efficiency, monitoring, waste water and waste gas treatments, or economics and cross media effects pertain to other relevant horizontal BREFs and may have not been developed or even covered in the present document;
  - generally applicable and specific information on particular processes or units covered by other vertical BREFs have not been covered, or may have been only partially covered in the present document, for example:
    - the steam cracker for the production of lower olefins, the production of aromatics (i.e. BTX), cyclohexane and cumene, or the alkylation of aromatics, that are already covered in the Large Volume Organic Chemicals (LVOC) BREF
    - the production of hydrogen by steam methane reforming, that is already covered by the Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers (LVIC-AFF) BREF. This BREF has been selected for including the generic information on this subject [IEF Strategy to review the Chemicals BREFs, March 2007]
    - the energy production techniques (i.e. boilers and furnaces) when commercial fuel oil, natural gas or gasoil are used when burning exclusively commercial fuels, that are already covered in the Large Combustion Plant (LCP) BREF [7, EC 2006].
Scope

Other BREFs reference documents which are of relevance for the sector covered in this document are the following:

<table>
<thead>
<tr>
<th>Reference document</th>
<th>Subject</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Waste Water and Waste Gas Treatment (CWW)</td>
<td>Waste water management and treatment techniques</td>
</tr>
<tr>
<td>Industrial Cooling Systems (ICS)</td>
<td>Cooling process</td>
</tr>
<tr>
<td>Economics and Cross-Media Effects (ECM)</td>
<td>Economics and cross-media effects of techniques</td>
</tr>
<tr>
<td>Emissions from Storage (EFS)</td>
<td>Storage, blending, loading and unloading of refinery materials</td>
</tr>
<tr>
<td>Energy Efficiency (ENE)</td>
<td>Energy efficiency and integrated refinery management</td>
</tr>
<tr>
<td>Large Combustion Plants (LCP)</td>
<td>Use of commercial fuels in refineries</td>
</tr>
<tr>
<td>Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (LVIC-AAF)</td>
<td>Steam reforming and hydrogen purification</td>
</tr>
<tr>
<td>Large Volume Organic Chemical Industry (LVOC)</td>
<td>Etherification process (MTBE, ETBE and TAME production)</td>
</tr>
<tr>
<td>General Principles of Monitoring (MON)</td>
<td>Emissions to air and water</td>
</tr>
<tr>
<td>Waste Incineration (WI)</td>
<td>Waste and waste water management</td>
</tr>
<tr>
<td>Waste Treatments Industries (WT)</td>
<td>Waste and waste water management</td>
</tr>
</tbody>
</table>

The scope of the BREF does not include matters that only concern safety in the workplace or the safety of products because these matters are not covered by the Directive. They are discussed only where they affect matters within the scope of the Directive.
Chapter 1

1 GENERAL INFORMATION

KOM conclusion 1.4:

- TWG to supply general info and data (in particular for new EU Member States)
- TWG to provide also background info through site questionnaires.

1.1 The purpose of refineries

The purpose of refining is to convert natural raw materials such as crude oil and natural gas into useful saleable products. Crude oil and natural gas are naturally occurring hydrocarbons found in many areas of the world in varying quantities and compositions. In refineries, they are transformed into different products as:

- fuels for cars, trucks, aeroplanes, ships and other forms of transport;
- combustion fuels for the generation of heat and power for industry and households;
- raw materials for the petrochemical and chemical industries;
- speciality products such as lubricating oils, paraffins/waxes and bitumen;
- energy as a by-product in the form of heat (steam) and power (electricity).

In order to manufacture these products, these raw materials are handled and processed in a number of different refining facilities, alone or as a mixture with biofuels. The combination of these processing units which convert crude oil and natural gas into products, including supporting units and facilities, is called a refinery. The market demand for the type of products, the available crude quality and certain requirements set by authorities influence the size, configuration and complexity of a refinery. As these factors vary from location to location no two refineries are identical.

1.2 Refinery sector in the EU

1.2.1 General

The economic and political worldwide refining industry has undergone considerable changes. The increased effort in oil and gas exploration and production as well as cost reductions achieved in these activities has resulted in at least a worldwide maintenance the stability of the total world recognised reserves worldwide.

In 2006, oil and gas provided respectively 42 % and 23 % of the European Union’s EU-27 final energy consumption. They represent the first and the second most important sources of energy in Europe. About 94 % of the fuels required for transport were originated from oil products, while natural gas represented 36 % of energy consumption for services and households, and 20 % of the energy used for power generation.

Despite the progressive increase of biofuels in the transport sector (increasing from less than 0.2 % prior to 2000 to 1.78 % in 2006 for EU-27), the health and viability of the refining industry remains of critical strategic importance to the Union EU for maintaining a successful and internationally competitive position for industry as a whole, and for providing competitively priced products to consumers [8, EUROSTAT 2008].
Chapter 1

1.2.1.1 Oil refining

In 2008, there were 662 refineries worldwide, with a total capacity of around 4 500 million t/year. The world's largest refining region is Asia (25 %) followed by North America and Europe (around 20 % each). The top refining countries in the world are the USA, followed by China, Russia and Japan.

The refining industry has suffered from a structural overcapacity for distillation most of the time since the oil crisis in 1973/1974. Only in the early 1980s, early 1990s and late 1990s were attractive margins achieved due to high oil prices at these times. Moreover, severe competition, environmental compliance of the refining industry and regulatory uncertainty have added to the decrease in profitability in certain periods. This long-lasting recession has led oil and gas companies to make significant adjustments in upstream and downstream operations such as cuts in production costs, innovations in technology and organisational restructuring. The ratio of refinery capacity to demand has declined from 113 % in 1990 to 103 % in 2004, despite chronic overcapacity in capacity due to demand accelerating at a faster rate. A respite from the economic crisis starting in 2008 has led to a decrease in demand on energy products.

However, cooperation in the form of partnerships, alliances, joint ventures or mergers between companies, governments and local communities, contractors and suppliers has led to significant cost reductions. This trend is also fuelled by increased environmental awareness in society, supported by the current process of harmonisation of legislation, particularly within Europe. Examples of new forms of co-operation are the recent (mid-1998) downstream merger between BP and Mobil, which started as a partnership in refining and marketing in 1996 and secured reportedly significant pre-tax cost savings. Recently Total-Fina Elf merger and an Esso-Mobil merger were concluded. A further recent example is the refining-capacity exchange between StatOil (Mongstad, Norway) and Shell (Sola/Pernis, Netherlands).

Some European oil refineries have closed in the last 20 years, followed by Ther has been a progressive increase of but crude oil processing capacity has increased since the 1990s recent years, mainly by capacity creep (de-bottlenecking, improvement in equipment reliability and longer cycles between turnarounds) to cope with the low but steady 1 – 2 % increase in product demand per year in Europe. Since 2005, there has been a stabilisation and even a slight decrease of the overall European demand. At the worldwide level, the capacity creep is estimated to be equivalent to six to ten additional world scale refineries going on stream every year.

Economic experts foresee low margins for future decades due to less possibility of capacity rationalization. As a general trend, investment has been shifted towards exploration and drilling. The crude oil refining industry is complex, with the following issues at stake in Europe:

The following refineries were recently removed or sold:

<table>
<thead>
<tr>
<th>Name</th>
<th>Location country</th>
<th>Crude b/cd</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2010)-Petrochina</td>
<td>Grangemouth, UK, EU</td>
<td>200 000</td>
<td>Sold</td>
</tr>
<tr>
<td>(2010)-Essar</td>
<td>Stanlow, UK, EU</td>
<td>240 000</td>
<td>Sold</td>
</tr>
<tr>
<td>(2011)-Total</td>
<td>Dunker, France, EU</td>
<td>137 000</td>
<td>Shut down</td>
</tr>
<tr>
<td>(2010)-Petroplus Intl.</td>
<td>Teesside England, UK</td>
<td>100 000</td>
<td>Shut down</td>
</tr>
<tr>
<td>(2010)-Shell Canada.</td>
<td>Montreal Canada-Quebec</td>
<td>121 000</td>
<td>Shut down</td>
</tr>
<tr>
<td>(2009)-Oil Co. Ltd.</td>
<td>Toyama Japan</td>
<td>57 000</td>
<td>Shut down</td>
</tr>
</tbody>
</table>

Source: [ 70. Oil & Gas 2010 ]
Within the context of a constant demand on transportation products for smaller environmental impact, the European Union is promoting biofuels, bioproducts and biorefinery investment to reduce EU dependency on fossil feedstocks and foreign raw materials.

### 1.2.1.2 Natural gas refining

In parallel to the consumption of petroleum products, the gross inland consumption of natural gas in EU-27 has progressively increased during the last decades, and reached a peak of around 446 Mtoe in 2005. Despite a slight decrease in 2006 and 2007, EU demand is still expected to grow rather significantly with a CAGR of around +1.8 % until at least 2020, mainly driven by thermoelectric requirements.

On the other hand, EU indigenous gas production has been stable over the last decade, but is now showing a clear decreasing trend starting in 2004. This production is expected to fall, notably in UK, Netherlands, Germany and Italy. Consequently, EU-27 dependence on gas importation could rise from a current level of 58 % in 2005 to approximately 81 % in 2025.

This context drives a significant number of projects for new infrastructures for importing, both for gaseous feedstock (new pipelines or pipeline connections to the existing network from Russia, the Caspian region, North Africa and the Middle East production fields) and for a number of new LNG terminals. According to some authors, 16 regasification plants devoted to imported liquefied natural gas (LNG) reception, storage and final process were in operation in 2008 in the EU, and five were under construction. Up to 35 new terminals are under consideration [10, Ruggeri 2008 ], [11, Van Putten 2008 ], [12, Basolas 2008 ] .

### 1.2.2 Feed stock

#### 1.2.2.1 Crude oil feed stock

After a period of steady production in Europe during the 1990s, a decreasing trend has been observed since 2002 and a shift towards lighter (North Sea) crudes specifically in the North of Europe. The world reserve of crude oil seems to guarantee the availability of raw materials for a reasonably long period (~40 years). Table 1.1 shows a summary of the world reserves and the consumption of crude oil per geographical area during the last decade.

<table>
<thead>
<tr>
<th>Reserves (Mt)</th>
<th>1990</th>
<th>2002</th>
<th>2005</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>2400</td>
<td>2800</td>
<td>3300</td>
<td>3400</td>
</tr>
<tr>
<td>North America</td>
<td>5300</td>
<td>8700</td>
<td>11500</td>
<td>12200</td>
</tr>
<tr>
<td>South and Central America</td>
<td>7700</td>
<td>11400</td>
<td>14600</td>
<td>16000</td>
</tr>
<tr>
<td>USSR (former)</td>
<td>8200</td>
<td>8700</td>
<td>9100</td>
<td>8900</td>
</tr>
<tr>
<td>China</td>
<td>3200</td>
<td>3400</td>
<td>3400</td>
<td>3400</td>
</tr>
<tr>
<td>Middle East</td>
<td>89300</td>
<td>92000</td>
<td>92400</td>
<td>92600</td>
</tr>
<tr>
<td>Africa</td>
<td>7800</td>
<td>10200</td>
<td>10700</td>
<td>11500</td>
</tr>
<tr>
<td>Other Regions</td>
<td>3000</td>
<td>2790</td>
<td>2400</td>
<td>2600</td>
</tr>
<tr>
<td>Total</td>
<td>136800</td>
<td>136670</td>
<td>140700</td>
<td>140800</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Consumption (Mt)</th>
<th>1990</th>
<th>2002</th>
<th>2005</th>
<th>2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe (perimeter)</td>
<td>217.5</td>
<td>256.6</td>
<td>328.1</td>
<td>755.2</td>
</tr>
<tr>
<td>North America</td>
<td>656.5</td>
<td>653.8</td>
<td>660.7</td>
<td>1047.1</td>
</tr>
<tr>
<td>South and Central America</td>
<td>229.8</td>
<td>257.0</td>
<td>313.9</td>
<td>218.8</td>
</tr>
<tr>
<td>USSR (former)</td>
<td>570.7</td>
<td>402.3</td>
<td>352.6</td>
<td>182.0</td>
</tr>
<tr>
<td>China</td>
<td>138.3</td>
<td>144.0</td>
<td>158.5</td>
<td>200.0</td>
</tr>
<tr>
<td>Middle East</td>
<td>861.9</td>
<td>945.8</td>
<td>983.3</td>
<td>215.0</td>
</tr>
<tr>
<td>Africa</td>
<td>320.7</td>
<td>332.2</td>
<td>359.6</td>
<td>115.6</td>
</tr>
<tr>
<td>Other Regions</td>
<td>184.7</td>
<td>190.8</td>
<td>204.9</td>
<td>728.7</td>
</tr>
<tr>
<td>Total</td>
<td>3180.1</td>
<td>3182.5</td>
<td>3361.6</td>
<td>3462.4</td>
</tr>
</tbody>
</table>

Table 1.1: Crude oil reserves and consumption per geographical region
Source: [247, UBA Austria, 1998], [246, BP AMOCO, 2001]
Table 1.1: Crude oil reserves and consumption per geographical region

<table>
<thead>
<tr>
<th>Region</th>
<th>Reserves (billion barrel)</th>
<th>1999</th>
<th>2008</th>
<th>2009</th>
<th>2009 share of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td></td>
<td>69.5</td>
<td>73.4</td>
<td>73.3</td>
<td>5.5</td>
</tr>
<tr>
<td>South and Central America</td>
<td></td>
<td>97.8</td>
<td>198.9</td>
<td>198.9</td>
<td>14.9</td>
</tr>
<tr>
<td>Europe and Eurasia</td>
<td></td>
<td>107.8</td>
<td>137.2</td>
<td>136.9</td>
<td>10.3</td>
</tr>
<tr>
<td>Middle East</td>
<td></td>
<td>685.8</td>
<td>753.7</td>
<td>754.2</td>
<td>56.6</td>
</tr>
<tr>
<td>Africa</td>
<td></td>
<td>84.7</td>
<td>127.5</td>
<td>127.7</td>
<td>9.6</td>
</tr>
<tr>
<td>Asia Pacific</td>
<td></td>
<td>39.9</td>
<td>41.7</td>
<td>42.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1085.6</td>
<td>1332.4</td>
<td>1333.1</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Region</th>
<th>Consumption (Mt)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td></td>
<td>23286</td>
<td>23795</td>
<td>22826</td>
<td>26.4</td>
</tr>
<tr>
<td>South and Central America</td>
<td></td>
<td>4905</td>
<td>5681</td>
<td>5653</td>
<td>6.6</td>
</tr>
<tr>
<td>Europe and Eurasia</td>
<td></td>
<td>19760</td>
<td>20193</td>
<td>19372</td>
<td>23.5</td>
</tr>
<tr>
<td>Middle East</td>
<td></td>
<td>4689</td>
<td>6864</td>
<td>7146</td>
<td>8.7</td>
</tr>
<tr>
<td>Africa</td>
<td></td>
<td>2490</td>
<td>3045</td>
<td>3082</td>
<td>3.7</td>
</tr>
<tr>
<td>Asia Pacific</td>
<td></td>
<td>20518</td>
<td>25662</td>
<td>25998</td>
<td>31.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>75648</td>
<td>85239</td>
<td>84077</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Source: [71, BP 2010]

KOM conclusion 2.2: TWG to supply prospective info and data at CONCAWE 'regional' level

The advent of North Sea crude oils and the continuous increase in the production of these light, low-sulphur crudes is mainly responsible for the lowering of the average sulphur content of the crude oils processed in European refineries. Since 1985 the average sulphur content has fluctuated by around 1.0 and to 1.1 %. However, the difference between type of crude processed in each European region should be noted, i.e. an average of 1.17 % S in the crude oils processed in the refineries of North West Europe, an average of 0.91 % S in the Atlantic region, 1.2 % S in the Mediterranean and 0.64 %S in the ‘Others’. The availability of the type of crude oil to refineries is not the same. Figure 1.1, shows the sulphur balance trend up to 2006. differences in average sulphur content of the crude feedstock processed in refineries in different regions/countries are stated.
Some local factors for these differences are the following:

- location close to oil fields where low-sulphur crudes are produced (freight for crude from the North Sea to Mediterranean costs up to USD 1/bbl, so low-sulphur crudes from the North Sea are rarely processed in the Mediterranean area.)
- refinery equipped with insufficient desulphurisation/upgrading capacity to process (heavy) high-sulphur crudes
- exclusion from markets where high-sulphur products can be sold (e.g. bitumen, bunker fuel)
- some other form of specialisation in the use of low-sulphur crudes (e.g. luboil production).

Any refinery that is not influenced by local factors such as those mentioned above will try to process high-sulphur crudes to the maximum extent, as their prices are considerably lower. (e.g. in September 1999 Platt’s quoted ‘Arab heavy’ with a sulphur content of 2.8% was USD 1.1/bbl cheaper than Arab Light with sulphur content of 1.8%). If the flexibility of refineries would be theoretically high, the product slate would be altered to suit market requirements irrespective of the crude type by the inclusion of conversion units. As consequence of that all refineries would continuously be running on the cheapest crude available, which probably would be very heavy and high-sulphur [253, MWV, 2000] [310, Swain, 2000].

### 1.2.2.2 Biofuels feedstock growth

Specific support policies worldwide aim to replace fossil fuel consumption with biofuels and stimulate biofuel production and expansion in domestic markets. They result in a fast growing production of these products (mainly bioethanol and biodiesel) which must be stored, handled, mixed up, and even progressively processed in conventional oil refineries together with petroleum products.

The following Figure 1.2 shows the quota (%) on blending versus the target set by the EU Directive on biofuel (2003/30/EC). Obviously this has led to an increase of the European consumption of these products for transport that are normally commercialized by the large oil companies.
Figure 1.2: Percentage of biofuel blend (Source: Biodiesel EurObserv’er)

Table 1.2: Biofuels consumption for transport by country (2009 - tonnes of oil equivalent)

<table>
<thead>
<tr>
<th>Country</th>
<th>Bioethanol</th>
<th>Biodiesel</th>
<th>Other</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>581.686</td>
<td>2,224,349</td>
<td>88.272</td>
<td>2,894,307</td>
</tr>
<tr>
<td>France</td>
<td>455.933</td>
<td>2,055,556</td>
<td></td>
<td>2,511,489</td>
</tr>
<tr>
<td>Italy</td>
<td>118,014</td>
<td>1,048,988</td>
<td></td>
<td>1,167,002</td>
</tr>
<tr>
<td>Spain</td>
<td>152,193</td>
<td>894,335</td>
<td>1,046,528</td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>159,000</td>
<td>822,872</td>
<td></td>
<td>981,872</td>
</tr>
<tr>
<td>Poland</td>
<td>136,043</td>
<td>568,997</td>
<td></td>
<td>705,040</td>
</tr>
<tr>
<td>Austria</td>
<td>64,249</td>
<td>424,901</td>
<td>13,369</td>
<td>502,519</td>
</tr>
<tr>
<td>Sweden</td>
<td>199,440</td>
<td>159,776</td>
<td>35,015</td>
<td>394,231</td>
</tr>
<tr>
<td>Netherlands</td>
<td>138,650</td>
<td>228,886</td>
<td></td>
<td>367,536</td>
</tr>
<tr>
<td>Belgium</td>
<td>37,577</td>
<td>221,252</td>
<td></td>
<td>258,829</td>
</tr>
<tr>
<td>Portugal</td>
<td>0</td>
<td>231,468</td>
<td></td>
<td>231,468</td>
</tr>
<tr>
<td>Romania</td>
<td>53,274</td>
<td>131,328</td>
<td></td>
<td>184,602</td>
</tr>
<tr>
<td>Hungary</td>
<td>64,488</td>
<td>119,303</td>
<td></td>
<td>183,791</td>
</tr>
<tr>
<td>Czeck Rep.</td>
<td>51,097</td>
<td>119,809</td>
<td></td>
<td>170,906</td>
</tr>
<tr>
<td>Finland</td>
<td>79,321</td>
<td>66,280</td>
<td></td>
<td>145,601</td>
</tr>
<tr>
<td>Ireland</td>
<td>19,733</td>
<td>54,261</td>
<td></td>
<td>73,994</td>
</tr>
<tr>
<td>Slovakia</td>
<td>6,820</td>
<td>55,041</td>
<td></td>
<td>61,861</td>
</tr>
<tr>
<td>Greece</td>
<td>0</td>
<td>57,442</td>
<td></td>
<td>57,442</td>
</tr>
<tr>
<td>Lithuania</td>
<td>14,091</td>
<td>37,770</td>
<td></td>
<td>51,861</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>740</td>
<td>39,915</td>
<td>498</td>
<td>41,153</td>
</tr>
<tr>
<td>Slovenia</td>
<td>1,859</td>
<td>27,993</td>
<td></td>
<td>29,852</td>
</tr>
<tr>
<td>Cyprus</td>
<td>0</td>
<td>15,024</td>
<td></td>
<td>15,024</td>
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<td>Bulgaria</td>
<td>0</td>
<td>6,186</td>
<td></td>
<td>6,186</td>
</tr>
<tr>
<td>Latvia</td>
<td>1,120</td>
<td>3,570</td>
<td></td>
<td>4,690</td>
</tr>
<tr>
<td>Denmark</td>
<td>3,913</td>
<td>243</td>
<td></td>
<td>4,156</td>
</tr>
<tr>
<td>Malta</td>
<td>0</td>
<td>583</td>
<td></td>
<td>583</td>
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<tr>
<td>Estonia</td>
<td>NA</td>
<td>NA</td>
<td></td>
<td>NA</td>
</tr>
<tr>
<td>TOTAL EU 27</td>
<td>2,339,241</td>
<td>9,616,128</td>
<td>137,154</td>
<td>12,092,523</td>
</tr>
</tbody>
</table>

Source: EurObserv’er
Bioethanol

Worldwide, USA and Brazil dominate the bioethanol production as observed in Figure 1.3. Worldwide production amounted to 22 Mtoe in 2006, with almost half of it was produced in USA from corn crops growth in the Midwest representing 2% - 3% of the countries fuel.

![World bioethanol fuel production](image)

The development of ethanol imports to the EU is illustrated below in figure XXX, with increasing shares especially from Brazil and Latin America, Asia and Africa from 2003 onwards. The total volume of trade grew almost 6 times from 120,000 m³ (0.1 Mtoe) in 2001 to 660,000 m³ (0.33 Mtoe) in 2005.

Biodiesel

Biodiesel remains a small fraction of the fuel used worldwide but, as seen on Figure 1.4, has experienced strong growth rates in the last years, especially in Europe where biodiesel (mainly from rapeseed and sunflower oil) accounts for 75% of the total EU biofuel production. In 2006 the European Union produced 4.7 Mt (3.2 Mtoe) experiencing a 66% growth compared to 2005. In 2007 this capacity grew more than double to 11 Mt (7.5 Mtoe) in Europe. Germany is the world’s leading biodiesel producer, making 40% of the world total in recent years, followed by France and Italy.
Chapter 1

According to the European Biodiesel Board, Europe is the largest biodiesel market in the world at the time of writing (2009). In 2007, Europe consumed over 7.5 Mm³ (5.15 Mtoe) of biodiesel. In December 2007, biodiesel imports to Europe had reached 0.8 Mt (0.6 Mtoe), which corresponds to a 500 % increase from 2006. Over 50 % of feedstock imports to Europe in 2007 came from Russia and Ukraine with 0.4 Mt (0.27 Mtoe).

1.2.2.3 Natural gas feedstock

In 2005, proven world gas reserves were equal to 60 years of gas production at current rates. Since 2005, the proven reserves increased faster than gas consumption and estimated reserves could represent the equivalent of another 200 years of consumption.

The highest percentage of gas supplied in the EU-27 comes from indigenous production, covering 37 % of total net supplies (432 Mtoe) in 2007. The main external sources are Russia (24 %), Norway (19 %), and Algeria (10 %). The decrease in the EU-27 indigenous production over the period is mainly compensated for by the growing imports from Norway.

LNG represented YY % in 200X of European gas importations. This figure is expected to reach ZZ % in 2020. This increasing trend is encouraged by a growing spot market as a consequence of Europe’s newly opened single market in gas.
Table 1.3: Natural gas proven reserves

<table>
<thead>
<tr>
<th></th>
<th>At end 1989</th>
<th>At end 1999</th>
<th>At end 2008</th>
<th>At end 2009</th>
<th>Share of total</th>
<th>R/P(*) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trillion cubic metres</td>
<td>Trillion cubic metres</td>
<td>Trillion cubic metres</td>
<td>Trillion cubic metres</td>
<td></td>
<td></td>
</tr>
<tr>
<td>US</td>
<td>4.73</td>
<td>4.74</td>
<td>6.93</td>
<td>6.93</td>
<td>0.037</td>
<td>11.7</td>
</tr>
<tr>
<td>Canada</td>
<td>2.73</td>
<td>1.72</td>
<td>1.75</td>
<td>1.75</td>
<td>0.009</td>
<td>10.9</td>
</tr>
<tr>
<td>Mexico</td>
<td>2.06</td>
<td>0.86</td>
<td>0.5</td>
<td>0.48</td>
<td>0.003</td>
<td>8.2</td>
</tr>
<tr>
<td>Total North America</td>
<td>9.52</td>
<td>7.32</td>
<td>9.18</td>
<td>9.16</td>
<td>0.049</td>
<td>11.3</td>
</tr>
<tr>
<td>Total S. and Cent. America</td>
<td>4.8</td>
<td>6.81</td>
<td>7.32</td>
<td>8.06</td>
<td>0.043</td>
<td>53.2</td>
</tr>
<tr>
<td>Azerbaijan</td>
<td>n/a</td>
<td>1.23</td>
<td>1.31</td>
<td>1.31</td>
<td>0.007</td>
<td>88.8</td>
</tr>
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<td>Denmark</td>
<td>0.11</td>
<td>0.14</td>
<td>0.06</td>
<td>0.06</td>
<td>0.005</td>
<td>7.6</td>
</tr>
<tr>
<td>Germany</td>
<td>0.29</td>
<td>0.23</td>
<td>0.1</td>
<td>0.08</td>
<td>0.003</td>
<td>6.4</td>
</tr>
<tr>
<td>Italy</td>
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<td>0.19</td>
<td>0.06</td>
<td>0.06</td>
<td>0.005</td>
<td>8.6</td>
</tr>
<tr>
<td>Kazakhstan</td>
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<td>1.78</td>
<td>1.82</td>
<td>1.82</td>
<td>0.01</td>
<td>56.6</td>
</tr>
<tr>
<td>Netherlands</td>
<td>1.57</td>
<td>1.55</td>
<td>1.14</td>
<td>1.09</td>
<td>0.006</td>
<td>17.3</td>
</tr>
<tr>
<td>Norway</td>
<td>1.73</td>
<td>1.25</td>
<td>2.22</td>
<td>2.05</td>
<td>0.011</td>
<td>19.8</td>
</tr>
<tr>
<td>Poland</td>
<td>0.16</td>
<td>0.15</td>
<td>0.11</td>
<td>0.11</td>
<td>0.001</td>
<td>26.6</td>
</tr>
<tr>
<td>Romania</td>
<td>0.13</td>
<td>0.35</td>
<td>0.63</td>
<td>0.63</td>
<td>0.003</td>
<td>57.9</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>n/a</td>
<td>42.44</td>
<td>43.3</td>
<td>44.38</td>
<td>0.237</td>
<td>84.1</td>
</tr>
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<td>Turkmenistan</td>
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<td>2.59</td>
<td>8.1</td>
<td>8.1</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td>Ukraine</td>
<td>n/a</td>
<td>1.01</td>
<td>0.98</td>
<td>0.98</td>
<td>0.005</td>
<td>51</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>0.56</td>
<td>1.27</td>
<td>0.29</td>
<td>0.29</td>
<td>0.002</td>
<td>4.9</td>
</tr>
<tr>
<td>Uzbekistan</td>
<td>n/a</td>
<td>1.58</td>
<td>1.68</td>
<td>1.68</td>
<td>0.009</td>
<td>26.1</td>
</tr>
<tr>
<td>Other Europe and Eurasia</td>
<td>47.41</td>
<td>0.43</td>
<td>0.45</td>
<td>0.44</td>
<td>0.002</td>
<td>46.6</td>
</tr>
<tr>
<td>Total Europe and Eurasia</td>
<td>52.28</td>
<td>56.17</td>
<td>62.26</td>
<td>63.09</td>
<td>0.337</td>
<td>64.8</td>
</tr>
<tr>
<td>Total Middle East</td>
<td>37.83</td>
<td>54.74</td>
<td>75.82</td>
<td>76.18</td>
<td>0.406</td>
<td></td>
</tr>
<tr>
<td>Total Africa</td>
<td>8.48</td>
<td>11.44</td>
<td>14.71</td>
<td>14.76</td>
<td>0.079</td>
<td>72.4</td>
</tr>
<tr>
<td>Total Asia Pacific</td>
<td>9.5</td>
<td>12.07</td>
<td>16</td>
<td>16.24</td>
<td>0.087</td>
<td>37</td>
</tr>
<tr>
<td><strong>Total World</strong></td>
<td>122.4</td>
<td>148.55</td>
<td>185.28</td>
<td>187.49</td>
<td>1</td>
<td>62.8</td>
</tr>
</tbody>
</table>

(*) Reserves-to-production (R/P) ratio - If the reserves remaining at the end of any year are divided by the production in that year, the result is the length of time that these remaining reserves would last if production were to continue at that rate

(**) >100 years

Source: BP Statistical review of world energy - 2010
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1.2.3 Europe refining capacity

1.2.3.1 European oil refining capacity

European refineries are characterised by an excess in primary processing capacity, and by some 'misfits' (incompatibility between production and market demand) and excess in conversion capacity. European downstream sectors show too many refineries producing too much gasoline. Table 1.6 shows, per type of process, the charge and production capacity of European oil refineries for European Union (EU-27) and for EU+ Countries, which will correspond hereafter in this document to EU-27 enlarged by associated and official candidate Countries: Croatia, Macedonia, Norway, Switzerland and Turkey. Switzerland and Norway (hereafter called EU+ or European). The table also reflects capacities per type of process.

The crude oil capacity in 1999 of the 116 plants operating in the EU-27 at the beginning of 2008 was a little below 1 billion tonnes per year, which was roughly equivalent to the USA capacity and corresponded to 20 % of the entire world capacity, with Italy and Germany having the greatest capacity. The average individual capacity of European sites was about 8.6 Mm³/yr, a little higher than in other parts of the world. As a comparison, at the same time, the refining crude oil capacity of the 130 plants operated in USA was also reaching around 1 billion m³/yr, leading to a slightly lower individual average capacity of 7.8 Mm³/yr. At the world level, 647 plants were under operation at the beginning of 2008, with an average individual capacity of 7.7 Mm³/yr for an overall crude capacity reaching approximately 5 billion Mm³/yr.

Refining distillation capacity decreased substantially in the early 1980s following the oil price shocks of the 1970s. At the same time, the industry had to invest heavily in conversion capacity to convert fuel oil and adapt to demand for lighter transport fuels. Official figures for nameplate capacity show small further capacity reductions until the end of 1995. Combined with a slow rise in demand since 1986 this has increased apparent distillation capacity utilisation from a low point of 60 % in 1981 to an average above 90 % in 1997, higher in northern Europe and lower in southern Europe.

There are differences in supply and demand balances between different countries, with Germany and Spain in particular having a large supply deficit. The growth of oil products demand in Iberia has been well above the average for the EU, particularly in transport fuels. However, oil demand growth in the 1990s showed the Mediterranean region to be in line with the rest of Europe.

Even in the most favourable scenario, European refining capacity will almost certainly exceed demand for at least the next decade. International trading opportunities will only have a limited impact on Europe's overcapacity. There is a refining capacity surplus of 70—100 million tonnes per year (equivalent to 9 to 13 refineries) in the EU.

For the future, according to the Commission [72, EC 2010] and based on specific modelling, the investments required to upgrade EU+3 (including Switzerland, Norway and Turkey) refining capacities could reach EUR 17.8 billion (including 3.3 for international maritime organization (IMO) changes) between 2005 and 2030. These amounts would be mainly dedicated to extra gasoil hydrodesulphurisation units.
Figure 1.5: Global oil refining capacities

1.2.3.2 European natural gas refining capacity

Note for TWG: See section 1.3.2 for the number of gas refineries identified.

There has been a mild decline in the European gas refining output. The following tables give some background information on the worldwide production and consumption of gas (1999-2009).

Table 1.4: Worldwide gas production (Source: BP Statistical review of world energy - 2010)

<table>
<thead>
<tr>
<th>Production expressed as million of tonnes oil equivalent (Mtoe)</th>
<th>1999</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009 variation</th>
<th>2009 share of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total North America</td>
<td>679.9</td>
<td>695.3</td>
<td>713.9</td>
<td>729.7</td>
<td>739.4</td>
<td>1.6 %</td>
</tr>
<tr>
<td>Total S. and Cent. America</td>
<td>82.8</td>
<td>136.0</td>
<td>139.6</td>
<td>141.4</td>
<td>136.4</td>
<td>-3.2 %</td>
</tr>
<tr>
<td>Azerbaijan</td>
<td>4.9</td>
<td>5.5</td>
<td>8.8</td>
<td>13.3</td>
<td>13.3</td>
<td>0.2 %</td>
</tr>
<tr>
<td>Denmark</td>
<td>7.0</td>
<td>9.4</td>
<td>8.3</td>
<td>9.1</td>
<td>7.6</td>
<td>-16.3 %</td>
</tr>
<tr>
<td>Germany</td>
<td>16.1</td>
<td>14.1</td>
<td>12.9</td>
<td>11.7</td>
<td>11.0</td>
<td>-6.3 %</td>
</tr>
<tr>
<td>Italy</td>
<td>14.4</td>
<td>9.1</td>
<td>8.0</td>
<td>7.6</td>
<td>6.7</td>
<td>-12.0 %</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>8.1</td>
<td>21.5</td>
<td>24.1</td>
<td>26.8</td>
<td>29.0</td>
<td>8.6 %</td>
</tr>
<tr>
<td>Netherlands</td>
<td>54.2</td>
<td>55.4</td>
<td>54.5</td>
<td>60.0</td>
<td>56.4</td>
<td>-5.6 %</td>
</tr>
<tr>
<td>Norway</td>
<td>43.6</td>
<td>78.9</td>
<td>80.7</td>
<td>89.3</td>
<td>93.1</td>
<td>4.5 %</td>
</tr>
<tr>
<td>Poland</td>
<td>3.1</td>
<td>3.9</td>
<td>3.9</td>
<td>3.7</td>
<td>3.7</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Romania</td>
<td>12.6</td>
<td>10.7</td>
<td>10.4</td>
<td>10.2</td>
<td>9.8</td>
<td>-4.2 %</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>482.2</td>
<td>535.6</td>
<td>532.8</td>
<td>541.5</td>
<td>474.8</td>
<td>-12.1 %</td>
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<td>Turkmenistan</td>
<td>18.6</td>
<td>54.3</td>
<td>58.9</td>
<td>59.5</td>
<td>32.7</td>
<td>-44.8 %</td>
</tr>
<tr>
<td>Ukraine</td>
<td>14.8</td>
<td>16.9</td>
<td>16.9</td>
<td>17.1</td>
<td>17.3</td>
<td>1.7 %</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>89.2</td>
<td>72.0</td>
<td>64.9</td>
<td>62.7</td>
<td>53.7</td>
<td>-14.1 %</td>
</tr>
<tr>
<td>Uzbekistan</td>
<td>45.3</td>
<td>49.0</td>
<td>53.2</td>
<td>56.0</td>
<td>58.0</td>
<td>3.9 %</td>
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<td>Other Europe and Eurasia</td>
<td>10.3</td>
<td>10.3</td>
<td>9.7</td>
<td>9.2</td>
<td>8.6</td>
<td>-6.8 %</td>
</tr>
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<td>Total Europe and Eurasia</td>
<td>824.2</td>
<td>946.5</td>
<td>947.9</td>
<td>977.7</td>
<td>875.7</td>
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<td>Total Middle East</td>
<td>175.5</td>
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<td>345.0</td>
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<td>6.5 %</td>
</tr>
<tr>
<td>Total Africa</td>
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<td>192.8</td>
<td>183.5</td>
<td>-4.6 %</td>
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<tr>
<td>Total Asia Pacific</td>
<td>236.3</td>
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<td>2667.8</td>
<td>2762.7</td>
<td>2696.0</td>
<td>-2.1 %</td>
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</table>
Chapter 1

Table 1.5: Worldwide gas consumption (Source: BP Statistical review of world energy - 2010)

<table>
<thead>
<tr>
<th>Consumption expressed as billion cubic metres</th>
<th>1999</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009 variation</th>
<th>2009 share %</th>
<th>% of total</th>
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</thead>
<tbody>
<tr>
<td>Total North America</td>
<td>759.2</td>
<td>771.9</td>
<td>813.9</td>
<td>822.0</td>
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<td>-1.2 %</td>
<td>27.8 %</td>
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<tr>
<td>Total S. and Cent. America</td>
<td>89.5</td>
<td>135.3</td>
<td>138.1</td>
<td>141.0</td>
<td>134.7</td>
<td>-4.2 %</td>
<td>4.6 %</td>
</tr>
<tr>
<td>Austria</td>
<td>8.5</td>
<td>9.4</td>
<td>8.9</td>
<td>9.5</td>
<td>9.3</td>
<td>-2.1 %</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Azerbaijan</td>
<td>5.4</td>
<td>9.1</td>
<td>8.0</td>
<td>9.2</td>
<td>7.7</td>
<td>-16.0 %</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Belarus</td>
<td>14.8</td>
<td>19.0</td>
<td>18.8</td>
<td>19.2</td>
<td>16.1</td>
<td>-16.0 %</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Belgium and Luxembourg</td>
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<td>17.0</td>
<td>16.9</td>
<td>17.0</td>
<td>17.3</td>
<td>2.1 %</td>
<td>0.6 %</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>3.0</td>
<td>3.2</td>
<td>3.3</td>
<td>3.3</td>
<td>2.5</td>
<td>-25.1 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>8.6</td>
<td>9.3</td>
<td>8.7</td>
<td>8.7</td>
<td>8.2</td>
<td>-5.6 %</td>
<td>0.3 %</td>
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<td>5.1</td>
<td>4.6</td>
<td>4.6</td>
<td>4.4</td>
<td>-3.6 %</td>
<td>0.1 %</td>
</tr>
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<td>Finland</td>
<td>3.7</td>
<td>4.2</td>
<td>3.9</td>
<td>4.0</td>
<td>3.6</td>
<td>-10.5 %</td>
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<td>37.9</td>
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<td>87.2</td>
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<td>81.2</td>
<td>78.0</td>
<td>-3.7 %</td>
<td>2.6 %</td>
</tr>
<tr>
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<td>3.2</td>
<td>4.0</td>
<td>4.2</td>
<td>3.4</td>
<td>-19.7 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Hungary</td>
<td>11.0</td>
<td>12.7</td>
<td>11.9</td>
<td>11.8</td>
<td>10.1</td>
<td>-14.3 %</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Iceland</td>
<td>-</td>
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1.2.4 Economics

Low refinery margins and low return on investment stimulate refiners either to look at other products such as electricity, hydrogen and petrochemicals with higher margins or to shut down (e.g. Sola in Norway).

Political: the political pressures and the economic recession in some regions of the world will have a significant bearing on European economies and the pace at which upgrading of refineries or even new refinery projects will be undertaken world-wide.
## Table 1.6: EU+ capacity for mineral oil refining

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<tr>
<th>Country</th>
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<th>Coking</th>
<th>Thermal operations</th>
<th>Catalytic cracking</th>
<th>Catalytic reforming</th>
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Source: [9, Koottungal 2008, reviewed by TWG 2010]
### Production capacity in Mm³/yr (except units mentioned specifically)

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<th>Aromatics</th>
<th>Isomerisation</th>
<th>Base oil production</th>
<th>Etherification</th>
<th>Hydrogen (MNm³/d)</th>
<th>Coke (t/d)</th>
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<td>0.23</td>
<td>0.30</td>
<td>3.34</td>
<td>420</td>
<td>0.33</td>
<td>0.46</td>
<td>0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>Italy</td>
<td>2.28</td>
<td>0.06</td>
<td>0.78</td>
<td>1.62</td>
<td>0.68</td>
<td>8.28</td>
<td>2046</td>
<td>1783</td>
<td>0.91</td>
<td>0.44</td>
</tr>
<tr>
<td>Lithuania</td>
<td>0.42</td>
<td>0.51</td>
<td>3.97</td>
<td>0.67</td>
<td>9.47</td>
<td>1642</td>
<td>120</td>
<td>0.96</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>Netherlands</td>
<td>0.20</td>
<td>0.60</td>
<td>1.35</td>
<td>1.03</td>
<td>4.73</td>
<td>560</td>
<td>1.94</td>
<td>0.33</td>
<td>0.15</td>
<td>0.44</td>
</tr>
<tr>
<td>Portugal</td>
<td>0.31</td>
<td>1.00</td>
<td>1.49</td>
<td>0.22</td>
<td>2.42</td>
<td>252</td>
<td>252</td>
<td>0.33</td>
<td>0.15</td>
<td>0.44</td>
</tr>
<tr>
<td>Romania</td>
<td>0.13</td>
<td>0.60</td>
<td>0.45</td>
<td>0.22</td>
<td>0.60</td>
<td>0.51</td>
<td>2555</td>
<td>4.67</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>Slovakia</td>
<td>0.26</td>
<td>0.54</td>
<td>0.35</td>
<td>0.12</td>
<td>2.54</td>
<td>270</td>
<td>0.15</td>
<td>0.44</td>
<td>0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>Slovenia</td>
<td>0.10</td>
<td>1.5</td>
<td>2.20</td>
<td>1.66</td>
<td>9.66</td>
<td>2390</td>
<td>1712</td>
<td>1.54</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>Spain</td>
<td>0.20</td>
<td>0.20</td>
<td>0.56</td>
<td>0.56</td>
<td>9.66</td>
<td>2390</td>
<td>1712</td>
<td>1.54</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>Sweden</td>
<td>5.35</td>
<td>0.79</td>
<td>6.99</td>
<td>1.39</td>
<td>4.31</td>
<td>79.98</td>
<td>13 899</td>
<td>24.30</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>UK</td>
<td>15.2</td>
<td>2.76</td>
<td>15.55</td>
<td>36.29</td>
<td>9.96</td>
<td>43.1</td>
<td>79.98</td>
<td>24.30</td>
<td>0.33</td>
<td>0.44</td>
</tr>
<tr>
<td>EU-27</td>
<td>13.5 %</td>
<td>22 %</td>
<td>20 %</td>
<td>36 %</td>
<td>22 %</td>
<td>40 %</td>
<td>21 %</td>
<td>7 %</td>
<td>19 %</td>
<td>20 %</td>
</tr>
<tr>
<td>Croatia</td>
<td>0.55</td>
<td>0.32</td>
<td>0.03</td>
<td>0.03</td>
<td>200</td>
<td>123</td>
<td>0.33</td>
<td>0.33</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Macedonia</td>
<td>0.25</td>
<td>0.22</td>
<td>0.22</td>
<td>0.02</td>
<td>610</td>
<td>23</td>
<td>0.33</td>
<td>0.33</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Norway</td>
<td>0.64</td>
<td>0.22</td>
<td>0.22</td>
<td>0.02</td>
<td>610</td>
<td>23</td>
<td>0.33</td>
<td>0.33</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Switzerland</td>
<td>0.22</td>
<td>0.58</td>
<td>0.38</td>
<td>0.79</td>
<td>0.3</td>
<td>0.33</td>
<td>0.15</td>
<td>0.33</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>Turkey</td>
<td>0.82</td>
<td>0.34</td>
<td>0.34</td>
<td>0.79</td>
<td>0.3</td>
<td>0.33</td>
<td>0.15</td>
<td>0.33</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>EU+</td>
<td>15.2</td>
<td>3.62</td>
<td>16.1</td>
<td>38.5</td>
<td>10.33</td>
<td>4.31</td>
<td>86.93</td>
<td>25.78</td>
<td>0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>% World capacity</td>
<td>13.5 %</td>
<td>29 %</td>
<td>21 %</td>
<td>38 %</td>
<td>23 %</td>
<td>40 %</td>
<td>23 %</td>
<td>7.5 %</td>
<td>20 %</td>
<td>22 %</td>
</tr>
</tbody>
</table>

Notes for Table 1.6 (first part):
- Vacuum distillation has been included in primary distillation sections in this document.
- Thermal operations include visbreaking (within this document) and thermal cracking (within LVOC BREF).
- Catalytic hydrocracking, hydrorefining and hydrotreatment are included in hydrogen-consuming processes.
- Catalytic hydrotreatment: Includes processes where 10% of the feed or less is reduced in molecular size. It includes desulphurisation of atmospheric residues and heavy fuel gas oil, catalytic cracker treatments and mid - distillates.
- Catalytic hydro treating: No reduction in molecular size of feed occurs. It includes pretreatment of catalytic reformer feed, naphtha desulphurisation, naphtha olefin/aromatic saturation, straight-run distillate, pretreating catalytic cracker feed, pretreatments of other distillates and polish of base oils.

Notes for Table 1.6 (second part):
- Aromatic production is included in the LVOC BREF, although some refineries have it.
1.2.5 Product market

1.2.5.1 Petroleum products

KOM conclusion 1.4: Outline for updating Chap.1 foresees EUROPIA/CONCAWE to supply necessary information.

The European market is characterised by a growing demand for petrochemicals, kerosene and diesel, a stable demand for gasoline, a declining demand for gasoline, light heating oil and heavy fuel oil. Competition is expected from refineries in the Russian Federation and the Middle East. There is ongoing competition because of the increasing capacity in the Middle East and Asia.

In the particular case of automotive fuels, and despite the progressive technical adaptation of European sites which lead them to produce (on average) more middle distillates than in every other region in the world except Asia (as seen in Table 1.7), EU refineries are still not producing the mix demanded by EU consumers due to their technical design. They cannot satisfy the existing demand for diesel and they continue to produce gasoline in excess. Due to favourable taxation, the share of diesel fleet has risen from 23 % in 1996 to 53 % in 2006, and is expected to increase by 60 – 65 % over the next decade.

Table 1.7: Product group consumption per region

<table>
<thead>
<tr>
<th>Product consumption</th>
<th>Light distillates</th>
<th>Middle distillates</th>
<th>Fuel oil</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>9998 10803</td>
<td>6628 6332</td>
<td>1415 814</td>
<td>5245 4877</td>
</tr>
<tr>
<td>Total US</td>
<td>8716 9221</td>
<td>5700 5281</td>
<td>814 518</td>
<td>4290 3666</td>
</tr>
<tr>
<td>S. and Cent. America</td>
<td>1650 1812</td>
<td>1625 2011</td>
<td>715 791</td>
<td>915 1040</td>
</tr>
<tr>
<td>Europe</td>
<td>4386 3328</td>
<td>6690 7642</td>
<td>2093 1491</td>
<td>2877 2947</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>880 1112</td>
<td>1022 1222</td>
<td>936 421</td>
<td>877 1210</td>
</tr>
<tr>
<td>Middle East</td>
<td>899 1583</td>
<td>1513 2257</td>
<td>1300 1776</td>
<td>978 1530</td>
</tr>
<tr>
<td>Africa</td>
<td>582 719</td>
<td>1006 1356</td>
<td>501 420</td>
<td>401 586</td>
</tr>
<tr>
<td>Asia Pacific</td>
<td>5553 7817</td>
<td>7613 9326</td>
<td>3694 3083</td>
<td>3657 5771</td>
</tr>
<tr>
<td>World</td>
<td>23948 27173</td>
<td>26096 30146</td>
<td>10655 8797</td>
<td>14949 17961</td>
</tr>
</tbody>
</table>

Source: BP Statistical review of world energy - 2010

<table>
<thead>
<tr>
<th>Region</th>
<th>Gasoline</th>
<th>Distillate</th>
<th>Residual</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>46.1</td>
<td>44.1</td>
<td>4.2</td>
<td>5.6</td>
</tr>
<tr>
<td>Canada</td>
<td>27.0</td>
<td>28.5</td>
<td>6.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Mexico</td>
<td>24.4</td>
<td>24.4</td>
<td>3.2</td>
<td>10.9</td>
</tr>
<tr>
<td>Central/South America</td>
<td>23.1</td>
<td>23.1</td>
<td>3.1</td>
<td>10.7</td>
</tr>
<tr>
<td>Western Europe</td>
<td>22.1</td>
<td>22.1</td>
<td>4.1</td>
<td>22.8</td>
</tr>
<tr>
<td>Middle East</td>
<td>42.2</td>
<td>38.4</td>
<td>35.4</td>
<td>22.6</td>
</tr>
<tr>
<td>Africa</td>
<td>18.5</td>
<td>26.1</td>
<td>36.1</td>
<td>23.8</td>
</tr>
<tr>
<td>Asia</td>
<td>18.4</td>
<td>30.7</td>
<td>14.3</td>
<td>33.5</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>19.3</td>
<td>30.3</td>
<td>25.0</td>
<td>25.5</td>
</tr>
<tr>
<td>World</td>
<td>26.1</td>
<td>28.4</td>
<td>14.4</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Refinery output by main categories of product as percentage of total (2003)
[20, Gary et al. 2007]
A picture for the demand in Western Europe is presented in Table 1.5.

<table>
<thead>
<tr>
<th>Refinery-products</th>
<th>Demand 1995 Mt</th>
<th>% of Total</th>
<th>Average annual growth in % 1995 - 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha chemical feed stock</td>
<td>40</td>
<td>2</td>
<td>4.5</td>
</tr>
<tr>
<td>Gasoline</td>
<td>125</td>
<td>20</td>
<td>0.7</td>
</tr>
<tr>
<td>Jet fuel (kerosene)</td>
<td>40</td>
<td>2</td>
<td>2.7</td>
</tr>
<tr>
<td>Diesel</td>
<td>115</td>
<td>19</td>
<td>2.3</td>
</tr>
<tr>
<td>Fuel oil (Light inland)</td>
<td>110</td>
<td>18</td>
<td>1.4</td>
</tr>
<tr>
<td>Heavy fuel oil for electricity</td>
<td>75</td>
<td>13</td>
<td>2.6</td>
</tr>
<tr>
<td>Heavy fuel oils for bunker</td>
<td>30</td>
<td>5</td>
<td>0.7</td>
</tr>
<tr>
<td>Other products *</td>
<td>65</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>TOTAL</td>
<td>600</td>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes:
Values in the table corresponding to Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, United Kingdom together.
*Other products (in 1995 at 65 Mt) include lubes and bitumen products and refinery fuel (estimated at 38.7 Mt/year).

Table 1.5: Product demand development Western Europe
Source: [118, VROM, 1999]

According to the Commission [72, EC 2010] the evolution of the petroleum product demand mix in the EU between 1990 and 2008 is the following:

- the share of jet fuel and kerosene has increased from 5.5 % to 9.4 %;
- the share of gasoil (including diesel, not heating oil) has increased from 17.7 % to 31 %;
- the share of gasoline has increased from 22.7 % to 16.1 %;
- the share of heavy fuel oil has increased from 16.3 % to 6.4 %.

At the time of writing (2010), the EU production-consumption gap is still closed via international trade in refined products. The EU imports diesel (mostly from the Russian Federation) and exports gasoline (mostly to the United States of America, and in a lesser extent, to Africa and the Middle East). As Figure 1.6 shows, this import-export EU market was almost balanced in 2005.

Figure 1.6: Transportation fuel balance between Europe, North America and the Former Soviet Union
However, the US, Middle Eastern and Asian countries have been increasing their refining capacity and North America is expected to become also an important diesel exporter already as early as 2011–2012. According to certain sources, Europe’s diesel deficit could be satisfied due to a combination of falling general demand, ongoing technological improvements on gasoline engines, rising imports from the US and new hydro cracking units that will come online.

Table 1.8: Worldwide import/export of products - 2009 (BP statisticals)

<table>
<thead>
<tr>
<th>Import/exports of products million of tonnes per year</th>
<th>Products exports</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>122.0</td>
</tr>
<tr>
<td>Canada</td>
<td>15.3</td>
</tr>
<tr>
<td>Mexico</td>
<td>21.0</td>
</tr>
<tr>
<td>S. and Cent. America</td>
<td>41.3</td>
</tr>
<tr>
<td>Europe</td>
<td>152.0</td>
</tr>
<tr>
<td>Former Soviet Union</td>
<td>3.2</td>
</tr>
<tr>
<td>Middle East</td>
<td>10.5</td>
</tr>
<tr>
<td>North Africa</td>
<td>10.0</td>
</tr>
<tr>
<td>West Africa</td>
<td>12.1</td>
</tr>
<tr>
<td>East and Southern Africa</td>
<td>5.7</td>
</tr>
<tr>
<td>Australasia</td>
<td>17.1</td>
</tr>
<tr>
<td>China</td>
<td>49.8</td>
</tr>
<tr>
<td>India</td>
<td>10.4</td>
</tr>
<tr>
<td>Japan</td>
<td>35.3</td>
</tr>
<tr>
<td>Singapore</td>
<td>79.8</td>
</tr>
<tr>
<td>Other Asia Pacific</td>
<td>127.6</td>
</tr>
<tr>
<td>Total world</td>
<td>714</td>
</tr>
</tbody>
</table>

Product quality: cleaner fuels. As far as the quality of refined products is concerned, the phasing out of lead from gasoline will be further pursued has been completed and new specifications (see Table 1.9) have required a reduction of the sulphur content for all types of automotive fuels, lower aromatics, particularly benzene in gasoline, and reduced polyaromatic hydrocarbons and a higher cetane number in diesel. The trend is that environmental quality requirements will become more stringent for all refinery products. These requirements will be especially true for automotive fuels (Auto Oil I and II). Moreover, EU acidification will put additional pressure on the sulphur content of liquid fuels, and therefore also on the sulphur content of the fuels used in refineries. Meeting these new specifications will require additional investment, particularly in desulphurisation capacity, adding more pressure to the restructuring process of the sector.

Environmental: emission reduction from refineries is a major issue. As regards the future, refinery fuel consumption will be higher because of increased conversion (consumption at 49 Mt/yr at current energy efficiency). The composition of the refinery fuel will be adapted and cannot excluded that the use of the liquid refinery fuel component (estimated at 11 Mt/yr in 1995) may be phased out. Such a reduction of use of liquid refinery fuels, some of them residual components, leads further to more distillation residue upgrading investments (like coking, thermocracking or gasification.) (on top of the reduced demand for HFO by some 25 Mt/yr by 2010). [118, VROM, 1999].
### Table 1.9: Evolution of mineral oil product specifications

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gasoline</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>ppm</td>
<td>500 max.</td>
<td>150 max.</td>
<td>50 max.</td>
<td>10 max</td>
</tr>
<tr>
<td>Lead</td>
<td>g/l</td>
<td>0.15</td>
<td>0.005 max</td>
<td>10 max</td>
<td>10 max</td>
</tr>
<tr>
<td>Aromatics</td>
<td>% v/v</td>
<td>none</td>
<td>42 max.</td>
<td>35 max.</td>
<td>35 max.</td>
</tr>
<tr>
<td>Olefins</td>
<td>% v/v</td>
<td>none</td>
<td>18 max.</td>
<td>18 max.</td>
<td>18 max.</td>
</tr>
<tr>
<td>Aromatics</td>
<td>% v/v</td>
<td>42 max.</td>
<td>35 max.</td>
<td>35 max.</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>% v/v</td>
<td>5 max.</td>
<td>1.0 max.</td>
<td>1.0 max.</td>
<td>1.0 max.</td>
</tr>
<tr>
<td>Evaporation at 100 °C (summer)</td>
<td>%</td>
<td>65/70 max.</td>
<td>46 min.</td>
<td>46 min.</td>
<td>46 min.</td>
</tr>
<tr>
<td>Evaporation at 150 °C (winter)</td>
<td>%</td>
<td>none</td>
<td>75 min.</td>
<td>75 min.</td>
<td>75 min.</td>
</tr>
<tr>
<td>RVP, summer</td>
<td>kPa</td>
<td>80</td>
<td>60 max.</td>
<td>60 max.</td>
<td>60 max.</td>
</tr>
<tr>
<td>Oxygen</td>
<td>%</td>
<td>2.5 max.</td>
<td>2.7 max.</td>
<td>2.7 max.</td>
<td>3.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>% v/v</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>% v/v</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Iso-propyl alcohol</td>
<td>% v/v</td>
<td>10</td>
<td>10</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Ter-butyl alcohol</td>
<td>% v/v</td>
<td>7</td>
<td>7</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Iso-butyl alcohol</td>
<td>% v/v</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Ethers &gt;C4</td>
<td>% v/v</td>
<td>15</td>
<td>15</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Other oxygenates</td>
<td>% v/v</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td><strong>Diesel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>ppm</td>
<td>500 max.</td>
<td>350 max.</td>
<td>50 max.</td>
<td>10 max</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>49 min.</td>
<td>51 min.</td>
<td>51 min.</td>
<td>51 min.</td>
</tr>
<tr>
<td>Density @ 15°C</td>
<td>kg/m³</td>
<td>860 max.</td>
<td>845 max.</td>
<td>845 max.</td>
<td>845 max.</td>
</tr>
<tr>
<td>Distillation 95 % (v/v)</td>
<td>°C</td>
<td>370 max.</td>
<td>360 max.</td>
<td>360 max.</td>
<td>360 max.</td>
</tr>
<tr>
<td>Polycyclic Aromatics</td>
<td>% m/m</td>
<td>none</td>
<td>11 max.</td>
<td>11 max.</td>
<td>8 max.</td>
</tr>
<tr>
<td>FAME - EN 14078</td>
<td>% v/v</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>7 max.</td>
</tr>
<tr>
<td><strong>Heating gas oil</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>% m/m</td>
<td></td>
<td></td>
<td>0.1 max</td>
<td></td>
</tr>
<tr>
<td><strong>Inland heavy fuel oil</strong></td>
<td></td>
<td></td>
<td>2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bunker fuel oil in SOx emission control zones</strong></td>
<td></td>
<td></td>
<td>IMO - 2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>% w/w</td>
<td></td>
<td></td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

At the time of writing (2011), the Commission made a proposal for amending directive 1999/32/EC on fuel specifications. This proposal aims at taking into account the more stringent rules for the sulphur content of fuels used by maritime transport agreed under International Maritime Organisation (IMO) through the revised Annex VI to MARPOL convention. It introduces, in particular, stricter sulphur limits for marine fuel:

- in Sulphur Emission Control Areas (SECAs): 1 % as of 1 July 2010 and 0.10 % as of 1 January 2015;
- in sea areas outside SECAs: 3.5 % as of 1 January 2012 and, in principle, 0.50 % as of 1 January 2020.

**Automation**: application of information techniques features such as enhanced process control and management’s systems. These investments have enabled considerable cost/manpower savings and efficiency improvements.
1.2.5.2 Natural gas

In 2007, the world’s largest exporter of natural gas was by far Russia (around 200 billion m³/yr), followed by Canada and Norway 2nd place with around 87 billion. The first EU-27 exporter, the Netherlands, ranked the 9th place with 30 billion.

Table 1.10: Natural gas transfers (2009)

<table>
<thead>
<tr>
<th>Transferred to</th>
<th>Pipeline Imports (billion m³)</th>
<th>LNG imports</th>
<th>Total imports</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>122.49</td>
<td>17.33</td>
<td>139.82</td>
</tr>
<tr>
<td>S. and Cent. America</td>
<td>12.49</td>
<td>3.28</td>
<td>15.77</td>
</tr>
<tr>
<td>Europe and Eurasia</td>
<td>443.97</td>
<td>69.02</td>
<td>512.99</td>
</tr>
<tr>
<td>Austria</td>
<td>7.98</td>
<td>–</td>
<td>7.98</td>
</tr>
<tr>
<td>Belgium</td>
<td>15.01</td>
<td>6.53</td>
<td>21.54</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>2.64</td>
<td>–</td>
<td>2.64</td>
</tr>
<tr>
<td>Croatia</td>
<td>1.20</td>
<td>–</td>
<td>1.20</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>9.40</td>
<td>–</td>
<td>9.40</td>
</tr>
<tr>
<td>Estonia</td>
<td>0.71</td>
<td>–</td>
<td>0.71</td>
</tr>
<tr>
<td>Finland</td>
<td>4.10</td>
<td>–</td>
<td>4.10</td>
</tr>
<tr>
<td>France</td>
<td>35.99</td>
<td>13.07</td>
<td>49.06</td>
</tr>
<tr>
<td>Germany</td>
<td>88.82</td>
<td>–</td>
<td>88.82</td>
</tr>
<tr>
<td>Greece</td>
<td>2.55</td>
<td>0.74</td>
<td>3.29</td>
</tr>
<tr>
<td>Hungary</td>
<td>8.10</td>
<td>–</td>
<td>8.10</td>
</tr>
<tr>
<td>Ireland</td>
<td>5.08</td>
<td>–</td>
<td>5.08</td>
</tr>
<tr>
<td>Italy</td>
<td>66.41</td>
<td>2.90</td>
<td>69.31</td>
</tr>
<tr>
<td>Latvia</td>
<td>1.19</td>
<td>–</td>
<td>1.19</td>
</tr>
<tr>
<td>Lithuania</td>
<td>2.77</td>
<td>–</td>
<td>2.77</td>
</tr>
<tr>
<td>Netherlands</td>
<td>17.21</td>
<td>–</td>
<td>17.21</td>
</tr>
<tr>
<td>Poland</td>
<td>9.15</td>
<td>–</td>
<td>9.15</td>
</tr>
<tr>
<td>Portugal</td>
<td>1.59</td>
<td>2.82</td>
<td>4.41</td>
</tr>
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<td>Romania</td>
<td>2.05</td>
<td>–</td>
<td>2.05</td>
</tr>
<tr>
<td>Slovakia</td>
<td>5.40</td>
<td>–</td>
<td>5.40</td>
</tr>
<tr>
<td>Slovenia</td>
<td>0.89</td>
<td>–</td>
<td>0.89</td>
</tr>
<tr>
<td>Spain</td>
<td>8.99</td>
<td>27.01</td>
<td>36.00</td>
</tr>
<tr>
<td>Sweden</td>
<td>1.31</td>
<td>–</td>
<td>1.31</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>30.88</td>
<td>10.24</td>
<td>41.12</td>
</tr>
<tr>
<td>Rest Europe and Eurasia</td>
<td>114.55</td>
<td>5.71</td>
<td>120.26</td>
</tr>
<tr>
<td>Middle East</td>
<td>30.42</td>
<td>0.89</td>
<td>31.31</td>
</tr>
<tr>
<td>Africa</td>
<td>5.25</td>
<td>–</td>
<td>5.25</td>
</tr>
<tr>
<td>Asia Pacific</td>
<td>19.16</td>
<td>152.27</td>
<td>171.43</td>
</tr>
<tr>
<td><strong>Pipeline exports</strong></td>
<td><strong>633.77</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>LNG exports</strong></td>
<td><strong>242.77</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total exports</strong></td>
<td><strong>876.54</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Source: BP Statistical Review Of World Energy 2010*

Unconventional gas: The use of horizontal drilling in conjunction with hydraulic fracturing has greatly expanded the ability of producers to profitably produce natural gas from low permeability geologic formations, particularly shale formations. Application of fracturing techniques to stimulate oil and gas production began to grow rapidly in the 1950s, although experimentation dates back to the 19th century.

Shale gas (see further definition) has become a ‘game changer’ for the natural gas market. The proliferation of activity into new shale plays has increased dry shale gas production in the United States from 11 billion cubic metres in 2000 to 136 in 2010, or 23 % of US dry gas production. Wet shale gas reserves have increased to about 1 700 billion cubic metres by year-end 2009, when they comprised about 21 % of overall US natural gas reserves, now at the highest level since 1971.
Thus, adding the identified shale gas resources to other gas resources increases total world technically recoverable gas resources by over 40% to 640 000 billion cubic metres.

Shale gas is extracted by fracking technique that involves high pressure injection of water, sand and chemical additives and thus environmental impact needs to be taken into consideration.

Some useful definitions about these new techniques are provided:

- **Shale gas** - Natural gas stored in extremely small pore spaces or bonded to organic material within rock composed mostly of consolidated clay and siltstone.
- **Tight gas** - Natural gas stored in small pore spaces in very low permeability underground formations, such as sandstone, siltstone or limestone.
- **Deep gas** - Unconventional natural gas that is located deep within geological formations.
- **Coalbed methane (CBM)** - Natural gas stored in naturally occurring fracture systems or bonded onto coal. A liquid, low-pressure sweet gas, CBM gas is used to fuel hot water heaters, furnaces and ranges.

Mid-size companies led this extraction activity: e.g. Chesapeake, Exco, XTO Energy, Atlas, Encana or Duvenay.

Table 1.11: Estimated technically recoverable shale gas resources in 32 countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Estimated technically recoverable reserves (billion m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>36 104</td>
</tr>
<tr>
<td>United States</td>
<td>24 409</td>
</tr>
<tr>
<td>Argentina</td>
<td>21 917</td>
</tr>
<tr>
<td>Mexico</td>
<td>19 284</td>
</tr>
<tr>
<td>South Africa</td>
<td>13 734</td>
</tr>
<tr>
<td>Australia</td>
<td>11 214</td>
</tr>
<tr>
<td>Canada</td>
<td>10 987</td>
</tr>
<tr>
<td>Libya</td>
<td>8 212</td>
</tr>
<tr>
<td>Algeria</td>
<td>6 541</td>
</tr>
<tr>
<td>Brazil</td>
<td>6 400</td>
</tr>
<tr>
<td>Poland</td>
<td>5 295</td>
</tr>
<tr>
<td>France</td>
<td>5 097</td>
</tr>
<tr>
<td>Norway</td>
<td>2 350</td>
</tr>
<tr>
<td>Chile</td>
<td>1 812</td>
</tr>
<tr>
<td>India</td>
<td>1 784</td>
</tr>
<tr>
<td>Paraguay</td>
<td>1 756</td>
</tr>
<tr>
<td>Pakistan</td>
<td>1 444</td>
</tr>
<tr>
<td>Bolivia</td>
<td>1 359</td>
</tr>
<tr>
<td>Ukraine</td>
<td>1 189</td>
</tr>
<tr>
<td>Sweden</td>
<td>1 161</td>
</tr>
<tr>
<td>Denmark</td>
<td>651</td>
</tr>
<tr>
<td>Uruguay</td>
<td>595</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>566</td>
</tr>
<tr>
<td>Colombia</td>
<td>538</td>
</tr>
<tr>
<td>Tunisia</td>
<td>510</td>
</tr>
<tr>
<td>Netherlands</td>
<td>481</td>
</tr>
<tr>
<td>Turkey</td>
<td>425</td>
</tr>
<tr>
<td>Morocco</td>
<td>311</td>
</tr>
<tr>
<td>Venezuela</td>
<td>311</td>
</tr>
<tr>
<td>Germany</td>
<td>227</td>
</tr>
<tr>
<td>Western Sahara</td>
<td>198</td>
</tr>
<tr>
<td>Lithuania</td>
<td>113</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>186 977</strong></td>
</tr>
</tbody>
</table>

Source: [73, US DOE 2011]  
NB: Italics: EU-27 member states
1.3 European refineries

1.3.1 Oil refineries

At the time of writing (2011), there are currently around 130 crude oil refineries spread around the EU+ countries. Of these refineries, 10 are specialist refineries producing mainly lubricating oil basestocks or bitumen. It is difficult to be precise about the actual numbers as there are several situations where, as a result of amalgamations, what were separate refineries are now managed as one, sharing some facilities, even though the component parts may be some kilometres apart. Germany and Italy are the countries with the most refineries in Europe. Luxembourg has none. Four on-shore natural gas plants have been identified in Europe—Figure 1.7 and the associated Table show the distribution of European refineries by country. As can be seen on the map, refineries are mainly placed close to the sea or to a big river, to satisfy their need for large amounts of cooling water as well as to facilitate the sea transport of raw materials and products. There are some places in Europe with a high concentration of refineries (e.g. Rotterdam in Netherlands (5); Antwerp in Belgium (5) and Sicily in Italy (4).

As a result of overcapacity in the European refinery sector, very few new oil refineries have been built in the last 25 years. In fact, only 9% of the existing refineries have been built in this period and only two % in the last ten years, 95 % being built before 1981 and 44 % before 1961 (see Table 1.12). Although most refineries will have had upgrades and new units built since they were first commissioned, their overall structure, and in particular items like the pattern of sewer systems, will have remained essentially unchanged.

Note for TWG (CONCAWE): if possible, it would be interesting to update the full Table with EU-27 data—No new data made available

Table 1.12: Percentage of refineries built during different time periods in EU-27

<table>
<thead>
<tr>
<th>Time period</th>
<th>Number of refineries built in the time period</th>
<th>Percentage of refineries built during the time period (%)</th>
<th>Cumulative percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before 1900</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1900 – 1910</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>1911 – 1920</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>1921 – 1930</td>
<td>9</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>1931 – 1940</td>
<td>7</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>1941 – 1950</td>
<td>8</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>1951 – 1960</td>
<td>17</td>
<td>17</td>
<td>44</td>
</tr>
<tr>
<td>1961 – 1970</td>
<td>41</td>
<td>40</td>
<td>83</td>
</tr>
<tr>
<td>1971 – 1980</td>
<td>12</td>
<td>12</td>
<td>95</td>
</tr>
<tr>
<td>1981 – 1990</td>
<td>3</td>
<td>3</td>
<td>98</td>
</tr>
<tr>
<td>1991 – 2000</td>
<td>2</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>2000 – 2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>103 (*)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) Refinery in Martinique not included within the table. Some refineries have been demolished recently.

Source: CONCAWE

1.3.2 Gas refineries

Four on-shore natural gas plants have been identified in Europe. Three have been identified in the Netherlands and one in Norway. Nine onshore natural gas plants have been identified in Europe. Three have been identified in the Netherlands and six in Norway, including LNG plants.
Figure 1.7: Geographical distribution of the European refineries
<table>
<thead>
<tr>
<th>ID</th>
<th>Country</th>
<th>Refinery location</th>
<th>ID</th>
<th>Country</th>
<th>Refinery location</th>
<th>ID</th>
<th>Country</th>
<th>Refinery location</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>Austria</td>
<td>Schwechat</td>
<td>47</td>
<td>Greece</td>
<td>Thessaloniki</td>
<td>87</td>
<td>Romania</td>
<td>Bacau</td>
</tr>
<tr>
<td>2-5</td>
<td>Belgium</td>
<td>Antwerpen</td>
<td>48</td>
<td>Elefsis</td>
<td>Aspropyrgos</td>
<td>88</td>
<td>Campina</td>
<td></td>
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<tr>
<td>6</td>
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<td>Burgas</td>
<td>49</td>
<td>Aspropyrgos</td>
<td>Aghhi Theodori</td>
<td>89</td>
<td>Onesti, Bacau</td>
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<tr>
<td>7</td>
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<td>Greece</td>
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<td>Hungary</td>
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<td>Nynashamn</td>
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<td>Zagreb</td>
<td>66</td>
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<td>Italy</td>
<td>Meilini, Sicily</td>
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<td>Brojorden - Lysekil</td>
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<td>Italy</td>
<td>S. Martino Di Trecate S.</td>
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<td>Cressier</td>
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<td>Lithuania</td>
<td>Mazeikiai</td>
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<td>Turkey</td>
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<td>Izmik</td>
</tr>
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<td>Croatia</td>
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<td>73</td>
<td>The Netherlands</td>
<td>Rotterdam</td>
<td>116</td>
<td>Turkey</td>
<td>Narli, Kahramannamara</td>
</tr>
<tr>
<td>31</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>74</td>
<td>The Netherlands</td>
<td>Vlissingen</td>
<td>117</td>
<td>Turkey</td>
<td>Batam, Siirt</td>
</tr>
<tr>
<td>32</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>75</td>
<td>The Netherlands</td>
<td>Amsterdam</td>
<td>118</td>
<td>Turkey</td>
<td>Mersin</td>
</tr>
<tr>
<td>33</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>76</td>
<td>The Netherlands</td>
<td>Pernis</td>
<td>119</td>
<td>Turkey</td>
<td>Narli, Kahramannamara</td>
</tr>
<tr>
<td>34</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>77</td>
<td>The Netherlands</td>
<td>Groningen</td>
<td>120</td>
<td>Turkey</td>
<td>Coryton Essex</td>
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<tr>
<td>35</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>78</td>
<td>The Netherlands</td>
<td>Stangen</td>
<td>121</td>
<td>Turkey</td>
<td>Eastham</td>
</tr>
<tr>
<td>36</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>79</td>
<td>Norway</td>
<td>Mongstad</td>
<td>122</td>
<td>United Kingdom</td>
<td>South Killingholme</td>
</tr>
<tr>
<td>37</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>80</td>
<td>Norway</td>
<td>Slagen</td>
<td>123</td>
<td>United Kingdom</td>
<td>Stanilow</td>
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<td>Zagreb</td>
<td>81</td>
<td>Norway</td>
<td>Jaslo</td>
<td>124</td>
<td>United Kingdom</td>
<td>South Killingholme</td>
</tr>
<tr>
<td>39</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>82</td>
<td>Poland</td>
<td>Gdansk</td>
<td>125</td>
<td>United Kingdom</td>
<td>Dundee</td>
</tr>
<tr>
<td>40</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>83</td>
<td>Poland</td>
<td>Gorlice</td>
<td>126</td>
<td>United Kingdom</td>
<td>Fawley</td>
</tr>
<tr>
<td>41</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>84</td>
<td>Poland</td>
<td>Plock/Trzebina</td>
<td>127</td>
<td>United Kingdom</td>
<td>Grangemouth</td>
</tr>
<tr>
<td>42</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>85</td>
<td>Portugal</td>
<td>Leça da Palmeira Porto</td>
<td>128</td>
<td>United Kingdom</td>
<td>Milford Haven</td>
</tr>
<tr>
<td>43</td>
<td>Croatia</td>
<td>Zagreb</td>
<td>86</td>
<td>Portugal</td>
<td>Sines</td>
<td>129</td>
<td>United Kingdom</td>
<td>Pembroke, Dyfed</td>
</tr>
</tbody>
</table>

**NB:** In italics: lubricant and bitumen specialised refineries

**Source:** [70, Oil & Gas 2010]
Chapter 1

1.3.3 Technical characteristics of European refineries

Compared to other parts of the world, refining configurations of Western European refineries reflect to some extent their technical adaptation to the local demands of middle distillates, in particular diesel and jet fuel: they show proportionally more hydrotreating and hydrocracking capacities and less catalytic cracking capacities than in North America. As shown in Table 1.13, the most complex refinery configurations are observed in North America refineries. As a result, they produce 3 times less heavy residues than in Europe, and 6 times less than in the Russian federation or in Africa.

Table 1.13: Refining configurations as a percentage of crude distillation

<table>
<thead>
<tr>
<th>World regions</th>
<th>Catalytic cracking</th>
<th>Catalytic reforming</th>
<th>Catalytic hydrocracking</th>
<th>Catalytic hydrotreating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>6.5</td>
<td>14.7</td>
<td>1.9</td>
<td>28.0</td>
</tr>
<tr>
<td>Asia</td>
<td>11.9</td>
<td>8.7</td>
<td>3.3</td>
<td>38.5</td>
</tr>
<tr>
<td>Eastern Europe</td>
<td>9.0</td>
<td>14.5</td>
<td>3.1</td>
<td>41.6</td>
</tr>
<tr>
<td>Middle East</td>
<td>5.1</td>
<td>9.2</td>
<td>8.3</td>
<td>29.2</td>
</tr>
<tr>
<td>North America</td>
<td>20.2</td>
<td>31.9</td>
<td>8.4</td>
<td>73.4</td>
</tr>
<tr>
<td>South America</td>
<td>19.6</td>
<td>6.4</td>
<td>2.1</td>
<td>28.9</td>
</tr>
<tr>
<td>Western Europe</td>
<td>15.0</td>
<td>14.3</td>
<td>7.0</td>
<td>66.7</td>
</tr>
</tbody>
</table>

Source: [20, Gary et al. 2007]

Table 1.14 shows the number of processes currently operating in the mineral oil refineries in each country. As can be seen, crude and vacuum distillations, catalytic hydrotreatment and catalytic reforming are the most common processes, as they are found in the simplest of refineries. It may be surprising that the number of catalytic hydrotreatment processes is higher than the number of refineries, but the reason is simply that there is, on average, more than one catalytic hydrotreatment in each European refinery. The least common processes in European refineries are coking and polymerisation/dimerisation.

Note for TWG: Please confirm your interest for this update, in particular for Table 1.15

Some of these refining processes have been analysed in order to determine the type of technique or techniques used to perform a certain process. For instance, there are currently two technologies to carry out alkylation, namely sulphuric and hydrofluoric. In this case these two technologies are competitors but in other cases, such as hydrotreating, one technique does not exclude another (these cases are marked with an asterisk in Table 1.15). The percentage of techniques for each process is shown in Table 1.15, based on data [73, Radler, 1998] reviewed by TWG members. As can be seen in that table, some techniques are really predominant in particular processes in European refineries. This category includes delayed coking, visbreaking, fluid catalytic cracking, hydrofluoric alkylation, C₃ and C₆ isomerisation, Methyl tert-butyl ether (MTBE) production and steam reforming for the production of hydrogen. Other processes where one technique is less predominant are catalytic reforming, catalytic hydrefining, catalytic hydrotreating and hydrogen recovery process.
Table 1.14: Number of type of processes per country

<table>
<thead>
<tr>
<th>Process</th>
<th>EU 27 number</th>
<th>EU+ number</th>
<th>World M barrel/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Fluid coking</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2 Delayed coking</td>
<td>13</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>3 Other</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td><strong>Coking</strong></td>
<td><strong>16</strong></td>
<td><strong>16</strong></td>
<td><strong>4.61</strong></td>
</tr>
<tr>
<td>1 Thermal cracking</td>
<td>14</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2 Visbreaking</td>
<td>52</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td><strong>Thermal ops</strong></td>
<td><strong>66</strong></td>
<td><strong>66</strong></td>
<td><strong>3.82</strong></td>
</tr>
<tr>
<td>1 Fluid</td>
<td>58</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>1 Other</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td><strong>Catalytic cracking</strong></td>
<td><strong>61</strong></td>
<td><strong>61</strong></td>
<td><strong>14.66</strong></td>
</tr>
<tr>
<td>1 Semiregenerative</td>
<td>58</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>2 Cyclic</td>
<td>13</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>3 Continuous regen</td>
<td>34</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>4 Other</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>Catalytic reforming</strong></td>
<td><strong>105</strong></td>
<td><strong>105</strong></td>
<td><strong>11.51</strong></td>
</tr>
<tr>
<td>1 Distillate upgrading</td>
<td>24</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>2 Residual upgrading</td>
<td>6</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>3 Lube oil manufacturing</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>4 Other</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>e Conventional</td>
<td>15</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>m Mild to moderate</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td><strong>Catalytic hydrocracking</strong></td>
<td><strong>38</strong></td>
<td><strong>38</strong></td>
<td><strong>5.41</strong></td>
</tr>
<tr>
<td>1 Pretreatment of cat. reformer feeds</td>
<td>81</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>2 Other naphta desulphurisation</td>
<td>26</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>3 Naphtha aromatics saturation</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>4 Kerosin/jet desulphurisation</td>
<td>35</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>5 Diesel desulphurisation</td>
<td>65</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>6 Distillate aromatics saturation</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>7 Other distillates</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>8 Pretreatment cat. crackers feed</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>9 Other heavy GO</td>
<td>13</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>10 Resid hydrotreating</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>11 Lube oil polishing</td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>12 Post hydrotreating of FCC naphtha</td>
<td>19</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>13 Other</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td><strong>Catalytic hydrotreating</strong></td>
<td><strong>309</strong></td>
<td><strong>309</strong></td>
<td><strong>45.43</strong></td>
</tr>
</tbody>
</table>

Source: [70, Oil & Gas 2010]
Table 1.15: Percentage of EU+ refineries that have a certain process (per type of process)

<table>
<thead>
<tr>
<th>Process</th>
<th>Technique used</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coking</td>
<td>Delayed coking</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Fluid coking</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Visbraking</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Thermal cracking</td>
<td>18</td>
</tr>
<tr>
<td>Thermal operations</td>
<td>Fluid</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>6</td>
</tr>
<tr>
<td>Catalytic cracking</td>
<td>Semiregenerative</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Continuous regenerative</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Cyclic</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>4</td>
</tr>
<tr>
<td>Catalytic reforming</td>
<td>Distillate upgrading</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Residual upgrading</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Lube oil manufacturing</td>
<td>0</td>
</tr>
<tr>
<td>Catalytic hydrocracking</td>
<td>Used for</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mild to moderate hydro cracking</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Conventional</td>
<td>64</td>
</tr>
<tr>
<td>Catalytic hydorefining</td>
<td>Used for</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mild distillate</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Heavy gas oil desulphurisation</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Catalytic cracker and cycle stock treatment</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Residual desulphurisation</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>3</td>
</tr>
<tr>
<td>Catalytic hydrotreating</td>
<td>Naphtha desulphurising</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Straight-run distillate</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Pretreatment cat reformer feeds</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Lube oil polishing</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Naphtha olefin or aromatic saturation</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Other</td>
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<td>Alkylation</td>
<td>Pre-treating cat cracker feeds</td>
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<tr>
<td></td>
<td>Hydrofluoric acid</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>Sulphuric acid</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>3</td>
</tr>
<tr>
<td>Polymerisation</td>
<td>Polymerisation</td>
<td>79</td>
</tr>
<tr>
<td>Dimerisation</td>
<td>Dimerisation</td>
<td>21</td>
</tr>
<tr>
<td>Aromatics (*)</td>
<td>BTX</td>
<td>59</td>
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<tr>
<td></td>
<td>Hydrodealkylation</td>
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<td>Cyclohexane</td>
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<td>Cumene</td>
<td>3</td>
</tr>
<tr>
<td>Isomerisation</td>
<td>C5 and C6 feed</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>C5 feed</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>C4 feed</td>
<td>9</td>
</tr>
<tr>
<td>Etherification</td>
<td>MTBE</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>TAME</td>
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<td>ETBE</td>
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</tr>
<tr>
<td>Hydrogen</td>
<td>Production</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Steam methane reforming</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Steam naphtha reforming</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Partial oxidation</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pressure swing adsorption</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Membrane</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Cryogenic</td>
<td>19</td>
</tr>
</tbody>
</table>

(1) For definitions of processes see bottom of Table 1.6.

Source: Data from [73, Radler, 1998] reviewed by the TWG.

Following the analysis of the type of processes, Table 1.16 shows the capacity ranges for the different processes found in EU+ refineries. As can be seen, the ranges are quite large, explaining again the diversity of type of refineries found in the EU+. For instance, there exist huge differences in the capacity of crude units or catalytic hydrotreating. Smaller differences exist in the coking processes and alkylation processes.
Table 1.16 — Capacity of the various processes in EU+ refineries

<table>
<thead>
<tr>
<th>Process</th>
<th>Maximum</th>
<th>Average</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude</td>
<td>23.21 Mm^3/yr</td>
<td>7.96 Mm^3/yr</td>
<td>0.46 Mm^3/yr</td>
</tr>
<tr>
<td>Vacuum distillation</td>
<td>10.73 Mm^3/yr</td>
<td>3.03 Mm^3/yr</td>
<td>0.26 Mm^3/yr</td>
</tr>
<tr>
<td>Coking</td>
<td>3.05 Mm^3/yr</td>
<td>1.73 Mm^3/yr</td>
<td>0.72 Mm^3/yr</td>
</tr>
<tr>
<td>Thermal operations</td>
<td>3.50 Mm^3/yr</td>
<td>1.45 Mm^3/yr</td>
<td>0.39 Mm^3/yr</td>
</tr>
<tr>
<td>Catalytic cracking</td>
<td>8.32 Mm^3/yr</td>
<td>3.33 Mm^3/yr</td>
<td>0.52 Mm^3/yr</td>
</tr>
<tr>
<td>Catalytic reforming</td>
<td>4.98 Mm^3/yr</td>
<td>1.96 Mm^3/yr</td>
<td>0.08 Mm^3/yr</td>
</tr>
<tr>
<td>Cat. hydrocracking</td>
<td>3.77 Mm^3/yr</td>
<td>1.63 Mm^3/yr</td>
<td>0.05 Mm^3/yr</td>
</tr>
<tr>
<td>Cat. hydrofining</td>
<td>6.06 Mm^3/yr</td>
<td>1.58 Mm^3/yr</td>
<td>0.23 Mm^3/yr</td>
</tr>
<tr>
<td>Cat. hydrotreating</td>
<td>3.01 Mm^3/yr</td>
<td>1.78 Mm^3/yr</td>
<td>0.02 Mm^3/yr</td>
</tr>
</tbody>
</table>

Production capacity, Mm^3/yr

<table>
<thead>
<tr>
<th>Process</th>
<th>Maximum</th>
<th>Average</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylation</td>
<td>4.89 Mm^3/yr</td>
<td>0.45 Mm^3/yr</td>
<td>0.14 Mm^3/yr</td>
</tr>
<tr>
<td>Pol./Dim.</td>
<td>0.67 Mm^3/yr</td>
<td>0.23 Mm^3/yr</td>
<td>0.03 Mm^3/yr</td>
</tr>
<tr>
<td>Aromatics</td>
<td>1.49 Mm^3/yr</td>
<td>0.36 Mm^3/yr</td>
<td>0.04 Mm^3/yr</td>
</tr>
<tr>
<td>Isomerisation</td>
<td>1.13 Mm^3/yr</td>
<td>0.55 Mm^3/yr</td>
<td>0.11 Mm^3/yr</td>
</tr>
<tr>
<td>Base Oil production</td>
<td>4.03 Mm^3/yr</td>
<td>0.33 Mm^3/yr</td>
<td>0.03 Mm^3/yr</td>
</tr>
<tr>
<td>Etherification</td>
<td>0.30 Mm^3/yr</td>
<td>0.11 Mm^3/yr</td>
<td>0.01 Mm^3/yr</td>
</tr>
<tr>
<td>Hydrogen (MNm^3/day)</td>
<td>3.23 Mm^3/yr</td>
<td>1.54 Mm^3/yr</td>
<td>0.003 Mm^3/yr</td>
</tr>
<tr>
<td>Coke (t/d)</td>
<td>2300 t/d</td>
<td>869 t/d</td>
<td>173 t/d</td>
</tr>
<tr>
<td>Sulphur (t/d)</td>
<td>650 t/d</td>
<td>130 t/d</td>
<td>2 t/d</td>
</tr>
<tr>
<td>Bitumen</td>
<td>116 t/d</td>
<td>44 t/d</td>
<td>0.02 t/d</td>
</tr>
</tbody>
</table>

For definitions of processes see bottom of Table 1.6.
Sources: [73, Radler, 1998] reviewed by the TWG members.

Table replaced by figure

Figure 1.8: Capacity of the various processes in the EU-27 refineries
There are various approaches to defining refinery complexity [287, Johnston, 1996]. The Nelson refinery complexity index was used for the construction of Figure 1.9. In Dutch notes [118, VROM, 1999] EU refineries are grouped by configuration, as shown in Table 1.17. CONCAWE [115, CONCAWE, 1999] has grouped refineries by types (that differ in definition from the configurations of Table 1.17) in Figure 1.10 as they existed in the period 1969–1997. Other definitions are used in the industry, such as FCC equivalent (used by CEC DG Transport reports on the refining industry) or the Equivalent Distillation Capacity as used by Solomon Associates.

Figure 1.9 tries to illustrate the variety of complexity of refineries within Europe. The Y axis represents refinery complexity calculated according to the Nelson refinery complexity index [287, Johnston, 1996]. The X axis represents the different EU+ countries. If we divide the Y gap of the EU+ refineries into four categories (less than 3.9, between 3.9 and less than 6.1, between 6.1 and 8.4 and more than 8.4), we see that 18% of the refineries belong to the lowest category, 30% belong to the second category, 41% to the third and 11% to the group of more complex refineries. Consequently, seven out of 10 refineries of the EU+ can be considered as refineries with medium complexity.

In some studies it is common to distinguish between several types of refinery configuration according to complexity (For further information see Annex 9.2). This classification of refineries is to define five different types of configuration, as shown in Table 1.17. According to this classification, some 26 hydroskimmers (with or without thermal crackers) are still in operation in Europe. The most common configuration in EU+ refineries is the catalytic cracker configuration.

Note for the TWG: Figure 1.9 has been completed with received data - OK for SK

---

(1) Nelson developed a system to quantify the relative cost of components that make up a refinery. It is a pure cost index that provides a relative measure of the construction costs of a particular refinery based on its crude and upgrading capacity. Nelson assigned a factor of 1 to the distillation unit. All other units are rated in terms of their cost relative to this unit.

(2) Limits of the categories calculated as average ± standard deviation
## Table 1.17: European refineries by configuration

<table>
<thead>
<tr>
<th>Country</th>
<th>No. refineries</th>
<th>Base-oil and bitumen refineries</th>
<th>Configuration 1 Hydrocracking + isomerisation unit</th>
<th>Configuration 2 Cat-cracker configuration</th>
<th>Configuration 3 Hydrocracker configuration</th>
<th>Configuration 4 Very-complex refinery with catcracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belgium</td>
<td>5</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denmark</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Finland</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>14</td>
<td>4</td>
<td>10</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Germany</td>
<td>17</td>
<td>3</td>
<td>2</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Greece</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iceland</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td>17</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Netherlands</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Norway</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portugal</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>10</td>
<td>1</td>
<td>2</td>
<td>6</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switzerland</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UK</td>
<td>13</td>
<td>3</td>
<td>7</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>104</td>
<td>10</td>
<td>26</td>
<td>42</td>
<td>14</td>
<td>12</td>
</tr>
</tbody>
</table>

Source: [118, VROM, 1999] reviewed by the TWG

Figure 1.10 shows the evolution of the complexity of EU+ refineries. It can be seen that the number of type I refineries has decreased over the years. To make more efficient use of the crude, increasingly deeper conversion units have been installed in European refineries.

Notes: Type I: Simple or non-conversion refinery. Composed of crude oil distillation, reforming, treatment of distillate products, including desulphurisation and/or other quality improvement processes (e.g. isomerisation or speciality manufacturing). Type II: Mild conversion (Type I plus thermal cracking or visbreaking). Type III: Complex (Type II plus fluidised catcracking and/or hydrocracking). Any of above types may have bitumen or luboil production, which clearly increases the relative complexity. No lubricating or bitumen refinery is included in this figure.
1.3.4 Employment in the European refinery sector

Note for TWG:
Asked CONCAWE/EUROPIA for update 5/09/11: No updated data made available/Propose to delete

It has been estimated that in 1998, there were 55000 direct employees of the refinery operators and 35000 contract workers (based on the numbers of man-hours worked reported to CONCAWE for their annual safety statistics report). These figures were calculated by dividing the reported man-hours by 1840 to give man-years. For the contractors, some of these will be employed full time at refineries, others will have been working there only during the duration of the contract. The number of actual people will therefore be larger.

In order to gain a rough idea of the employment generated by a single refinery, the number of employees (annual average employment) for different EU refineries is shown as a function of the complexity of the refineries (Figure 1.11) and as a function of the crude capacity of the refineries (Figure 1.12). Indirect or induced employment has also been plotted in both graphs where the data is available. As can be seen, the employment generated increases as the complexity or the crude capacity increases.
Big differences in employment are found for refineries with the same capacity or same complexity. For instance, employment at refineries with a capacity of 5 million of tonnes per year ranges from less than 300 to almost 900. Bigger differences can be found in the plot with the Nelson complexity index.
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1.4 Main environmental issues in the refining sector

Refineries are industrial sites that manage huge amounts of raw materials and products, and they are also intensive consumers of energy and water used to carry out the process. In their storage and refining processes, refineries generate emissions to the atmosphere, to water and to the soil. Environmental management has become a major factor for refineries. The refining industry is a mature industry, and pollution abatement programmes have been carried out in most refineries for a long time to different extents. As a result, the emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.

It is important to know, with respect to the quality and quantity of refinery emissions, that on a macro scale the crude oils vary only to a limited extent in their composition. Moreover, refineries are often limited to a comparatively narrow range of crude oil diets. Normally, when switching from one crude oil to another within this range, large variations in refinery emissions are not expected. Consequently the type and quantity of refinery emissions to the environment are well known during normal operations. However, from time to time, processing of crude oils previously unknown to the refinery can have unforeseen impacts on the performance of refinery processes; leading to an increase in emissions. This is particularly likely to affect aquatic emissions and to a lesser extent air emissions.

1.4.1 Emissions to the atmosphere

According to available European emission inventories [34, EEA 2009] [35, EEA 2009], oil refining is responsible for a significant contribution to air emissions generated by industrial activities. In the particular case of sulphur oxides, this contribution is significant (around 7%) when even observed at the level of the overall emissions by all human activities.

The following Table 1.18 gives an estimation of the contribution of oil refineries with regard to emissions reported in 2007 and 2009 in the European Union for some main parameters.

Table 1.18: Contribution of oil refining to the EU-27 air emissions (in 2007)

<table>
<thead>
<tr>
<th>Main air pollutants</th>
<th>Overall emissions from human activities (kt)</th>
<th>Emissions from the energy production and use (1) (kt)</th>
<th>Oil refining emissions 2007(2) (kt) (#sites)</th>
<th>Part of emissions from the energy production and use (%)</th>
<th>Part of all emissions from human activities (%)</th>
<th>Oil refining emissions 2009(2) (kt) (#sites)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenhouse gases (CO₂-equivalent)</td>
<td>4 638 000</td>
<td>2 201 000</td>
<td>158 880 (105)</td>
<td>7.2</td>
<td>3.4</td>
<td>146 745 (100)</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>27 921</td>
<td>4634</td>
<td>58 (27)</td>
<td>1.3</td>
<td>0.2</td>
<td>55 (27)</td>
</tr>
<tr>
<td>Fine particulates (PM₁₀)</td>
<td>1 952</td>
<td>312</td>
<td>8 (44)</td>
<td>2.6</td>
<td>0.4</td>
<td>7 (40)</td>
</tr>
<tr>
<td>Fine particulates (PM₂₅)</td>
<td>1 266</td>
<td>224</td>
<td>11</td>
<td>4.9</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen oxides (NOₓ)</td>
<td>10 939</td>
<td>3991</td>
<td>193 (110)</td>
<td>4.8</td>
<td>1.8</td>
<td>162 (105)</td>
</tr>
<tr>
<td>Sulphur oxides (SOₓ)</td>
<td>7 442</td>
<td>6024</td>
<td>574 (111)</td>
<td>9.5</td>
<td>7.7</td>
<td>426 (103)</td>
</tr>
<tr>
<td>Volatile organic compounds (NMVOCs)</td>
<td>8 951</td>
<td>265</td>
<td>180 (98)</td>
<td>67.9</td>
<td>2.0</td>
<td>138 (93)</td>
</tr>
</tbody>
</table>

(1) This sector covers the production of energy from fossil fuels for power and heat generation and industrial manufacturing (NFR Sectors 1A1 and 1A2).
(2) Figures given for NFR Sector 1A1b

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NOₓ), particulates, and sulphur oxides (SOₓ) to the atmosphere.
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Refinery processes require a lot of energy; typically more than 60% of refinery air emissions are related to the production of energy for the various processes.

Sulphur recovery units and flares also contribute to these emissions. Catalyst changeovers and cokers release particulates. Volatile organic compounds (VOCs) are released from storage, product loading and handling facilities, oil/water separation systems and, as fugitive emissions, from flanges, valves, seals and drains. Other emissions to the atmosphere are H₂S, NH₃, BTX, CS₂, COS, HF and metals as constituents of the particulates (V, Ni and others). Table 1.19 shows a very brief summary of the main pollutants emitted by a typical refinery, with their main sources.

Table 1.19: Main air pollutants and their main sources emitted by refineries

<table>
<thead>
<tr>
<th>Main air pollutants</th>
<th>Main sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>Process furnaces, boilers, gas turbines</td>
</tr>
<tr>
<td></td>
<td>Fluidised catalytic cracking regenerators</td>
</tr>
<tr>
<td></td>
<td>CO boilers</td>
</tr>
<tr>
<td></td>
<td>Flare systems</td>
</tr>
<tr>
<td></td>
<td>Incinerators</td>
</tr>
<tr>
<td></td>
<td>LNG plant CO₂ separation</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Process furnaces and boilers</td>
</tr>
<tr>
<td></td>
<td>Fluidised catalytic cracking regenerators</td>
</tr>
<tr>
<td></td>
<td>CO boilers</td>
</tr>
<tr>
<td></td>
<td>Sulphur recovery units</td>
</tr>
<tr>
<td></td>
<td>Flare systems</td>
</tr>
<tr>
<td></td>
<td>Incinerators</td>
</tr>
<tr>
<td>Nitrogen oxides (NO, NO₂)</td>
<td>Process furnaces, boilers, gas turbines</td>
</tr>
<tr>
<td></td>
<td>Fluidised catalytic cracking regenerators</td>
</tr>
<tr>
<td></td>
<td>CO boilers</td>
</tr>
<tr>
<td></td>
<td>Coke calciners</td>
</tr>
<tr>
<td></td>
<td>Incinerators</td>
</tr>
<tr>
<td></td>
<td>Flare systems</td>
</tr>
<tr>
<td>Nitrogen peroxide (N₂O)</td>
<td>Fluidised catalytic cracking regenerators</td>
</tr>
<tr>
<td>Particulates (including metals)</td>
<td>Process furnaces and boilers, particularly when firing liquid refinery fuels</td>
</tr>
<tr>
<td></td>
<td>Fluidised catalytic cracking regenerators</td>
</tr>
<tr>
<td></td>
<td>CO boilers</td>
</tr>
<tr>
<td></td>
<td>Coke plants</td>
</tr>
<tr>
<td></td>
<td>Incinerators</td>
</tr>
<tr>
<td>Sulphur oxides</td>
<td>Process furnaces, boilers, gas turbines</td>
</tr>
<tr>
<td></td>
<td>Fluidised catalytic cracking regenerators</td>
</tr>
<tr>
<td></td>
<td>CO boilers</td>
</tr>
<tr>
<td></td>
<td>Coke calciners</td>
</tr>
<tr>
<td></td>
<td>Sulphur recovery units (SRU)</td>
</tr>
<tr>
<td></td>
<td>Flare system</td>
</tr>
<tr>
<td></td>
<td>Incinerators</td>
</tr>
<tr>
<td>Volatile organic compounds (VOCs)</td>
<td>Storage and handling facilities</td>
</tr>
<tr>
<td></td>
<td>Gas separation units</td>
</tr>
<tr>
<td></td>
<td>Oil/water separation systems</td>
</tr>
<tr>
<td></td>
<td>Fugitive emissions (valves, flanges, etc.)</td>
</tr>
<tr>
<td></td>
<td>Vents</td>
</tr>
<tr>
<td></td>
<td>Flare systems</td>
</tr>
</tbody>
</table>

Carbon dioxide (CO₂) is the greenhouse gas which receives the most attention in the debate about global climate change. The main source of CO₂ emissions is the production of energy. Since the first oil crisis in 1973, refineries have made a concerted effort to enhance energy efficiency. Despite these energy conservation measures, refinery energy demand has increased due to tightened product specifications and a shift over the years from producing heavy fuel oils.
to transport fuels. The fuel used for petroleum refining increased by about 15% in the EU-27 between 1990 and 2007, which represents the third largest key source increase during this period, after road transportation and public electricity and heat production. Even if gaseous fuels use has more than doubled since 1990, liquid fuels still represented in 2007 over 90% of all fuel used. The Netherlands and Italy are, with respectively 5 and 4.5%, the two Member States with the highest relative importance of CO₂ emissions from petroleum refining in their total greenhouse gas emissions.

Carbon monoxide (CO) always appears as an intermediate product of the combustion processes, in particular in under stoichiometric combustion conditions. However, the relevance of CO releases from refineries is not very high compared to CO₂.

Oxides of nitrogen (NOₓ), when emitted to the air, can combine with water and form a component of ‘acid rain’. Further, NOₓ in combination with volatile organic compounds and sunlight, can lead to the formation of ground-level ozone. The source of NOₓ is mainly the combustion processes; during the combustion of fuel, nitrogen (mainly originating from the combustion air itself) is transformed to a mixture of NO₂ and NO. Combustion conditions play an important role here. N₂O (laughing gas) is a powerful greenhouse gas that contributes to the stratospheric ozone depletion.

Particulate emissions (PM) have become a focus of attention because of their potential adverse health effects, in particular for the smallest particulate matter with an aerodynamic diameter <10 µm (PM10 - EN12341) and <2.5 µm (PM2.5 - EN14907). Particulate emissions are caused by the combustion of fuel oils, especially when there is sub-optimal combustion. Another significant source is the cat cracker. The particulate content of toxical compounds (e.g. heavy metals and polycyclic aromatic hydrocarbons) is of primary interest in the refining context.

Sulphur oxides (SOₓ), when emitted to the air, can combine with water and form a component of ‘acid rain’. The main source of SOₓ is the production of energy; during combustion, the sulphur in the fuel is transformed to a mixture of SO₂ and SO₃. Another source, typically smaller, is the flue-gas from the sulphur recovery units. There is a direct relation between the sulphur in the feed to a combustion process and the sulphur oxides in its flue-gas. Generally speaking the sulphur content of the refinery fuel pool is a careful balance between energy required, the type of crude processed, the emission limits and economic optimisations.

Volatile organic carbons compounds (VOC), as mentioned above, can react with NOₓ in the presence of sunlight to form low-level atmospheric ozone. Furthermore, the emission of VOC can give rise to odour problems, which may result in complaints from nearby residents. The source of VOC emissions is the evaporation and leakage of hydrocarbon fractions during potentially associated with all refining activities, e.g. fugitive emissions from pressurised equipment in process units, storage and distribution losses, and waste water treatment evaporation. Hydrocarbons may also be emitted during non-optimal combustion conditions, but these are only a small contribution.

Given the progress that refineries have made in the abatement of sulphur emissions to air, the focus has started to shift towards VOC (including odour), particulates (size and composition) and NOₓ, as it has in the environmental debate generally. When the carbon dioxide emissions debate gathers momentum, it will also strongly affect refineries.

### 1.4.2 Emissions to water

Water is used intensively in a refinery as process water and for cooling purposes. Its use contaminates the water with oil products mainly increasing the oxygen demand of the effluent. Refineries discharge waste water which originates from:
Process water, steam and wash water. These waters have been in contact with the process fluids, and apart from oil, will also have taken up hydrogen sulphide (H₂S), ammonia (NH₃) and phenols. The more severe the conversion processes, the more H₂S and NH₃ are taken up by the process water. The process water is treated in several, well known steps before discharge to the environment.

Cooling water, once through or circulating systems. This stream is theoretically free of oil. However, leakage into once through systems, even at low concentrations, can result in significant mass losses because of the large volume of water involved.

Rainwater from process areas. This type of water has not been in contact with the process fluids, but it comes from rainfall on surfaces which are possibly oil-polluted. It is often referred to as ‘accidently oil-contaminated’ water and is typically treated prior to discharge to the environment.

Rainwater from non-process areas. This stream is oil-free.

Oil and hydrocarbons are the main pollutants found in waste water generated by refineries. Other pollutants found in waste water generated by refineries are hydrogen sulphide, ammonia, phenols, benzene, cyanides and suspended solids containing metals and inorganic compounds (e.g. halides, sulphates, phosphates, sulphides). Table 1.20 gives a summary of the main water pollutants as well as their main sources.

Petroleum refineries consume water on a continuous basis to maintain the water balances in the steam, cooling water, utility service water, and emergency fire water supply circuits. Water is also consumed for process and maintenance use purposes.

The losses from the steam and cooling water circuits include, but are not limited to:

- condensate purge;
- consumed steam;
- evaporation;
- cooling water purge, and circuit leaks.

The losses from the emergency fire water supply circuits may include scheduled maintenance purges, water used to test and/or utilize emergency fire fighting equipment, and circuit leaks. Some of the consumed steam that is input into processing systems comes in direct contact with various fractions of hydrocarbons and substances. The condensates resulting from these uses are separated and extracted from the processing system. Condensates may be collected and processed through a steam stripper to separate and extract hydrogen sulfide (H₂S) and ammonia (NH₃) from the water. The stripped water may then be used for other refining processes such as crude desalting or water washing of process streams.

The water used for process purposes such as crude desalting or water washing will come in direct contact with either crude oil or other various fractions of hydrocarbons and substances. Wash water and/or steam used to clean and purge systems for maintenance activities can also generate waste water that has been in direct contact with these substances.

Other sources of waste water include, but are not limited to:

- water separated and removed from crude oil, intermediate, and product tanks;
- storm water, utility service water, steam condensate and/or emergency firewater that comes in contact with crude oil, intermediates, products, additives, chemicals, and/or lubricating oils in the drainage area;
- water originating from ballast water tanks of vessels off loading or loading petroleum based materials;
- routine and/or special waste solid-liquid separation activities;
- routine and/or special ground water extraction activities;
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- water discarded from periodic tank and piping system hydro test and metal passivation activities;
- water for sanitary usage.

Rain water falling onto the site can also come into contact with crude oil and various fractions of hydrocarbons and substances due to entry into some tank systems, secondary containment systems, loading and offloading areas for trucks, railcars, and vessels, production areas that include equipment containing these substances and maintenance work areas.

Rain water falling onto some non-process areas of the site may have a relatively low risk for coming into contact with materials and substances and therefore may not require a treatment technique prior to discharge into the environment.

A refinery site, therefore, produces a collective mix of waste water streams containing insoluble and soluble substances which become pollutants when released.

Waste water treatment techniques are therefore applied to control the amounts of these pollutants. Treatment techniques are typically directed at reducing the amount of pollutants and the oxygen demand exerted by the waste water before it is released.

The main pollutant parameters include:
- total hydrocarbon content (THC);
- biochemical oxygen demand (BOD);
- chemical oxygen demand (COD);
- ammoniacal nitrogen, total nitrogen;
- total suspended solids (TSS);
- total metals.

Other pollutant parameters include:
- total organic carbon (TOC);
- cyanides;
- fluorides phenols;
- phosphates;
- sulfides and other micro-pollutants.

Table 1.20 provides a summary of some of the main water pollutants and their sources within a refinery.

<table>
<thead>
<tr>
<th>Water pollutant Source</th>
<th>Water pollutant</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary/domestic blocks</td>
</tr>
<tr>
<td>H₂S (RSH)</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary/domestic blocks</td>
</tr>
<tr>
<td>NH₃(NH₄⁺)</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, sanitary/domestic blocks</td>
</tr>
<tr>
<td>Phenols</td>
<td>Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water</td>
<td>Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary/domestic blocks</td>
</tr>
<tr>
<td>Organic chemicals (BOD, COD, TOC)</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary/domestic blocks</td>
<td>Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, sanitary/domestic blocks</td>
</tr>
<tr>
<td>CN⁻, (CNS⁻)</td>
<td>Visbreaker, catalytic cracking, spent caustic, ballast water</td>
<td>Visbreaker, catalytic cracking, spent caustic, ballast water</td>
</tr>
<tr>
<td>TSS</td>
<td>Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary/domestic blocks</td>
<td>Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary/domestic blocks</td>
</tr>
<tr>
<td>Amines compounds</td>
<td>CO₂ removal in LNG plants</td>
<td>CO₂ removal in LNG plants</td>
</tr>
</tbody>
</table>

Source: [115, CONCAWE, 1999]
Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted
to prevention and reduction of contaminated waste water streams to the final treatment units.

Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted
to prevention and reduction. Reduction of water use and/or the concentration of pollutants in the
water, can have effects in reducing the final emission of pollutants.

Table 1.21: Evolution of some water pollutants released from refineries

<table>
<thead>
<tr>
<th>EPRTR data</th>
<th>Tonnes/year 2004</th>
<th>Number of sites 2004</th>
<th>Tonnes/year 2007</th>
<th>Number of sites 2007</th>
<th>Tonnes/year 2009</th>
<th>Number of sites 2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>6.475</td>
<td>42</td>
<td>7.951</td>
<td>42</td>
<td>6.074</td>
<td>41</td>
</tr>
<tr>
<td>Phenols</td>
<td>45</td>
<td>56</td>
<td>59</td>
<td>59</td>
<td>42</td>
<td>59</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>2.769</td>
<td>25</td>
<td>2.245</td>
<td>20</td>
<td>2.103</td>
<td>21</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>133</td>
<td>10</td>
<td>201</td>
<td>12</td>
<td>99</td>
<td>11</td>
</tr>
</tbody>
</table>

Source: [74, EC 2010]

1.4.3 Waste generation

The amount of waste generated by refineries is small if it is compared to the amount of raw
materials and products that they process. Table 1.23 shows the production and different waste
routes according to the European Pollutant Release and Transfer Register (E-PRTR)
declarations. Oil refinery waste normally covers three categories of materials:

- sludges, both oily (e.g. tanks bottoms) and non-oily (e.g. from waste water treatment
  facilities),
- other refinery wastes, including miscellaneous liquid, semi-liquid or solid wastes (e.g.
  contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash,
  spent caustic, spent clay, spent chemicals, acid tar) and,
- non-refining wastes, e.g. domestic, demolition and construction.

Table 1.22 shows a summary of the main types of solid wastes generated in a refinery and their
sources.
Table 1.22: Main solid wastes generated by refineries

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Category</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oiled materials</td>
<td>Oily sludges</td>
<td>Tank bottoms, biotreatment sludges, interceptor sludges, waste water treatment sludges, contaminated soils, desalter sludges</td>
</tr>
<tr>
<td></td>
<td>Solid materials</td>
<td>Contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon</td>
</tr>
<tr>
<td>Non-oiled materials</td>
<td>Spent catalyst (excluding precious metals)</td>
<td>Fluid catalytic cracking unit catalyst, hydrosulphurisation/hydrotreatment) catalyst, polymerisation unit catalyst, residue conversion catalyst</td>
</tr>
<tr>
<td></td>
<td>Other materials</td>
<td>Resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes</td>
</tr>
<tr>
<td>Drums and containers</td>
<td></td>
<td>Metal, glass, plastic, paint</td>
</tr>
<tr>
<td>Radioactive waste (if used)</td>
<td></td>
<td>Catalysts, laboratory waste</td>
</tr>
<tr>
<td>Scales</td>
<td></td>
<td>Leaded/unleaded scales, rust</td>
</tr>
<tr>
<td>Construction/demolition debris</td>
<td></td>
<td>Scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood</td>
</tr>
<tr>
<td>Spent chemicals</td>
<td></td>
<td>Laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/diethanol amine), TML/TEL (tetra methyl/ethyl lead)</td>
</tr>
<tr>
<td>Pyrophoric wastes</td>
<td></td>
<td>Scale from tanks/process units</td>
</tr>
<tr>
<td>Mixed wastes</td>
<td></td>
<td>Domestic refuse, vegetation</td>
</tr>
<tr>
<td>Waste oils</td>
<td></td>
<td>Lube oils, cut oils, transformer oils, recovered oils, engine oils</td>
</tr>
</tbody>
</table>

Source: [108, USAEPA, 1995]

Table 1.23: Waste production declaration

<table>
<thead>
<tr>
<th>Waste types</th>
<th>Waste routes</th>
<th>2007</th>
<th>2009</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Thousand of tonnes/year</td>
<td>Number of sites</td>
<td>Thousand of tonnes/year</td>
<td>Number of sites</td>
</tr>
<tr>
<td>Hazardous waste in country</td>
<td>Disposal</td>
<td>294</td>
<td>103</td>
<td>405</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td>306</td>
<td>98</td>
<td>372</td>
<td>103</td>
</tr>
<tr>
<td>Hazardous waste outside the country</td>
<td>Disposal</td>
<td>3</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td>34</td>
<td>30</td>
<td>19</td>
<td>23</td>
</tr>
<tr>
<td>Non hazardous waste</td>
<td>Disposal</td>
<td>372</td>
<td>60</td>
<td>262</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td>538</td>
<td>61</td>
<td>500</td>
<td>64</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>1 547</td>
<td>61</td>
<td>1 562</td>
<td>64</td>
</tr>
</tbody>
</table>

Source: E-PRTR and CONCAWE data 2007-2009

Oil retained in sludges or other types of waste represents a loss of product and, where possible, efforts are made to recover such oil. Waste disposal depends very much on its composition and on the local refinery situation. Because of the high operating costs of waste disposal, much priority has been given to waste minimisation schemes.

Waste generation trends show that oily sludge production is declining, mainly through housekeeping measures, whereas biological sludge generation has increased as a result of increased biotreatment of refinery effluent. Spent catalyst production is also increasing through the installation of new hydrocrackers, hydrotreatment facilities and catalytic cracker dust collectors. For all these waste categories, increased use is made of third party waste contractors for off-site treatment and disposal.
Chapter 1

1.4.4 Soil and groundwater contamination

Most refineries have some areas that are contaminated by historical product losses. Current refinery practices are designed to prevent spillages and leaks to the ground. In the past, the awareness of the potential risks of these contaminated areas was low. The two main issues here are the prevention of new spills and the remediation of historic contamination. As mentioned within the scope, soil remediation is not included in the scope of this document. Most oil fractions are biodegradable, given time. The thinking about the cleaning-up of these contaminated areas has changed over the years. Increased knowledge about soil sciences and the difficulty of soil remediation on a site that is still in operation, has lead to the pragmatic approach of managing the risks of these contaminated sites to ensure their fitness for use and ensuring that pollution does not spread beyond the site. There are a number of ongoing research initiatives for improving the performance of on site remediation techniques.

The main sources of contamination of soil and groundwater by oil are typically these places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground. These are commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon-containing water. The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists.

1.4.5 Other environmental issues

Besides the environmental issues mentioned in the above sections, especially for refineries situated near residential areas, environmental nuisances have become an issue of discussion with both local authorities and with representatives of the local population in so-called neighbourhood councils. Topics such as noise, light, and smoke emission (flaring) and smell odour which directly impact the residents receive much more emphasis in these neighbourhood councils than the above-mentioned “major” emissions which tended to receive more attention historically.

Aggravation by light can be caused through flaring at night by refineries and petrochemical plants located near densely populated areas.

Potential environmental issue regarding heat discharged by cooling water to the sea or rivers may also be considered. Since the 1970s, refineries have devoted considerable resources to increase process safety, both in design and operation by training, procedures and personal protection equipment. Increased attention, training, safe design and adequate tools and personal protection equipment has resulted in a steady decrease in the number of unsafe acts, accidents, incidents and near misses.

Occupational health is included in the operational safety procedures aimed at protecting workers from exposure to toxic materials and providing them with all necessary facilities which contribute to their well-being and their sense of security and safety. Instructions, information exchange and the training of personnel, the provision of personal protection equipment as well as strict adherence to stringent operational procedures have contributed to a steady decrease in accidents and health incidents. Typical refinery pollutants and products with a health risk include hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NOx and SOx, for which legally binding maximum acceptable concentrations values prevail.

The design of the refinery installations and the process control systems need to include provisions for a safe shutdown with minimum emissions from the unit involved. During unplanned operational upsets, these provisions should guarantee that feed supply is terminated followed by subsequent pre-programmed automated activation of pumps, relief systems, purging systems, flares and other equipment. Examples of such occurrences are utility failure, the breakdown of equipment, a fire or an explosion. Emergency situations leading to direct
spills occurring in parts of the plant which are neither fully contained nor fully automated, such as pipeline and tank bottom rupture, have to be addressed with standing emergency procedures. These procedures should aim at the minimisation and containment of the spills, followed by the rapid clean-up in order to minimise the environmental impact.
2 APPLIED PROCESSES AND TECHNIQUES

This section describes the major activities and processes that may be found within the natural gas plant sector and the petroleum-refining industry, including the materials and equipment used and the processes employed. This chapter is designed for those interested in gaining a general understanding of the processes and activities that can be found in these two industrial sectors, and for those interested in the interrelationship between the industrial process and the topics described in subsequent chapters of this document which include emission, consumption and best available techniques for the different processes. This section does not attempt to replicate published engineering information that is available for this industry in the general literature.

The major production unit operations and activities typically involved at petroleum refineries are described briefly, in alphabetical order, in this chapter. For many of these production operations, a number of different techniques and/or unit operations are used in the industry. While the major techniques used for each process/activity are described, the intention is not to describe all of the different processes currently in use. This chapter specifically describes the purpose and principle of the process, feed and product streams, a brief process description of commonly used production processes/activity and operability. This information, coupled with schematic drawings of the identified processes, provides a concise description of the process/activity.

The first section is dedicated to a general technical description of refineries, and the subsequent 24 sections cover all the processes and activities within the scope of the BREF. The processes of natural gas plants are included in one independent section (Section 17). These sections do not pretend to be of equal importance from the environmental impact point of view. Some sections have more relevance than others, but this approach allows for clearer presentation of the BAT assessment for the mineral oil and gas refinery sectors. No pollution abatement technique is included in this chapter. However, some of the processes (e.g. hydrotreatments) have an environmental aspect. Environmental implications of production techniques can be found in Chapter 3. Discussion on good environmental practices (prevention techniques) of production techniques can be found in Chapter 4. As a consequence of that, no information about emissions can be found in Chapter 2. Information on, for instance, flares, sulphur recovery units, waste water systems and waste management is not included in this chapter because these activities are not considered production activities. They are security or environmental techniques that are applied in both sectors.

2.1 General overview of the refinery processes

Crude oil and natural gas are mixtures of many different hydrocarbons and small amounts of impurities. The composition of these raw materials can vary significantly depending on the source (see Section 9.3 for type of crude oils). Petroleum refineries are complex plants, where the combination and sequence of processes are usually very specific to the characteristics of the raw materials (crude oil) and the products to be produced. In a refinery, portions of the outputs from some processes are fed back into the same process, fed to new processes, fed back to a previous process or blended with other outputs to form finished products. One example of that can be seen in Figure 2.1, which also shows that all refineries are different regarding their configuration, process integration, feedstock, feedstock flexibility, products, product mix, unit size and design and control systems. In addition, differences in owner strategy, market situation, location and age of the refinery, historic development, available infrastructure and environmental regulation are amongst other reasons for the wide variety in refinery concepts, designs and modes of operation. The environmental performance can also vary from refinery to refinery.

The production of a large number of fuels is by far the most important function of refineries and will generally determine the overall configuration and operation. Nevertheless some refineries can produce valuable non-fuel products such as feedstocks for the chemical and petrochemical
industries. Examples are mixed naphtha feed for a steam cracker, recovered propylene, butylene for polymer applications and aromatics manufacture covered under the Large Volume Organic Chemical Industry BREF. Other speciality products from a refinery include bitumen, lubricating oils, waxes and coke. In recent years the electricity boards in many countries have been liberalised, allowing refineries to feed surplus electricity generated into the public grid.

Refining crude oil into usable petroleum products can be separated into two phases and a number of supporting operations.

The first phase is the desalting of crude oil (Section 2.9) and the subsequent distillation into its various components or ‘fractions’ (Section 2.19). A further distillation of the lighter components and naphtha is carried out to recover methane and ethane for use as refinery fuel, LPG (propane and butane), gasoline-blending components and petrochemical feedstocks. This light product separation is done in every refinery.

The second phase is made up of three different types of ‘downstream’ processes: combining, breaking and reshaping fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. The goal of these processes is to convert some of the distillation fractions into marketable petroleum products (see Section 10.3) through any combination of downstream processes. These processes define the various refinery types, of which the simplest is the ‘hydroskimming’, which merely desulphurises (Section 2.13) and catalytically reforms (Section 2.6) selected cuts from the distillation unit. The amounts of the various products obtained are determined almost entirely by the crude composition. If the product mix no longer matches the market requirements, conversion units have to be added to restore the balance.

The market demand has for many years obliged refineries to convert heavier fractions to lighter fractions with a higher value. These refineries separate the atmospheric residue into vacuum gasoil and vacuum residue fractions by distillation under high vacuum suction (Section 2.19), and then feed one or both of these cuts to the appropriate conversion units. Thus by inclusion of conversion units, the product slate can be altered to suit market requirements irrespective of the crude type. The number and the possible combinations of conversion units are large.

The simplest conversion unit is the thermal cracker (Section 2.22) by which the residue is subjected to such high temperatures that the large hydrocarbon molecules in the residue convert into smaller ones. Thermal crackers can handle virtually any feed, but produce relatively small quantities of light products. An improved type of thermal cracker is the coker (Section 0), in which all of the residue is converted into distillates and a coke product. In order to increase the degree of conversion and improve product quality, a number of different catalytic cracking processes have evolved, of which fluid catalytic cracking (Section 2.5) and hydrocracking (Section 2.13) are the most prominent. Recently, residue gasification processes (Section 2.14) have been introduced within refineries, which enable refineries to eliminate heavy residues completely and to convert them into clean syngas for captive use and the production of hydrogen, steam and electricity via combined cycle techniques.

Supporting operations are those not directly involved in the production of hydrocarbon fuels but serve in a supporting role. They may include energy generation, waste water treatment, sulphur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and storage of products.

As mentioned in Section 1.3.1, there are various approaches to compare refineries due to the difference in complexity that they have. This can be done by defining refinery complexity indexes as they have been explained in Section 1.3.1. The Nelson refinery complexity index was used for the construction of Figure 1.9 [287, Johnston, 1996]. In Dutch notes [118, VROM, 1999] EU refineries are grouped by configuration, as shown in Table 1.17. CONCAWE [115, CONCAWE, 1999] has grouped refineries by types (that differ in definition from the
configurations of Table 1.17 in Figure 1.10 as they existed in the period 1960–1997. Other definitions are used in the industry, such as the FCC equivalent (used by CEC DG Transport reports on the refining industry) or the Equivalent Distillation Capacity as used by Solomon Associates. Some of these parameters will be used in the document.

Table 2.1 summarises the main products obtained from the main refinery processes. As can be seen, many of the products are obtained from different units and consequently it gives an idea of the technical complexity and the modes of operation that may be found in a refinery. This is one aspect of the technical complexity and the variety of modes of operation that may be found in a refinery.

An overview of the general scheme of a complex refinery is provided in Figure 2.1. This figure can be used as a synoptic of Chapters 2, 3 and 4 of this BREF Document. For each of the displayed units or processes, it provides, in particular (in red), the corresponding section number which is used over these three chapters, according to the general structure given in the Scope section (see page 43).
Figure 2.1: General scheme of a complex oil refinery

DAO: Deasphalted oil  
HDS: Hydro desulphurisation  
DEA: Diethylamine  
FCC: Fluid catalytic cracker  
HGO: Heavy gas oil  
LGO: Light gas oil  
HC: Hydrocracking  
VGO: Vacuum gas oil
Table 2.1: Refinery units and their main products

<table>
<thead>
<tr>
<th>Products → refinery units</th>
<th>Section</th>
<th>LPG</th>
<th>Gasoline</th>
<th>Kero/naphtha</th>
<th>Heating oil/diesel</th>
<th>HFO</th>
<th>Base oil</th>
<th>Coke/bitumen</th>
<th>Special</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon No range</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Alkylation</td>
<td>2</td>
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<td>Base oil production</td>
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<td>Bitumen production</td>
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<td>Catalytic cracker</td>
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<td>Residue cracking</td>
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<td>Catalytic reforming</td>
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<td>Delayed coking</td>
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<td>Gasification</td>
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<td>Etherification</td>
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<td>Gas separation processes</td>
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<td>Hydrogen plant</td>
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<td>Residue Hydroconversion</td>
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<td>Hydrocracker</td>
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<td>Hydrodesulphurisation</td>
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<td>Crude atmospheric distillation</td>
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<td>Vacuum distillation</td>
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<tr>
<td>Thermal cracking/Visbreaking</td>
<td>22</td>
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<tr>
<td>Sulphur recovery unit</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Carbon No range: C3-C4, C4-C12, C8-C17, C8-C25, >C8, >C15, >C30
- Alkylation: Wax
- Base oil production: H2
- Bitumen production: Low joule gas
- Catalytic cracker: Syngas
- Residue cracking: MTBE
- Catalytic reforming: Refinery fuel gas
- Delayed coking: H2
2.2 Alkylation

Purpose and principle
The purpose of alkylation is to yield high-quality motor fuel after blending. The term alkylation is used for the reaction of olefins with isobutane, to form higher molecular-weight isoparaffins with a high octane number. The process involves low-temperature reaction conditions conducted in the presence of strong acids.

Feed and product stream
Low molecular weight olefins (C3-C5) and isobutane are used as alkylation unit feedstocks. The major sources of low olefins are catalytic crackers and cokers. Isobutane is produced by hydrocrackers, cat crackers, catalytic reformers, crude distillation and natural gas processing. In some cases, n-butane is isomerised (see Section 2.16) to produce additional isobutane. The product is alkylate (a high-octane gasoline component) with some propane and butane liquids. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range. Dissolved polymerisation products are removed from the acid as thick dark oil.

Process description
Two processes have dominated historically where in the alkylation unit, hydrofluoric acid (HF) or sulphuric acid (H2SO4) were used as a catalyst. When the concentration of acid becomes low, some of the acid must be removed and replaced with fresh acid. Safety incidents and accidents in the HF units have set a new process scenario:

- sulphuric acid dominated the new investments since 1980.
- additives are now available to reduce the HF volatility and several mitigation systems have been developed to improve safety.
- soli-acid catalyst alternatives have improved in later years but industrial sites have not yet reported successful start-up or operational results. OandG Journal world refinery survey January 2011. Baku Heydar Aliyev Refinery (Azerbaijan) 75, OandG Journal 2011 selected a soli-acid alkylation unit for the basic design. Several available commercial processes are described in Chapter 6 Emerging Techniques.
- ionic liquid technology has gathered new patents and developments. A 65 000 tonnes per year plant in China has been retrofitted and has reported successful results (see chapter 6). There are also techniques to facilitate the retrofitting of a HF plant into a H2SO4 unit

Both process options need safety requirements because of large LPG volume. HF is more specifically hazardous due to possible skin penetration and destruction at tissue levels (and pulmonary oedema). In section 4.2.4, the trade-off between process alternatives is described.

In the hydrofluoric acid process, the slipstream of acid is redistilled. The concentrated hydrofluoric acid is recycled and its net consumption is relatively low. In this process (Figure 2.2), the feed enters the reactor and is mixed with the recycled isobutane and HF from the settler. Both the olefin and isobutane feeds are dehydrated first (not in Figure 2.2), as this is essential to minimise the potential corrosion. The reactor, operating at 25 - 45 °C and 7 – 10 barg, is cooled to remove the heat generated by the reaction. In the settler, alkylate and excess isobutane are separated from the HF. The HF is recycled to the reactor. A slipstream is regenerated by distillation. The organic phase from the settler consisting of the alkylate and unreacted isobutane flows to the isostripper. There, the isobutane and some other light components are stripped from the alkylate. This is routed as product to storage after treating it with potassium hydroxide (KOH). The decomposition of any organic fluoride formed is promoted by the high tube wall temperatures. The butane feed (n and iso) is normally fed to the isostripper. Saturated butanes are normally distilled outside the alkylation unit to produce a concentrated stream of isobutane, which is fed to the alkylation unit with the olefin feed. The isostripper overhead, essentially isobutane, is returned to the reactor. A small overhead slipstream is sent to a depropaniser, where propane is removed. The bottoms of the depropaniser (isobutene plus isobutane) are routed to the isobutane circulation stream, while the depropaniser
overhead stream (propane) passes through a HF stripper to remove traces of HF and is sent to storage after final KOH treatment. From the unit feed stream, normal butanes Normal butanes which come in with the unit feed streams are drawn off as a side-stream from the iso stripper, treated with KOH and sent to storage.

In the sulphuric acid process, (see Figure 2.3 below), the reactor operates at 4-15 °C, which requires chilling. Spent sulphuric acid generation is substantial and the sulphuric acid removed must be regenerated in a sulphuric acid plant (not considered as part of the alkylation unit). In this process, the olefin feed and recycled isobutane are introduced into the stirred, autorefrigerated reactor. Mixers provide intimate contact between the reactants and the acid catalyst and the reaction heat is removed from the reactor. The hydrocarbons that are vaporised from the reactor are routed to the refrigeration compressor where they are compressed, condensed and returned to the reactor. A depropaniser, which is fed by a slipstream from the refrigeration section, is designed to remove any propane introduced to the plant with the feeds. The reactor product is sent to the settler where the hydrocarbons are separated from the acid that is recycled. The hydrocarbons that are sent to the deisobutaniser together with make-up isobutene and isobutane, and the isobutene isobutane rich overhead is recycled to the reactor. The bottoms are then sent to a debutaniser to produce alkylate product. The aim is to produce high octane branched chain hydrocarbons for the gasoline pool. The process combines olefin and butylene feeds in the presence of strong sulphuric acid. Feed contact the recycle stream of \( \text{H}_2\text{SO}_4 \) in the reactor. The reactor circulation stream enhances a large interfacial area at low temperature (4-15 °C). Reaction products are first separated in a flash drum and then through a debutaniser. Onsite acid regeneration is also feasible (i.e. WSA technique).
Figure 2.3: Simplified process flow scheme for sulphuric acid alkylation

The AlkyClean soli-acid process is addressed in Chapter 6, Text has been moved to Chapter 6 Emerging techniques.
2.3 Base oil production

Although only 20% of EU refineries produce base oil, some actually specialise in it. Figure 1.7 (in Chapter 1) identifies the refineries specialised in the production of lubricant and bitumen. More extensive information about the processes can be found in the general literature (e.g. [319, Sequeira, 1998]).

Purpose and principle
Lubricants are a blend of different grades of base oils and special additives. To produce a suitable lubricant, certain properties of the base oil are very important: viscosity, viscosity index (high VI means that the viscosity changes very little as temperature changes, and vice versa), high resistance to oxidation, low pour point and good dope susceptibility or compatibility. The principle of base oil production is to separate the desired boiling range components from the atmospheric residue by vacuum distillation (Section 2.19); unwanted components are subsequently removed by different processes and optional hydrofinishing. Base oil is a speciality product and consequently not all crudes are suitable. Heavy crudes are frequently used as feedstock to conventional base oil complexes.

Feed and product stream
The feedstocks of a conventional base oil complex are waxy distillate side-streams from vacuum distillation units (Section 2.19) and the extracts from deasphalting units. Atmospheric residue feedstock to the vacuum distillation unit consists of various types of hydrocarbon compounds with different suitability for base oils:

a. **aliphatic or paraffinic**: Normal (n-)paraffins and iso (i-)paraffins form this group. The n-paraffins have a high VI and melting points, and at ambient conditions form crystals, which must be removed to reduce the pour point of lubricating. I-paraffins have lower melting points, very high VI but lower viscosity;

b. **naphthenic**: The naphthenic rings lend high viscosity, low melting point and a good VI (less than paraffins) to lubricant oils;

c. **aromatic**: The aromatic rings lend high viscosity and low melting point to compounds but a low VI to the oils. For this reason they are considered the least satisfactory type of compounds for lubricants. The ratio in which the three groups are present varies from crude to crude.

In the various processes of the base oil production, significant quantities of by-products such as bitumen, extracts and wax are produced. Based on a total feedstream to the vacuum distillation unit, on average some 20 – 25% end up as final base oil product.

Process description
A base oil complex consists typically of a vacuum distillation tower (Section 2.19), a deasphalting unit, an aromatic extraction unit, a dewaxing unit and an optional high-pressure hydrogenation unit and hydrofinishing unit to improve colour and stability, meet product specifications and remove impurities. Figure 2.4 shows a simplified block diagram of a base oil manufacturing plant.
A conventional base oil complex is very labour intensive mainly due to its batch operation, the many grades of base oil normally produced and the associated intensive product handling operations.

There are many possible routes for improving base oil quality. Continued evolution of the all-hydroprocessing route is one likely possibility. Selectivity toward desired molecular compositions could be bettered by improving the catalysts and the processing technology. Improving the feedstock can also improve the product. Four hydrosprocessing technologies are available to produce improved base oils of API group II and III quality level oils:

- integrated solvent hydrosprocessing;
- catalytic hydrosprocessing;
- very high viscosity index (VHVI) base oils from slack wax hydroisomerization;
- very high viscosity index (VHVI) base oils from fuel hydrocracker bottoms.

Several trademark processes have been developed to reach the corresponding performance characteristics.

For the future, the trend is toward even higher base oil purity, higher viscosity index, lower volatility, and longer life.

**Deasphalting**

Solvent deasphalting produces lubricating oil base stocks by extracting high-boiling lighter paraffinic and naphthenic hydrocarbons (asphaltenes and resins) from the vacuum residue of the vacuum distillation unit. This process makes the deasphalted oil extract light and paraffinic and the bitumen raffinate heavy and aromatic. Propane or propane-butane mixtures are usually used as solvents. At specific operating conditions, 37 – 40 bar and 40 – 70 °C, lower boiling paraffinic and naphthenic hydrocarbons are very soluble in propane. At higher temperatures (100 °C) all hydrocarbons are almost insoluble in propane. The solvent deasphalting process is a typical extraction process consisting of an extractor and recovery sections, flash evaporation and stripping, to separate the propane solvent from the oil and bitumen phase. The deasphalted oil product stream is run down to intermediate storage; the bitumen product stream can be blended to heavy fuel, used as feedstock for the coker or used for the bitumen product.

More recently, solvent deasphalting has been adapted for the preparation of catalytic cracking, hydrocracking, hydrodesulphuriser feeds and hard bitumen (deep deasphalting). For these purposes, heavier-than-propane solvents (butane to hexane mixture) are used together with higher operating temperatures. This maximises the yield of valuable deasphalted oil and minimises the yield of hard bitumen with a softening point usually over 150 °C.
Aromatic extraction
Aromatic extraction uses solvents to remove aromatics from base oil feedstocks, improving viscosity, oxidation resistance, colour and gum formation. A number of different solvents can be used (furfural, N-methyl-2-pyrrolidone [NMP], phenol, cresol or liquid sulphur dioxide). These processes are typical extraction processes consisting of an extractor and recovery sections, flash evaporation and stripping to separate the solvent from the oil-rich raffinate and aromatic-rich extract stream. Typically, feed lube stocks are contacted with the solvent in a packed tower or rotating disc contactor. Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The raffinate stream is rundown to intermediate storage. The extract, after solvent recovery, is likely to contain high concentrations of sulphur, aromatics, naphthenes and other hydrocarbons, and is often fed to the hydrocracker or cat cracker unit.

High pressure hydrogenation unit
The hydrogenation process is used to reduce aromatics and olefinic compounds found in the base oil streams.

Dewaxing
Dewaxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures. This process is used when paraffinic-rich crude oils are processed. Solvent dewaxing is more prevalent. In these units, the high pour point constituents (mainly paraffins) are removed from the raffinate streams. The oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallised, and then filtered to remove the wax. Solvents used for the process include propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK), toluene or chlorinated hydrocarbons. Solvent is recovered from the oil and crystallised wax through heating, two-stage flashing, followed by steam stripping. The wax is removed from the filters, melted and subsequently fed to a solvent recovery unit to separate the solvent from the wax. The wax is either used as feed to the catalytic cracker or is de-oiled and sold as industrial wax.

Hydrofinishing
In this unit, the colour and colour stability is improved and the organic acid components are removed. Sulphur content is also reduced. The need for hydrofinishing depends on the crude oil processed and to a certain extent on the patent owner and the design of the preceding units. The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).

Text partially moved from Section 4.3.5.

In standalone lube oil refineries, the small amounts of H₂S generated due to hydrotreatment are normally incinerated because the erection of a Claus unit is not available justified economically. Instead of hydrotreatment, sulphuric acid and clay treatments may typically be used in old plants.

Reference literature
[19a, Irish EPA, 1993], [268, TWG, 2001], [76, Hydrocarbon processing, 2011].

2.4 Bitumen production
Bitumen is a residue derived from certain crude oils (e.g. Middle East, Mexico or South America) after vacuum distillation has removed waxy distillates. Bitumen is normally mixed with other components (e.g. gravel) to produce asphalt that is used in road paving, roof coating and pipe sealing or coating. Bitumen production only appears in some refineries (45% of the EU refineries). There are also some refineries that specialise in producing these components. Figure 1.7 (in Chapter 1) identifies the lubricant-and bitumen-specialised refineries.
Purpose and principle

The desired properties of bitumen may be achieved either by adjusting distillation conditions or by ‘blowing’. In the latter process, air is blown into hot bitumen causing dehydrogenation and polymerisation reactions and creating a harder product with higher viscosity, higher softening point and a reduced penetration. (The penetration, often used as the main criterion, refers to the depth of penetration by a standard needle in a bitumen sample at standard conditions.). The properties of the blown bitumen are determined by the residence time in the oxidation vessel, the air rate and the liquid temperature. If any of these parameters is increased, the penetration is reduced and the softening temperature is raised.

Feed and product streams

In most applications the hydrocarbon feed stream to a bitumen blowing unit (BBU) is the bottom residue stream from a vacuum unit (Section 2.19) and in some instances the residue (extract) from a deasphalting unit (Section 2.3).

Normally, a number of different grades of bitumen are produced in campaigns and these are further modified by blending with other high-boiling components such as vacuum residue, heavy gas oil or synthetic polymers. In this way a single blowing unit is able to cater for a wide range of bitumen grades for various applications.

Polymer additives Styrene Butadiene Styrene(SBS), Ethylene Vinyl Acetate (EVA), Natural rubber,… are used for heavy duty service bitumen production. They do not change chemical structure of the bitumen but change its mechanical properties. The polymers modify the bitumen’s properties such as the softening or brittleness point, and aim at improving longevity.

Process description

The BBU will either operate on a continuous basis or in batch mode depending on the quality of the vacuum residue feedstock and the required bitumen product specification. Continuous processes are more common in refineries. A simplified process flow diagram of the BBU is shown in Figure 2.5 which represents a typical, continuously-operated BBU receiving its hot feed directly from the vacuum distillation unit. Where the bitumen feed is received from storage, an additional fired heater may be required to preheat the feed to a temperature of about 200 - 250°C, but it can be up to 550 °C. With a batch-operated BBU, a feed buffer vessel is usually included to store the hot feedstream from the vacuum unit.
The residue feedstream is pumped into the top of the oxidation vessel. Operating pressure in the top of the oxidation vessel is normally around 1 barg and in the bottom around 2 barg, depending on the height of the vessel. As air is sparged into the base of the vessel, oxidation of the residue takes place, resulting in heat. The temperature in the oxidation vessel, which determines to a certain extent the bitumen grade, is normally controlled between 260 and 300 °C. Different options are applied for adjusting the temperature, which include taking in the addition of colder feed to the oxidation vessel, the recirculation of cooled bitumen product from the bitumen rundown cooler, and in older units even direct water quenching is applied. The blown bitumen is removed from the bottom of the oxidation vessel and cooled by raising steam before being sent to storage.

The air rate is normally well in excess of stoichiometric requirements and so a considerable quantity of oxygen is present in the upper vapour space of the oxidation vessel. To avoid an explosion in the vapour space, in most units, steam is injected at a rate necessary to keep the oxygen concentration below the lower flammable limit (5 – 6 % v/v.). In some units a small amount of water is also injected into the vapour outlet of the oxidation vessel to reduce the vapour temperature. This is sometimes considered necessary to prevent afterburning in the overhead system that could lead to severe coke formation.

The overhead vapours are first passed through a vent gas scrubber to remove oil and other oxidation products. In most cases gasoil is used as once-through scrubbing liquid. The vent gas from the scrubber is subsequently cooled to condense light hydrocarbons and sour water, sometimes in a water spray contact condenser or scrubber. The remaining gas, consisting mainly of light hydrocarbons, N₂, O₂, CO₂ and SO₂, is incinerated at high temperatures (~800 °C) to ensure complete destruction of minor components such as H₂S, complex aldehydes and organic acids and phenolics, which have a highly unpleasant odour.

The majority of the BBUs produce the higher grades of bitumen (roof and pipe coatings) and normally operate continuously throughout the year. The BBUs which are used to produce road bitumens operate only when the demand for road asphalt is high.

### 2.5 Catalytic cracking

**Purpose and principle**

Catalytic cracking is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons. It uses heat and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Unlike the hydrotreater process, no hydrogen is used and consequently, limited desulphurisation takes place. Compared to other heavy oil catalytic conversion processes, the fluid catalytic cracking (FCC) process is superior in being able to handle larger quantities of metals, sulphur and asphaltenes. One drawback is the **minimal** limited flexibility in changing the product yields even if recent developments in catalysts allow, depending on the catalyst selection, an increase of LPG yield or a further reduction of the bottom products.

**Feed and product streams**

Normally the main feed stream to a catalytic cracking unit (cat cracker) is the heavy vacuum distillate stream from the vacuum distillation unit. Fluid catalytic cracking units can be designed to process heavy vacuum gasoils (HVGO) from the vacuum distillation unit, or bottom streams, also called ‘long resid’ (LR) from the atmospheric distillation unit. Most often, units designed for HVGO also treat some LR, and vice versa. These two unit types will be referred to as the FCC unit and the RCC unit respectively.
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Other process streams may be blended into the cat cracker feed such as heavy gasoil from the atmospheric distillation unit, coker or visbroken gasoil, deasphalted oil and extracts from lube oil units and sometimes a small quantity of atmospheric residue. These streams may be hydrotreated to make them suitable for the cat cracker to adjust the desired product’s yields and properties.

Compared to other conversion processes, the catalytic cracker process is characterised by a relatively high yield of good quality gasoline and relatively high quantities of C3 and C4. Both products are highly olefinic and therefore are ideal feedstreams for the alkylation, etherification and petrochemical industries. One drawback of the FCC process is the very low quality of the mid-distillate products in terms of sulphur, olefins, aromatics and cetane index. The residue catalytic cracking (RCC) unit is a cat cracker unit used to upgrade heavier fractions such as atmospheric residue. The majority of the products need further treatment prior to storage.

Process description

A number of different catalytic cracking designs are currently in use worldwide, including fixed-bed reactors, moving-bed reactors, fluidised-bed reactors and once-through units. The fluidised- and moving-bed reactors are by far the most prevalent in world refineries.

Fluid catalytic cracking (FCC) units are by far the most common catcracking units. The FCC unit consists of three distinct sections, the reactor-regenerator section including the air blower and the waste heat boiler, the main fractionator section including the wet gas compressor and the unsaturated gas plant section. A simplified flow scheme is shown in Figure 2.6.

In the FCC process, oil and oil vapour preheated to 250 to 425 °C come into contact with hot catalyst (zeolite) at about 680 – 730°C in the riser reactor. To enhance vapourisation and subsequent cracking, the feed is atomised with steam. The cracking process takes place at temperatures between 500 and 540 °C and a pressure of 1.5 – 2.0 barg. Most catalysts used in catalytic cracking are contain zeolites (for more details on zeolites see Annex 9.7 ) with metals and rare-earths (some 15 % w/w) supported by amorphous synthetic silica different types of aluminas and clays with metals. The catalyst is in a fine, granular form which mixes intimately with the vapourised feed. The fluidised catalyst and the reacted hydrocarbon vapour are separated mechanically in a (two-stage) cyclone system and any oil hydrocarbon remaining on the catalyst is removed by steam stripping. The amount of lost catalyst as fines in the reactor and regenerator cyclones system is balanced by the addition of fresh catalyst.

The catalytic cracking processes produce coke which collects on the catalyst surface and diminishes its catalytic properties. The catalyst therefore needs to be regenerated continuously or periodically, essentially by burning the coke off the catalyst at high temperatures. The method and frequency with which catalysts are regenerated are a major factor in the design of catalytic cracking units. The catalyst flows into a separate vessel(s) for either single- or two-stage regeneration, done by burning off the coke deposits with air. However, in time, the catalyst deactivates gradually and irreversibly due to high-temperature exposure and metal poisoning (mainly vanadium). The hot regenerated catalyst flows back to the base of the reactor riser, where it is cooled by vapourisation of the feed and by the heat absorption required for cracking reactions.

The cracked oil hydrocarbon vapours are then fed to a fractionation tower where the various desired fractions are separated and collected. The streams are steam stripped to remove volatile hydrocarbons prior to cooling and sending to storage. Slurry oil is taken from the bottom of the column and part of it is cooled by heat exchange with the reactor feed stream and by steam generation, and is then returned to the column. The recycled slurry oil is used as wash oil and as a quench for the hot reactor overhead vapours to prevent aftercracking. The rest of the slurry oil is filtered or decanted to remove catalyst fines, cooled and sent to storage. The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate it into three phases: gas, liquid and sour water streams. The liquid and gas streams are both fed to the gas
plant (Section 2.12) for further separation and the sour water stream is sent to the sour water stripper for purification (Section 2.25).

Various types of equipment are usually used for recovering energy from this process. The hot flue-gases from the regenerator are cooled by means of steam generation in a waste heat boiler or, in case of partial CO \textit{burn} combustion, in a CO boiler. Prior to steam generation, electricity can also be produced by expansion of the flue-gases in a turbo-expander. And, in particular for units processing large quantities of residue, additional heat removal from the regenerator can be achieved with catalyst coolers for steam generation.

Note to TWG: Following text partially moved from Chapter 4 –

\textit{Full combustion mode}

Total combustion mode is typically applied to vacuum distillate feedstocks. Low Conradson carbon feeds are typically processed in full combustion FCCs.

In the full combustion mode, the following precautions should be taken in order to optimise the emission of pollutants from the FCC are the following:

- when operating a FCC in full combustion mode, and \textit{With an excess of oxygen not greater than 2 \%, the amount of CO produced can be limited to a range from 35 to 250 mg/Nm\textsuperscript{3} with an excess of oxygen greater than 2 \%, (value attainable in continuous operations. Emissions values as a daily half hourly average). mean values Note for TWG: a larger reference period (1/day + 1/year) would be better but no data has been made available.}
- in full combustion mode, A CO oxidation promoter can be added to the regenerator to catalyse the oxidation of CO. However, this promoter also catalyses the oxidation of the fuel nitrogen in the coke, increasing the NO\textsubscript{x} levels (especially NO). A platinum catalyst may promote the generation of N\textsubscript{2}O. Consequently, the amount of CO promoter varies the relationship between the NO\textsubscript{x} emissions and CO emissions. However, values of 300 - 700 mg/Nm\textsuperscript{3} of NO\textsubscript{x} (3 \% O\textsubscript{2}) can be achieved.
- For residual feedstock cracking using antimony addition, NO\textsubscript{x} emissions can raise to 1000 mg/Nm\textsuperscript{3} (3 \% O\textsubscript{2}) if no other reduction technique is used.
- Minimisation of the use of aeration and purge steam can decrease particulate emissions significantly. Aeration/steam rates are based on achieving a stable catalyst circulation in the catalyst lines between the reactor and the regenerator.

- Proper loading and pre-sulphiding procedures, good reactor temperature control and good flow distribution can reduce catalyst losses.
- Stripping of the catalyst before reaction or before regeneration reduce the HC content in coke to be burnt \textit{helps to reduce the coke formation.}
- Temperature adjustment in the riser by injection of a recycle stream above the zone of the fresh feed injection.
- Modification of the design and operation of the regenerator especially to avoid high temperature spots that tend to increase the NO\textsubscript{x} formation.

Considering for example dust emissions, the basic design of an FCC includes two-stage cyclones in the regenerator vessel, which prevent the bulk of the fine catalyst used from escaping from the system. However, smaller catalyst particles, some of which are introduced with fresh catalyst and some mostly created by attrition in the circulating system, are not easily retained by the two-stage cyclone system. Consequently, in many cases, other abatement techniques have to be included to complement the process abatement techniques discussed here.

A reduction of the regeneration temperatures under the usual conditions (700-750 °C) would not have a significant impact in the NO\textsubscript{x} emissions but could require a CO boiler it will increase CO
concentration in the flue-gas and increase coke formation. A change in the design or operation of the regeneration may increase the CO concentration.

When excess O$_2$ is reduced to around 0.5 %, NO$_x$ production is dramatically reduced. This is due to the increase in CO from less available O$_2$ which can help reduce NO$_x$ back to N$_2$. Additionally, many FCC/RCC units cannot operate at these low O$_2$ levels and still maintain regenerator temperatures within safe operating limits, and low O$_2$ levels will increase CO emissions. Finally, SO$_x$ production is typically increased at low O$_2$ when SO$_x$-additives are being used since there is not enough O$_2$ for the SO$_2$ to oxidise to SO$_3$ and be captured by the additive.

### Partial combustion mode

In general, feed having a Conradson carbon figure up to 2 – 3 % may be treated in a ‘standard’ FCC without a CO boiler as well as partial-combustion FCC. A Conradson figure from 2 – 5 % would require a CO boiler and from 5 – 10 % a cat cooler would be needed. It should be noted that the above figures are only indicative and depend also on the severity of the cracking.

In the partial combustion mode considerable CO is present in the flue-gas and it is consumed downstream of the regenerator in a CO boiler, both to recover the energy produced in a CO boiler and to meet environmental requirements. This system can be seen as two-stage regeneration in comparison with the total combustion mode, where a single regeneration step is present.

Residue catalytic cracking (RCC) is basically the same process as FCC, with the difference that it often has a CO boiler and a catalyst cooler. Sometimes FCC units are equipped with both a CO boiler and a catalyst cooler and can consequently be used as RCC unit. Due to the higher coke laydown on the catalyst as a result of the heavier feeds, the heat balance around the regenerator may require additional measures for catalyst cooling. As the heavier feed normally has a higher metal content, especially Ni and V, the catalyst deactivation rate is so fast that the catalyst needs to be removed continuously, to be replaced by fresh catalyst. Increasing rates of fresh catalyst addition induces higher entrainment rates due to fines present in the fresh catalyst as well as fines produced by attrition. Therefore, higher particulate emissions from the regenerator are expected and should be taken into account for the choice and size of the flue-gas PM abatement technique to be implemented.

When processing residues containing very high levels of metals (Ni, V and Na) and CCR values of 3 – 10 wt %, two-stage regenerators can be used (Axens R2R™ technology). Two stage regenerator processes are tolerant of feedstocks having high Conradson Carbon Residue (CRR) values (3-10 % wt) and containing high levels of metals (Ni, V and Na). The first regenerator burns 30 – 70 % of the coke and essentially all the hydrogen in it. Regeneration conditions are kept mild and vanadium on the catalyst cannot form V$_2$O$_5$. In the second regenerator, full catalytic activity is restored by completely removing the remaining coke in a dry atmosphere, as hydrogen has been previously removed. V$_2$O$_5$ is now formed at high temperature, but as there is little moisture available to form vanidic acid the catalyst is preserved. The 2-stage regeneration system allows a R2R resid cracker RCC to operate at significantly higher metal levels on the catalyst, thereby reducing the catalyst make up requirements and operating costs.

### Reference literature

[76, Hydrocarbon processing 2011 ] [ 9, Koottungal 2008 ].

In the Thermofor Catalytic Cracking (TCC), the preheated feedstock flows by gravity through the catalytic reactor bed. The vapors are separated from the catalyst and sent to a fractionating tower. The spent catalyst is regenerated, cooled, and recycled. The flue-gas from regeneration is sent to a carbon monoxide boiler for heat recovery.
In the moving-bed process, oil is heated to 400 – 700 °C and is passed under pressure through the reactor, where it comes into contact with a catalyst flow in the form of beads or pellets. The cracked products then flow to a fractionating tower where the various compounds are separated. The catalyst is regenerated in a continuous process. Some units also use steam to strip the remaining hydrocarbons and oxygen from the catalyst before the catalyst is fed back to the oil stream. In recent years, moving-bed reactors have largely been replaced by fluidised-bed reactors.

2.6 Catalytic reforming

Purpose and principle
The heavy naphtha leaving the hydrotreating units is a very poor gasoline blend component due to its low octane. The purpose of a catalytic reformer is to upgrade the octane of these streams for use as a gasoline blendstock. The burning characteristics (octane number) of heavy naphtha are improved significantly by catalytic reforming. The most important characteristic of the reformate product is the octane number. Octane numbers are very low for n-paraffins, slightly better for naphthenes and isoparaffins and are highest for aromatics. There are four major types of reactions which occur during the reforming processes:

1. dehydrogenation of naphthenes to aromatics
2. dehydrocyclisation of paraffins to aromatics
3. isomerisation
4. hydrocracking.

Because the recently reformulated gasoline specifications have limited the allowable amount of benzene in gasoline (e.g. Auto Oil 1 see Table 1.9), and possibly in the future the aromatics content, catalytic reformer operation may be driven by hydrogen production needs more than to produce additional aromatic. EU gasoline market is in decline and reformulated specifications (see Table 1.9) limit the allowable amount of benzene and aromatics in gasoline, catalytic reformer operation is driven more by hydrogen production needs for diesel production than to produce additional aromatics and gasoline blend components, which has been traditionally been the case.
Feed and product streams
The typical feedstocks to catalytic reformer units are the hydrotreated straight-run heavy naphtha stream from the crude distillation unit and, if applicable, the hydrotreated heavy naphtha stream from the hydrocracker unit or coking unit, and medium catcracked naphtha stream from an FCC unit. A catalytic reformer produces hydrogen, which is essential for use in hydrotreaters (Section 2.13) and may be used in hydrocracking processes. Products from a reformer include, in addition to the hydrogen: refinery fuel gas; LPG; isobutene; n-butane and reformate. The reformate may be blended to gasoline or further separated into components as chemical feedstocks like benzene, toluene, xylene, and naphtha cracker feeds.

Some catalytic reformers operate under more severe conditions, resulting in an increased aromatics content in the reformate product. Some catalytic reformers are also used for the production of aromatics as a (chemical) product (see Large Volume Organic Chemical Industry BREF).

Process description
Feedstocks to catalytic reforming processes are usually hydrotreated first to remove sulphur, nitrogen and metallic contaminants. The catalysts used in catalytic reforming processes are usually very expensive (containing platinum [Pt]) and extra precautions are taken to ensure that catalyst is not lost. There are several catalytic reforming processes in use today. In general they can be classified into three categories: continuous, cyclic or semi-regenerative, depending upon the frequency of the catalyst regeneration. The fixed-bed or moving-bed processes are used in a series of three to six reactors.

Continuous catalytic regeneration (CCR) reforming process
In this process, the catalyst can be regenerated continuously and maintained at a high activity rate. The ability to maintain high catalyst activities and selectivities by continuous catalyst regeneration is the major advantage of this type of unit. Figure 2.7 shows a simplified process flow diagram of a continuous catalytic reformer.

Interheaters are needed between the reactors to provide the heat required for the endothermic dehydrogenation reaction. As the naphtha feed charge proceeds through the reactors, the reaction rates decrease and the reheat needed lessens. Freshly regenerated catalyst is introduced at the top of the first reactor and flows by gravity from top to bottom. From here it is passed on to the next reactor. Partially-aged catalyst is removed from the bottom of the lowest reactor and sent to an external regenerator where the carbon is burned from the catalyst. The catalyst is
acidified and reduced before being returned to the upper lead reactor. The reaction mixture from the last reactor is used to preheat the fresh feed and further cooled down prior to being fed to the low-pressure separator. There the hydrogen-rich gas is separated from the liquid phase. The gas is compressed and partially recycled to the naphtha feed. The remaining vapour is then further compressed, recontacted with the liquid from the low-pressure separator, cooled and fed to the high-pressure separator. The recompression and recontacting is included to maximise recovery of the C5/C4 fraction from the hydrogen-rich gas stream. Any excess of this hydrogen-rich gas is bled to the refinery fuel gas grid, routed to the refinery hydrogen system to be used in hydrogen consuming units like hydrotreaters. The selection of the reformer operating pressure and the hydrogen/feed ratio form a compromise between maximum yields and coking rate. stable operation.

Note to TWG: Information moved from section 4.6.2

The CCR reforming process has higher energy efficiency per tonne of desired product than the semi-regenerative process due to better yields and improved heat recovery from the products. As the CCR process is the latest and most modern type of catalytic reformer process, it has generally a design with a higher heat integration than the semi-regenerative process and lead to a higher energy efficiency. Appropriate revamping of semi-regenerative units can also achieve it through the same recovery from products, from pumparounds and integration with topping and vacuum.

The use of a CCR generates more dioxins than a semi-regenerative process during the regeneration of the catalyst. For more information, see Section 3.6.

Operational data
This technique operates at lower pressures (3.5 – 10 bar) than and at the same temperature as semi-regenerative processes. It uses mono (Pt) or bi-metallic catalysts (Pt-Re, Pt-Sn). Hydrogen is also produced in these processes. A continuous regeneration reformer produces around 350 Nm³ of hydrogen per tonne of feedstock. Since the increased coke laydown and the thermodynamic equilibrium yield of reformate are both favoured by low-pressure operation, the ability to maintain high catalyst activities and selectivities by continuous catalytic regeneration is the major advantage of the continuous process type of unit.

Disadvantages of the CCR reforming process include its ability to make reformates with high aromatic contents >70 vol % and CCR reformer reformates tend to be higher boiling compared to the semi-regenerative reforming process. These qualities can impact blending CCR reformer reformates into the gasoline pool with gasoline specification of less than 35 % v/v aromatics. Compared to the other reforming technologies, much of the value from CCR reforming is it improved yields at high octane; however, with bio-fuels blending and decreasing octane demand, the economics for converting other reforming technologies to CCR reforming technology is diminishing.

Economics
As an example, the investment costs based on a 3975 m³/d continuous octanising unit (battery limits, erected cost, 1998 Gulf Coast) was 10 000 USD per m³/d. The erected costs based on a 3180 m³/d unit (4Q95, US Gulf Coast) has been USD 48.3 million (USD15200 per m³/d). In addition, catalyst costs add another USD 2.6 million.

Example plant(s)
Nowadays, only continuous catalytic reformer units are built. New reforming units larger than 15 000 bpd (2400 m³/d) are typically designed as continuous catalyst regeneration reformer units. Smaller reformer units may be continuous catalyst regeneration or semi-regenerative designs as the cost of the CCR can become cost prohibitive with smaller scale units.

Reference literature
[212, Hydrocarbon processing, 1998], [166, Meyers, 1997], [268, TWG, 2001] [77, REF TWG 2010].
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Cyclic reforming process
The cyclic reforming process is characterised by having a swing reactor in addition to these on-stream, in which the catalyst can be regenerated without shutting the unit down. When the activity of the catalyst drops below the desired level, this reactor is isolated from the system and replaced by the swing reactor. The catalyst in the replaced reactor is then regenerated by introducing hot air into the reactor to burn the carbon from the catalyst. Typically, one reactor is always being regenerated.

Semi-regenerative reforming process
In this process design, regeneration requires the unit to be taken off-stream. Depending upon the severity of operation, regeneration is required at intervals of three to 24 months. High hydrogen recycle rates and operating pressures are utilised to minimise coke laydown and the associated loss of catalyst activity.

The reactors operate at temperatures in the range of 400 - 560°C and pressures in the range of 15 – 35 bar. This type of process produces between 130 and 200 Nm³ of hydrogen per tonne of feedstock.

Economics
The erected cost of a semiregenerative unit of 3180 m³/d is 33 million USD (10 400 USD per m³/d). In addition, catalyst costs add another 3.4 million USD (1995 - US Gulf Coast)

Many applications exist in Europe as well as in the rest of the world.

Cross-media effects
In semi-regenerative reforming, the unit catalyst is regenerated at intervals of three to 24 months, depending on the intensity of the process. The emission factor of dioxins per tonne of feedstock is much lower than in the case of continuous regeneration. For more information, see Section 3.6.

2.7 Coking processes

Purpose and principle
Coking is a severe thermal cracking process used primarily to reduce the refinery production of low-value residual fuel oils and transform them into transportation fuels, such as gasoline and diesel. As part of the process, coking also produces petroleum coke, which is essentially solid carbon with varying amounts of impurities. When high-quality coke is required (e.g. to produce anodes for metals industry) green coke needs to be process in a calciner.

Feed and product streams
As the coking process is a thermal destruction process, the quality of the feed in terms of metal content, Concarbon number and other contaminants is not critical. As a matter of fact, coking is predominantly used when the feed has a high Concarbon number and contains high quantities of impurities which cannot be handled in catalytic conversion processes. All this produces high feedstock flexibility. The feed to a delayed coking unit can consist of atmospheric residue, vacuum residue, shale oils, tar sands, liquid and coal tar, which results in a petroleum coke used for fuel applications. Aromatic oils and residues such as heavy cycle oils from a catalytic cracking unit and thermal tars are suitable feed stocks for the production of needle coke and anode coke. The feed to a fluid coker is the vacuum residue, sometimes mixed with refinery sludges, tar sands, bitumen and other heavy residues.

The products from the coking fractionator are refinery fuel gas, LPG, naphtha and light and heavy gas oils. Petroleum coke is another product, with the type depending upon the process used, operating conditions and feedstock used. Coke produced by the coker is called ‘green’ coke and still contains some heavy hydrocarbons left from incomplete carbonisation reactions. More information about the properties of the coke can be found in Section 10.3.2.
Process description
Two types of coking processes exist: the delayed and fluid coking processes that produce coke and the flexicoking process that gasifies the coke produced in a fluid coking process to produce coke gas.

Delayed and fluid coking
The basic process is the same as thermal cracking (Section 2.22), except that feed streams are allowed to react for longer without being cooled. Figure 2.8 shows a simplified process flow diagram of the delayed coking unit.

The delayed coking feed stream of residual oils is first introduced to a fractionating tower, where residual lighter materials are drawn off and the heavy ends are condensed (not shown in Figure 2.8). The heavy ends are removed, heated in a furnace and then fed to an insulated vessel called the coke drum, where the cracking takes place. In the case of fluid coking, a fluidised-bed is used. Temperature (440 – 450 °C), pressure (1.5 – 7.0 barg) and recycle ratio are the main process variables which contribute to the quality and yields of delayed coking products. When the coke drum is filled with product, the feed is switched to an empty parallel drum (dotted drum in Figure 2.8).

When the coke drum is full, steam is then injected to remove hydrocarbon vapours. The coke bed is then quenched with water and the cokes are cut out with high pressure water. The cutting water passes to dedicated settlement where coke solids settle out and the clarified water is recycled. The wet green coke is conveyed to designated open stock piles, where water drains out and is recycled. Green coke can already be sold and used for energy production. The yield of delayed coking is usually above 80 % (25-30 % to coke, 65 -75 % to light products) conversion of feed to products. The production of petroleum coke is of the ratio of 0.13 tonnes of petroleum coke produced per tonne of feedstock.

Hot vapours from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulphide and ammonia, are fed back to the fractionator where they can be treated in the sour gas treatment system or drawn off as intermediate products. Condensed hydrocarbons are re-
processed and collected water is reused for coke drum quenching or cutting. Any remaining vapours commonly pass to the flare system. Normally, products such as naphtha are totally fed to the naphtha hydrotreater for further processing. The heavier products are suitable feedstock for catalytic reforming after proper hydrotreatment. Light oil needs further treatment before being sent to the gasoil blending pool. The heavy gasoil is preferably sent to a hydrocracker unit (Section 2.13) for further conversion into light components. When no cracking units are available, it is blended in the heavy fuel oil pool.

**Calciner**
For certain applications, green coke should be calcinated before being used or sold. The incinerator kilns are direct fuel gas or coke fine fired at the discharge end. The coke is calcinated at up to 1380 °C, driving off volatile matter and burning it within the kiln. Exhaust gases discharge from the feed end and are incinerated to burn off residuals and coke fines. Hot flue-gases pass through a waste heat boiler and gas cleaning by multi-cyclones. Collected fines from the cyclones are pneumatically conveyed to a silo with exit air filters. The calcined coke discharges to a rotary direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and the water scrubber. Collected cyclone fines may be recycled to product, which is oil sprayed as a dust suppressant, or may be incinerated or sold as a fuel.

**Flexicoking**
The flexicoking process typically converts 84 – 88 % w/w of the vacuum residue to gaseous and liquid products. Virtually all metals in the feed are concentrated in the 2 % solids purged from the process. Flexicoking is a very robust process in which coking and gasification are fully integrated. The process is advanced compared to the classic delayed coker in terms of operation and labour intensity.

The flexicoking process uses three major vessels: the reactor, the heater and the gasifier. As auxiliary facilities, the system includes a heater overhead cooling system and a fines removal system, a coke gas sulphur recovery unit and reactor overhead scrubber (Figure 2.9). The preheated vacuum residue feed is sprayed into the reactor, where it is thermally cracked, typically at 510 – 540 °C. The freshly-formed coke is deposited on the surface of the fluidised recirculated coke particles. In the gasifier, the coke is reacted at elevated temperatures, typically 850 - 1000 °C, with air and steam to form coke gas, a mixture of hydrogen, carbon monoxide and dioxide and nitrogen. Sulphur in the coke is converted in the gasifier primarily to hydrogen sulphide, plus traces of carbonyl sulphide (COS). Nitrogen in the coke is converted to ammonia and nitrogen. Unlike normal gasifiers which are fed with pure oxygen, the flexicoking gasifier is fed with air, resulting in a coke gas with a relatively low calorific value, as it contains a high quantity of nitrogen inerts.
Figure 2.9: Simplified process flow scheme for a flexicoker

The cracked hydrocarbon vapour product from the reactor is passed through cyclones to remove coke particles and is subsequently quenched in a scrubber section located at the top of the reactor. Material boiling above 510 – 520 °C is condensed in the scrubber and recycled to the reactor. The lighter material goes overhead to conventional fractionation, gas compression and light ends recovery sections. The treatments and use of the products are very similar to the ones already described in the delayed coker. Pressure relief from the fractionator of the coking processes passes to flare and from the coke drums to the quench tower system.

2.8 Cooling systems

Under the IPPC process, a horizontal BREF on Industrial Cooling Systems [69, European Commission 2001] has been produced that covers many topics of relevance to the refineries sector. To avoid repetition, therefore, this section on cooling addresses only topics not covered by that horizontal BREF. Moreover, some cooling water pollution issues have already been studied in the OSPAR (North Sea) and HELCOM (Baltic) processes.

Purpose and principle

In a refinery, the cooling of feed and product streams is required to allow refinery process operations to take place at the right temperatures, and to bring products to their appropriate storage temperature. Even though heat integration of process systems ensures that significant cooling can be achieved by exchanging heat between streams to be cooled and streams to be heated, additional cooling is still required. This additional cooling should be provided by an external cooling medium: water and/or air.

Process description

A wide range of techniques is used for cooling purposes in oil refineries. Most refineries use a combination of the techniques available. The selection of a cooling system depends on the required cooling temperature, the cooling capacity, contamination risk (primary or secondary cooling loop) and local circumstances. A simplified diagram of the cooling techniques is shown in Figure 2.10 and briefly described below:
Air cooling
In an air cooler (forced or induced draught), the process stream in the tubes is cooled against the air delivered by a fan. An induced draught air cooler is illustrated in Figure 2.10.

Water cooling
Direct water cooling (i.e. quenching)
Because of the high contamination generated by this type of cooling, quenching is only used in cokers (Section 2.7), in gasifiers and in some sludge incinerators.

Once-through system (seawater, river water, etc.)
In a typical once-through cooling system, water is extracted from a surface water body, filtered if necessary and sometimes treated with biocide to inhibit fouling. It is then passed around the refinery to enable cooling through heat exchangers. The cooling water is passed through a process unit once and is then discharged directly without treatment in the waste water treatment plant. There are several ways to use water for once-through cooling in refineries that carry a different risk of contamination by process streams which are described below:

- Once-through cooling water used for cooling non-polluting streams, e.g. in power generation. A cooling tower system is generally applied when the thermal loading of the surface water is too high (Figure 2.10 A and B).
- Once-through cooling water used for heat exchange with a recirculating water system which then cools the process streams (Figure 2.10 C).
- Once-through cooling water is used to cool process streams directly (via heat exchangers) (Figure 2.10 A and B).
Circulation system (tempered water, cooling water)
In this system, most cooling water is repeatedly recycled through cooling towers using ambient air. In order to control the concentration of contaminants and the solids content in the cooling water, a blowdown stream is used, which is sent to the waste water treatment unit, and make-up water is added. A certain amount of water also exits the system through evaporation (Figure 2.10 D).

Wet closed system (normally water)
Tempered water is used when process streams to be cooled should not be exposed to the (low) cooling water temperatures (Figure 2.10 F).

Hybrid systems
In these cases hybrid systems, both air and water are used as the cooling media. These systems normally maximise the use of air cooling and the rest is done by water cooling. Two types of systems are available and they are shown in Figure 2.10 G and H.

Refrigeration systems
In specific cases when process streams have to be cooled below ambient temperatures, refrigeration systems are applied. This can be either a direct refrigeration system, i.e. using the refrigerant (propane or ammonia) in the process, or an indirect system (Figure 2.10 F) using a circulation system (e.g. brine, glycol) where the refrigerant cools the circulating liquid.

2.9 Desalting

Purpose and principle
Crude oil and heavy residues can contain varying quantities of inorganic compounds such as water soluble salts, sand, silt, rust and other solids, together characterised as bottoms sediment. The salt in the crude is primarily in the form of dissolved or suspended salt crystals in water emulsified with the crude. These impurities, especially salts, can lead to fouling and corrosion of heat exchangers (crude preheaters) and especially the crude distillation unit overhead system (Section 2.19). Salts are detrimental to the activity of many of the catalysts used in the downstream conversion processes and sodium salts stimulate coke formation (e.g. in furnaces). Some inorganic impurities are chemically bound, such as vanadium and nickel are often referred to as oil-soluble salts. These cannot be eliminated in a desalter. Moreover, water should preferably be removed if the water content of the crude is relatively high. Therefore, desalting of the incoming crude oil is generally applied before separation into fractions (in Section 2.19).

The principle of desalting is to wash the crude oil or heavy residues with water at high temperature and pressure to dissolve, separate and remove the salts and solids.

Feed and product streams
Crude oil and/or heavy residues (oily feedstock) and reused and fresh water are the feedstreams to the desalter and washed crude oil and contaminated water are the outputs of the desalting processes. The water phase from the overhead crude distillation unit of the overhead and other used water streams are normally fed to the desalter as washwater. Efforts are made in the industry to minimise water content of the crude to less than 0.3 % and bottoms sediments to less than 0.015 %. The concentrations of inorganic impurities in the cleaned stream are highly dependent on the design and operation of the desalter as well as the crude source.

Process description
After preheating to 115 – 150 °C, the oily feedstock is mixed with water (fresh and preused water) in order to dissolve and wash out the salts. Intimate mixing takes place between the oil and the wash water together in a globe valve mixer, a static mixer or a combination of both. The water must then be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals to assist in breaking up the emulsion and/or, more commonly, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The
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separation efficiency depends on pH, density and viscosity of the crude oil, as well as the volume of wash water used per volume of crude. Either AC or DC fields may be used and potentials from 15 to 35 kV are used to promote coalescence. Many refineries have more than one desalter. Multiple-stage desalters also exist. The washwater containing dissolved hydrocarbons, free oil, dissolved salts and suspended solids is further treated in an effluent treatment plant (Section 4.26). Where bottoms sediments are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids. Figure 2.11 shows a simplified process flow diagram of a modern design crude desalter.

![Figure 2.11: Simplified flow diagram of a crude desalter](image)

2.10 Energy system

Although heat-producing plants are an essential and integral part of most refining processes/activities, the systems tend to be very similar and they are therefore dealt with in this horizontal section. Consequently, as a consequence of that energy management issues, fuel management, energy production techniques (e.g. boilers, furnaces, gas turbines) and steam management are included in this section.

Heat-producing plants are an essential and integral part of most refining processes/activities. An important aspect of the refining energy system is the effective use of internal residue streams as part of the energy mix. This chapter describes some principles of energy production and management in the context of refinery fuels.

**Purpose and principle**

Heat and electricity are needed to run a refinery. The extensive heat requirement is generally satisfied by fuel combustion either directly (by heaters, furnaces) or indirectly via steam. Heat can be provided to process streams and unit operations directly (by heaters) or indirectly (e.g. steam). Steam is usually produced inside the refinery. This is increasingly coupled to the generation of electricity in surplus because it can be sold on the external market (as with steam if there is local demand) or, more and more, imported from adjacent facilities like collective CHP plants designed for supplying the refinery together with several other industrial facilities within a petrochemical platform, or as a by-product from an associated dedicated steam methane reformer. Electricity can be generated in the refinery (e.g. CHP, gas/steam turbines, IGCC) and it can be or bought from the grid. Moreover, energy (steam and power) is recognised by refiners as another output that can be produced in-house and be sold.

An emerging proposition is full commercialisation where (some) steam and electricity production is outsourced to a power company specialist. Some refineries have switched to importing their base load steam and electricity needs from third party companies based locally.
Fuels and fuel systems

The fuel required for the production of steam and power or for the firing of the furnaces originates either from fuels that are produced by the refinery itself (refinery fuels) or from natural gas that is bought outside, or a combination of both. Normally, most or all of the entire gaseous and liquid refinery fuels used are by-products of refinery processes. The composition and quality of these fuels vary with the crude oils processed. Generally speaking, the refinery fuel pool is a careful balance between energy required, type of crude processed, emission limits and economics.

Refinery fuel gas (RFG)
The majority of the fuel used in a refinery is refinery fuel gas (RFG) gas (methane, ethane and ethylene in combination with excess hydrogen) which is internally generated in the different refinery processes and collected in the refinery gas system, but has to be used quickly and cannot normally be sold as a valuable product. RFG, if properly treated, is a low-polluting fuel. This is a mixture of methane, ethane, ethylene and hydrogen and may contain some CO and small amounts of C₃, C₄, N₂ and H₂S. RFG is produced and collected in the refinery gas system, but has to be used quickly and cannot normally be sold as a product. The composition may change over time depending on refinery operations and the feedstock being processed and will be different from site to site again depending on feedstock and installed plants, for example if the refinery has a coker that supplies syngas (CO + H₂) to the RFG system. Most of the refinery fuel gas systems have two or three alternative sources of supply: refinery gas, imported gas (normally natural gas) and liquefied petroleum gas (LPG). External supplies usually become part of the RFG system although dedicated units may run on commercial fuel. RFG, if properly treated, is a low-polluting fuel. More information on RFG is provided in Section 4.10.2. These gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking, coking and all hydrodesulphurising processes). In the latter case the gas streams are normally treated by amine scrubbing to remove H₂S before being released to the refinery fuel gas system, and dust removal and COS conversion if necessary (Section 4.25). Coke gas forms a main refinery gas source if coking takes place in the refinery. Sulphur content in the form of H₂S is normally below 100 – 2620 mg/Nm³, and will strongly depend on the pressure used in the amine treating units. But levels of 20 – 40 mg/Nm³ are possible for gas treated at high pressure (20 bars), and lower levels, of 2 – 15 mg/Nm³ can even be reached with very high pressure (50 bars). Residual H₂S concentration which can be achieve by using a refinery fuel gas treatment are shown in Table 4.86 of Section 4.25.5.1. The nitrogen content is negligible.

Fuel gas system

Figure 2.12 shows a schematic diagram of a typical fuel gas system. The fuel gas is supplied from the different refinery units. In this diagram, back-up supply is provided by imported natural gas and by internally-produced LPG, which is vaporised and routed into the fuel gas header. The condensation of heavier hydrocarbons and/or water is critical for the fuel gas system. Normally all units have their own fuel gas knock-out drum, in which condensate formed in the fuel gas distribution system is separated. The fuel gas lines from this drum need to be steam-traced to avoid condensation in the supply lines to the individual burners. Liquids from the fuel gas knock-out drum are drained to a closed slops system.
Liquid refinery fuel (heavy fuel oil, HFO) used in the refinery is normally a mixture of the residues from atmospheric and/or vacuum distillation and conversion and cracking processes. Liquid refinery fuels are available in various grades, viscosity being the main parameter. The lower the viscosity, the more expensive the fuel. The heavier (more viscous) grade fuels require heating to reduce their viscosity before combustion. They contain sulphur (<0.1 – 0.6 %), particle-promoters metals (e.g. V, Ni) and nitrogen (0.1 – 0.8 %) resulting, after direct combustion, in high SO$_2$, particulates and NO$_x$ emissions. They can also be gasified in the Integrated gasification combined cycle (IGCC) plant where virtually any refinery residue (visbroken or thermal tars, etc.) can be converted to heat and power.

Provided that the crude oil is properly desalted, the ash content of the fuel will be directly related to the total solids, the amount being proportional to the sum of the nickel and vanadium present (Ni-V value: 0.03 – 0.15 % w/w depending on the residue source and crude origin). To arrive at the metal content of the HFO, the metal content of the crude is multiplied by a factor of 4 - 5 (dependent on the yield of residue and the residue content of the crude). The metal content of the HFO can vary between 40 and 600 ppm for HFO from a North Sea crude and Arabian Heavy crude respectively, generating particulate concentration in the flue-gas of 150 - 500 mg/Nm$^3$. The most prominent metals indigenous to the crude are vanadium and nickel. Other metals such as cadmium, zinc, copper, arsenic and chromium have been detected [43a, Dekkers and Daane, 1999]. Table 2.2 shows the metal content of residual fuel oil typically used in refineries.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration range (ppm)</th>
<th>Average concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>7.23 – 540</td>
<td>160</td>
</tr>
<tr>
<td>Ni</td>
<td>12.5 – 86.13</td>
<td>42.2</td>
</tr>
<tr>
<td>Pb</td>
<td>2.49 – 4.55</td>
<td>3.52</td>
</tr>
<tr>
<td>Cu</td>
<td>0.28 – 13.42</td>
<td>2.82</td>
</tr>
<tr>
<td>Co</td>
<td>0.26 – 12.68</td>
<td>2.11</td>
</tr>
<tr>
<td>Cd</td>
<td>1.59 – 2.27</td>
<td>1.93</td>
</tr>
<tr>
<td>Cr</td>
<td>0.26 – 2.76</td>
<td>1.33</td>
</tr>
<tr>
<td>Mo</td>
<td>0.23 – 1.55</td>
<td>0.95</td>
</tr>
<tr>
<td>As</td>
<td>0.17 – 1.28</td>
<td>0.8</td>
</tr>
<tr>
<td>Se</td>
<td>0.4 – 1.98</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Source: [322, HMIP UK, 1995]
Liquid refinery fuel system
As has already been stated, liquid refinery fuels are heavy residues that should be stored in a separate storage tank at an elevated temperature to reduce the high viscosity. A typical refinery fuel oil system (schematic diagram, see Figure 2.13) includes a dedicated mixing tank (normally off-site), a circulation pump and heater (when required). The system discharges fuel oil at a constant pressure and at the required condition of temperature and viscosity, so that atomisation and efficient combustion are possible. If the fuel consumption is low, the cost of installing heated storage, preheat, etc. may not be justified for the use of heavy fuels and so a light fuel oil will be used. Liquid refinery fuels are normally used for process start-ups.

Solid fuels such as petroleum coke can be gasified as a refinery fuel gas source for refineries (Flexicoking, Section 0). Coke is burnt in the catalytic cracking regenerator (Section 2.5) and coking process (Section 0) and represents a heat production source in the refinery. Coal, as imported fuel, is not applied in European refineries.

![Simplified flow diagram of a heavy fuel oil system](image)

Figure 2.13: Simplified flow diagram of a heavy fuel oil system

Energy production techniques
It is not the intention of this section to include a detailed description of energy production techniques (steam and power), since one can be found in the Large Combustion Plant (LCP) BREF [7, EC 2006].

Furnaces and boilers
Many of the individual refinery processes and utility systems combust fuel (gas and/or liquid) in dedicated furnaces and boilers to supply the heat necessary for the process. Fired process heaters and boilers are the main heat producers. The former transfer the heat released in the combustion process directly to the process stream and the latter produce steam that will be used somewhere in the refinery. The principle of steam generation is the heating of boiler feed water, under pressure in a specified fuelled boiler or a waste-heat boiler consisting of heat exchanger bundles (economisers and superheaters). In this document no distinction is made between furnaces and boilers except when relevant.

A variety of furnaces and burner types are used in refineries, largely determined by the heat-release characteristics required by a particular process. Many but not all furnaces are dual (oil/gas) fired to allow flexibility in the refinery fuel system. Refinery process heaters are typically rectangular or cylindrical enclosures with multiple-fired burners of specialised design using mainly low-combustion intensity. Boilers (fixed or fluidised bed) are generally fairly standard steam-producing units of medium or high-combustion intensity. Waste heat boilers may also be present in the furnaces of stacks. Well maintained and operated direct-fired heaters and boilers normally achieve thermal efficiencies of over 85%. If air preheat is applied and the
combustion products (flue-gas) are cooled close to their dew point, the thermal efficiency can be as high as 93%. Boilers consume about 10 - 20% of refinery energy requirements.

**Gas and steam turbines**

Gas turbines work as follows: fresh air at ambient conditions is drawn into the compressor where its temperature and pressure are raised. The high-pressure air proceeds into the combustion chamber, where the fuel is burned at a constant pressure. The resulting high-temperature gases then enter the turbine where they expand to atmospheric pressure, thus producing power. Steam turbines are used to transform the steam pressure to power. Combined-cycle processes combine the gas and steam turbine processes to produce power at higher efficiency than is reached with open-cycle turbines (steam and gas). More information about gas and steam turbines as well as combined cycles can be found in the LCP BREF [7, EC 2006].

**Cogeneration plants (CHP)**

These systems are designed for the co-production of heat and power. The fuel for this type of facility is usually natural gas. It is, however, also possible to fire refinery gas as part of the fuel slate, thus potentially reducing the amount of refinery gas available for combustion in boilers and furnaces. The steam and power cogeneration concept can also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

**Integrated gasification combined cycle (IGCC)**

Integrated gasification combined cycle is a technique for producing steam, hydrogen (optional) and electrical energy from a variety of low-grade fuel types with the highest conversion efficiency possible. During the gasification of the oil with oxygen and/or air, syngas is also produced and used for energy production, typically in a combined cycle for the production of heat and electricity. Hydrogen can also be separated from the syngas for use in the refinery (Section 2.14).

The principle is based on the high-temperature and high-pressure reaction of organic carbons or coke with steam and under stoichiometric amounts of oxygen (partial oxidation) to produce syngas (CO+H₂). After the combustion chamber, the system contains a number of sophisticated energy recovery systems to produce steam and electricity. Figure 2.14 shows a block flow diagram of an IGCC plant. In the partial oxidation of hydrocarbons, the product gas contains a certain amount of free carbon (soot). The soot particles are removed from the gas together with the ash in a two-stage water wash.
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Figure 2.14: Block flow scheme for IGCC

The gasification plant consists of two integrated complex units. In the first, syngas manufacturing process plants (SMPP), the gasification of heavy fractions takes place and the syngas is produced and purified. In the second the combined-cycle power plants, the syngas is fed to a combined-cycle thermoelectric unit. The SMPP includes the two sections described below.

- **Gasification and carbon extraction**: in the gasification section, the feedstock is gasified through a non-stoichiometric reaction with pure oxygen and water; the reaction occurs in the gasifier, a non-catalytic vessel internally-coated with refractory, operating at a high temperature (about 1300 °C) and pressure (about 65 bar).

- **Gas cooling and purification**: in the gas-cooling section, the waste heat from syngas is recovered by the generation of steam at three pressure levels. A small quantity of carbon, formed in the gasifiers is removed from the gas by direct contact with water in a scrubber. Water is then treated in the grey water treatment and then sent to the existing refinery biotreatment plant. A solid effluent in the form of a filter cake is discharged from this unit and sent to external plants for the recovery of the metals. In addition, a COS hydrolysis reactor is provided to convert the small amount of COS produced in the gasifier to H₂S. This section also includes a gas expander for the recovery of the pressure energy of the syngas (pressure in gasifiers is about 65 bar). This system contains an acid-gas removal process which consists of a circulating amine stream used to selectively absorb the H₂S formed in the gasifier and in during the COS hydrolysis. It also contains an air separation unit. This unit produces the oxygen required for the gasification and the Claus plant, and the nitrogen for syngas conditioning. It is based on conventional cryogenic air fractionation. And finally, it contains a sulphur recovery unit where Claus units recover elemental sulphur from the H₂S recovered in the acid-gas removal section. This, along with a tail gas treatment section maximise the overall sulphur recovery.

After the cooling and purification sections, the purified syngas is sent to the combined cycle power plant, for power generation. It mainly consists of a conventional cycle with a gas turbine, a heat-recovery steam generator and a steam turbine.
Chapter 2

Products from the energy system
As mentioned at the beginning of this section, the energy system of a refinery (or any other industrial complex) is there to provide the heat and power necessary to carry out the process. A short description of the types of products produced by the energy system of a refinery (steam and power) is given below.

Steam
The different steam qualities generated in the boilers of the refinery have the general characteristics described below (the heat content ranges from about 2700 MJ/t for low-pressure steam to 3200 MJ/t for super heated high pressure steam at 50 bar):

- High-pressure (HP) steam network (>30 bar, 350 – 500 °C), generated in waste heat boilers (cooling of hot off-gases and/or hot products in catalytic processes and hydrocrackers) and in fired boilers. HP-steam is mainly used in turbines to produce electrical power (and medium pressure steam);
- Medium pressure (MP) steam network (7 – 20 bar, 200 – 350 °C), generated by pressure reduction of HP steam, is used within the refinery for stripping, atomisation, vacuum generation and heating (e.g. reboilers, tanks);
- Low pressure (LP) steam network (3.5 – 5 bar, 150 – 200 °C), generated in heat exchangers by cooling of hot products, and by pressure reduction of MP steam. LP steam is used for heating, stripping and tracing.

Steam is produced by heating demineralised water, ‘boiler feed water’ (BFW), under pressure in a steam boiler. Steam-raising plants are normally fuelled with refinery fuel gas or liquid. The refinery is equipped with dedicated steam boilers in virtually all process units, containing a HP-, MP- and LP-steam distribution network and with HP-, MP- and LP-condensate collection networks, which are connected with the BFW preparation unit and the condensate storage tank. (Reference is made to Figure 2.15 and to the LCP BREF [7, EC 2006].)

Steam used in turbines and heaters after cooling is usually recovered as condensate. BFW is therefore a mixture of fresh demineralised make-up water (quality dependent on steam pressure) and recovered condensate. BFW make-up can be brought in but can also be prepared at the refinery using drinking water, filtered groundwater, seawater distillation, surface water or even treated effluent by using a combination of treatment operations, such as sand filtration or microfiltration (to remove suspended solids) and demineralisation which is accomplished by subsequent cation and anion exchange (see dotted area in Figure 2.15). Reverse osmosis (to remove ions, colloids and large organic molecules) is usually applied in new plants and is followed in some cases by mixed-bed ion exchange and active carbon filtration for final polishing. The condensate tank is generally equipped with an oil detection system and an oil skimming device. To avoid corrosion in the steam and condensate systems, oxygen and carbon dioxide are removed in deaerators, and oxygen scavengers and corrosion inhibitors are added. After conditioning, the BFW is pumped to the boilers. In boilers, the hot flue-gases and BFW flow countercurrently; BFW is preheated in the economiser and further heated in the first and second superheater. In order to keep the concentration of dissolved compounds and suspended solids in the steam drum constant, a condensate blowdown of 1 – 2 % is normally required.
**Electrical power**

Power is mainly generated in turbines with high-pressure steam but can also be produced in gas turbines on site and/or bought from the grid (e.g. hydrogenerated power). Electricity is necessary to run pumps, compressors, control systems, valves, etc. Refinery electrical systems are therefore extensive.

**Energy management**

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal aim is to continuously match the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This issue is also analysed in this document and Section 2.15 examines the integration of all techniques that may be used in a refinery. This section is included here because the energy efficiency of a refinery can be increased not only by improving the energy efficiency of the individual processes (which is addressed in each section) or energy efficiency of the energy production system but also by improving energy management, energy conservation and heat integration/recovery within the refinery as a whole.

Energy management has long been an important issue for refineries. For example, management techniques such as the ISO 14000 system series, the EN 16001 System or EMAS can provide an appropriate framework to develop suitable energy management systems and can increase the energy efficiency of the refinery as a whole. Energy conservation techniques such as reporting and giving incentives for energy savings, carrying out combustion improvements or reviewing the energy integration of the refinery are some of the techniques that may have a great impact on reducing energy consumption and consequently on increasing the energy efficiency of a refinery. Other technical tools to increase efficiency are the heat integration/recovery techniques, of which examples are: the installation of waste heat boilers, the installation of expanders to recuperate power and increasing the insulation of buildings and process units to reduce heat losses. Steam management is another good tool for increasing energy efficiency.
2.11 Etherification

Purpose and principle
A number of chemicals (mostly alcohols and ethers) are added to motor fuels either to improve performance or to meet environmental requirements. Since the 1970s, alcohols (methanol and ethanol) and ethers have been added to gasoline to increase octane levels, reduce carbon monoxide generation and reduce atmospheric ozone due to the lower reactivity of resulting VOC emissions. The octane improvement has been a factor in the phase out of lead as a fuel additive. These additives replaced the lead additives which were being phased out as required by the Auto-Oil I programme. As a result, a number of different ethers are currently added to the gasoline and are better able to meet both the new oxygen requirements and the vapour pressure limits. The most common ethers being used as additives are methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME). Some refineries (~30 % of EU refineries) manufacture their own supplies of these ethers.

Feed and product streams
Isobutylene and/or isoamylene and methanol (or ethanol) are necessary to produce MTBE (or ETBE) and/or TAME. Isobutylene is obtained from a number of refinery sources including: the light naphtha from the FCC and coking units; the by-product from steam cracking of naphtha processes described in LVOC BREF [85, EC 2003] or light hydrocarbons during the production of ethylene and propylene also in LVOC BREF; catalytic dehydrogenation of isobutane also in LVOC BREF and conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides within LVOC BREF. Methanol (ethanol) is bought in comes from an external supply.

Process description
Multiple variations of commercial processes are available. Most processes can be modified to react isobutylene or isoamylene with methanol or ethanol to produce the corresponding ether. All use an acidic ion exchange resin catalyst under controlled temperature and pressure conditions. Temperature control of the exothermic reaction is important to maximise conversion and minimise undesirable side effects and catalyst deactivation. The reaction is usually carried out in two stages with a small excess of alcohol to achieve isoolefin conversions of over 99 % and the methanol consumption is essentially stoichiometric. The basic difference between the various processes is in reactor design and the method of temperature control.

**MTBE production process**
Figure 2.16 shows an example of a simplified process flow diagram of an MTBE plant. The feed stream is cooled prior to entering the top of the primary reactor. The resin catalyst in the primary reactor is a fixed-bed of small beads. The reactants flow down through the catalyst bed and exit the bottom of the reactor. Effluent from the primary reactor contains ether, methanol and unreacted isoolefin and usually some paraffins from the feed. A significant amount of the effluent is cooled and recycled to control the reactor temperature. The net effluent feeds to a fractionator with a section containing catalyst or to a second reactor. Ether is withdrawn as the bottom product; and unreacted alcohol vapour and isoolefin vapour flow up into the catalyst reaction to be converted to ether. The process usually produces an ether stream and a relatively small stream of unreacted hydrocarbons and methanol. The methanol is extracted in a water wash and the resulting methanol-water mixture is distilled to recover the methanol for recycling. The excess methanol and unreacted hydrocarbons are withdrawn as net overhead product, and fed to a methanol recovery tower. In this tower the excess methanol is extracted by contact with water. The resultant methanol-water mixture is distilled to recover the methanol, which is then recycled to the primary reaction.
ETBE production process
The MTBE unit is able to produce ETBE with minor modifications and elimination of bottlenecking (increase capacity of the column and cooler, increase bottom temperature on catalytic column, change top and bottom temperature on ethanol/water column).

TAME production process
In this process, C\textsubscript{5} isoamylenes are separated from the light catcracked spirit stream (LCCS) from the FCC unit and catalytically reacted with methanol in the presence of hydrogen to produce TAME. The main stages for TAME production are pentane removal, scavenging, reaction and purification. Figure 2.17 shows a simplified scheme for the TAME production.

C\textsubscript{5} removal is achieved by distillation (depentaniser) of the LCCS feedstock. Overheads are condensed and the hydrocarbons are returned as reflux while gases go to the refinery flue-gas system. A C\textsubscript{5} side-stream is withdrawn from the column as feed to the TAME unit. Column bottom liquids (C\textsubscript{6+}) are routed to re-blending with the eventual product from the TAME unit.

The C\textsubscript{5} stream is then scavenged to remove catalyst poisons by passing it through an ion exchange resin to remove basic nitrogen compounds, e.g. ammonia, and any metallic contamination. A hydrogen feed is also scavenged to remove any acidic components. The feedstock, containing injected methanol and hydrogen, is fed to the reactor section. Hydrogen is used to convert dienes into monoolefins and prevent gum formation during the reaction. This takes place over a palladium-impregnated ion-exchange resin and the isoamylenes are converted to TAME.

The TAME product stream is purified by fractional distillation, washing and phase separation. Fractionator overheads pass to a reflux drum with the gaseous phase of low-boiling hydrocarbons (C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{4}, etc.) together with unreacted hydrogen before being vented to refinery fuel gas or flare. The bottom product of TAME gasoline with some methanol is cooled and mixed with recycled water from the methanol recovery plant, then routed to a settler for phase separation. The TAME gasoline fraction from this is blended with the depentaniser bottoms C\textsubscript{6+} stream and passed to storage. The methanol/water fraction is recycled to the methanol recovery plant feed drum.
Methanol is recovered by distillation in a common still with the overhead’s methanol being condensed and passed to buffer storage for recycling to the TAME plant or other uses. The bottoms are essentially water with some contaminants and are mainly recycled with a purge to effluent treatment to avoid formic acid buildup.

Figure 2.17: Simplified process flow scheme for TAME production

2.12 Gas separation processes

Purpose and principle
Low-boiling hydrocarbons are usually treated in a common separation plant operating at elevated pressures. The purpose of a gas plant is to recover and to separate \( \text{C}_1 - \text{C}_5 \) and higher compounds from various refinery off-gases by distillation. In mineral oil refineries, one (or more) gas plant is present to handle different gas streams from different processes. (e.g. cat reformers, cat crackers, distillation units). These plants are the core for installations refining natural gas (Section 2.17) where the different components are separated. Depending on application of the products, some refineries remove mercury from LPG, tops and naphtha.

Feed and product streams
The feed of the gas plant consists of gas and liquid streams from crude distillation, cat crackers, catalytic reformers, alkylation, desulphurisation and similar units. Pretreatment of some feedstocks may be necessary, typically by hydro-desulphurisation (Section 2.13) or amine treating (H\(_2\)S removal, see Section 4.25.5.1). The compounds recovered depend on the composition of the feed and the market requirements. The gas streams are normally separated into \( \text{C}_1 \) and \( \text{C}_2 \) fractions for sale or use as refinery fuel gas, LPG (propane and butane) and a light gasoline (\( \text{C}_3 \) and higher) stream. Olefins, isoparaffins and n-paraffins can be also separated in the process.

Process description
As a minimum, the gas plant consists of two columns where the first one, an absorber/stripper column (deethaniser) strips all light \( \text{C}_2 \)-minus components to maximise recovery of \( \text{C}_3 \)-plus
components from the feed streams. Figure 2.18 shows a simplified process flow diagram of a gas plant.

![Simplified process flow scheme for a part of a gas plant](image)

**Figure 2.18:** Simplified process flow scheme for a part of a gas plant

The feed stream to the gas plant is cooled and chilled, the residual vapour phase from this being routed to a refrigerated absorber, meeting chilled recycled light gasoline absorbent. Absorber overhead is the C\textsubscript{1}, C\textsubscript{2} fraction. The bottoms are combined with the liquid stream from chilling, and pass to the first fractionator or deethaniser. The first fractionator overheads (essentially C\textsubscript{2}-ethane) are combined with the absorber overheads while the bottoms pass to the second fractionator to produce a C\textsubscript{3}/C\textsubscript{4} overheads stream and debutanised gasoline bottoms. A recontacting section, where vapours from various units are compressed and recontacted with the deethaniser overhead can be installed to maximise the C\textsubscript{3}/C\textsubscript{4} recovery. The bottoms of the deethanizer column, mainly C\textsubscript{3}/C\textsubscript{4} compounds, are fed to the depropaniser column. This overheads stream is routed to a third fractionator to split the C\textsubscript{3} and C\textsubscript{4} streams as overheads (propane) and bottoms (butane) respectively. Products pass to pressurised storage via any final sweetening by selective molecular sieve adsorption. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the refinery fuel gas system.

The gasoline bottom stream passes to a fourth fractionator to produce a depanentised fraction for use as chilled, recycled gasoline on the absorber. The net output is blended to form the gasoline product. A drying step before sending to storage can be necessary (not shown). Also, a vessel containing a bed of caustic pellets (not shown) can be installed in the butane system as an additional guard, although water and H\textsubscript{2}S should have been removed in the top of the deethaniser and depropaniser column. If no (or insufficient) upstream treatment has taken place, this can also be done in the unit itself, e.g. with an amine H\textsubscript{2}S absorber followed by a mercaptan oxidation/extraction of the deethaniser bottoms with amine H\textsubscript{2}S absorption of the deethaniser net overhead gas.

If thermal and/or catalytic cracking units are present, recovery of olefinic components may also be worthwhile. It is also possible to separate isobutane from n-butane. The isobutane can be used as feed to an alkylation unit, while the n-butane (or part of it) can be used as a blending component in the gasoline pool or isomerisation.
2.13 Hydrogen-consuming processes

Two types of processes are included in this section: hydrocracking and hydrotreatments. Both processes take place over a metal catalyst in a hydrogen atmosphere. Many of these processes are found in a refinery, normally named according to the type of feed to treat and the reaction conditions. The common denominator to these processes is that all rely on hydrogenation processes and consequently consume hydrogen. Isomerisation processes of alkanes or olefins also consume some hydrogen, but these processes are included in a separate section (Section 2.16).

Purpose and principle

Hydrotreating and hydroprocessing

Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulphur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from the crude distillation units, also cracks these heavier molecules to lighter, more saleable products. Both processes are usually placed upstream of these processes in which sulphur and nitrogen could have adverse effects on the catalyst, such as catalytic reforming and hydrocracking units. The processes use catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen.

Hydrotreating can be divided into a number of reaction categories: hydrodesulphurisation, hydrodenitrification, saturation of olefins and saturation of aromatics. A hydrotreater unit specifically employed to remove sulphur is usually called a hydrodesulphurisation unit (HDS). In this section the standard hydrotreating of naphtha, mid-distillate and residue-type feed streams is discussed and includes the items described below.

- A naphtha hydrotreater unit normally serves three purposes: desulphurisation, denitrogenation and stabilising the naphtha feed stream to the downstream isomerisation and reformer units. Stabilising the naphtha streams usually requires the conversion of unsaturated hydrocarbons produced in thermal and catalytic cracking processes into paraffins. The selective hydrogenation of light dienes that are contaminants of many light olefin streams may also be partially hydrogenated. Hydrogenation of aromatics is a variant of either naphtha or of processed distillate. Gasoline desulphurisation is dominated by sulphur removal from FCC naphtha, which accounts for about 35 % of gasoline pool but over 90 % of sulphur in gasoline. Deep reduction of gasoline sulphur (to below 10 ppm) must be made without decreasing octane number or losing gasoline yield. The problem is complicated by the high olefins contents of FCC naphtha which contributes to octane number enhancement but can be saturated under HDS conditions.

- A mid-distillate hydrotreater unit normally has two purposes: desulphurisation and hydrogenation of the mid-distillate stream. Stabilising mid-distillate streams is required when large quantities of cracked components are blended to the mid-distillate pool, and usually requires partial saturation of aromatics and olefins and a reduction of the N-content. The full saturation of aromatics may be required to prepare naphtha, kerosene, and diesel feedstocks. Among the applications of this process are smoke-point improvements in aircraft turbine fuels, reduction of the aromatic content of solvent stocks to meet requirements for air pollution control, production of cyclohexane from benzene (LVOC) and cetane number improvement in diesel fuels.

- Diesel oil deep desulphurisation (Hydrofining) is normally done to heating and diesel oils to meet product sulphur specifications. Large decreases of diesel sulphur are dictated by 4,6-dimethyl dibenzothiophene, as it is the least reactive sulphur compounds that have substitutions on both 4- and 6-positions. The deep HDS problem of diesel streams is
exacerbated by the inhibiting effects of co-existing poly-aromatics and nitrogen compounds in the feed as well as H₂S in the product. Other reasons are to improve colour and sediment stability.

- Residue hydrotreating is mainly applied to improve the residue feed quality (normally atmospheric residue) to a residue catalytic cracker (RCC) unit. RCCs are restricted to process residue streams by their metal content and Concarbon number.

Hydroprocessing may also be designed to remove low-levels of metals from the feed. The metals to be removed include nickel and vanadium, which are native to the crude oil, as well as silicon and lead-containing metals that may be added elsewhere in the refinery.

Hydrocracking is one of the most versatile of all refining processes, capable of converting any fraction, from atmospheric gasoils to residual (deasphalted) oil into products with a lower molecular weight than the feed. The hydrocracking reactions occur under high hydrogen partial pressure in the presence of a catalyst with a two-fold function: hydrogenation and cracking. Hydrocracking may also be used for the cracking of superior fuels and the production of lubricants (dewaxing is discussed in Section 2.3). The type of catalyst maximises the production of naphtha, mid-distillates or lube production. The presence of hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products, giving net products, which are a mixture of pure paraffins, naphthenes and aromatics. Hydrocracking produces mid-distillates with outstanding burning and cold flow properties as follow:

- kerosene with low freezing points and high smoke points;
- diesel fuels with low pour points and high cetane numbers;
- heavy naphthas with a high content of single-ring hydrocarbons;
- light naphthas with a high isoparaffin content;
- heavy products that are hydrogen-rich for feed FCC units, ethylene plants (LVOC), or lube oil dewaxing and finishing facilities (Section 2.3).

When hydrocracking is applied to heavy residues, a pretreatment is needed to remove high metal content before the hydrocracking reaction is produced. Residue hydroconversion is a type of hydrocracking applied to convert low-value vacuum residue and other heavy residue streams into lighter low-boiling hydrocarbons by reacting them with hydrogen.

**Feed and product streams**

Hydrotreating and hydroprocessing

These processes are applied to a wide range of feedstocks, from LPG up to heavy residue and mixture thereof. Table 2.3 summarises the feeds, products and process objectives for each type of hydrotreatment.
### Table 2.3: Feedstocks, desired products and process objectives of hydrotreatments

<table>
<thead>
<tr>
<th>Feedstocks</th>
<th>Desired products</th>
<th>For the removal of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clean LPG</td>
<td>S, olefins</td>
</tr>
<tr>
<td>LPG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthas</td>
<td>Catalytic reformer feed</td>
<td>S (&lt;0.5 ppm), N, olefins</td>
</tr>
<tr>
<td></td>
<td>(S: 0.05 – 0.5 % w/w)</td>
<td></td>
</tr>
<tr>
<td>LPG, naphthas</td>
<td>Low diene contents</td>
<td>Dienes (25 – 1 ppm) in product</td>
</tr>
<tr>
<td>Cat. cracked naphtha</td>
<td>Gasoline blending component</td>
<td>S</td>
</tr>
<tr>
<td>Atmospheric gas oils</td>
<td>Ethylene feedstock (LVOC)</td>
<td>S, aromatics</td>
</tr>
<tr>
<td></td>
<td>Jet</td>
<td>S, aromatics</td>
</tr>
<tr>
<td></td>
<td>Diesel</td>
<td>S, aromatic and n-paraffins</td>
</tr>
<tr>
<td>Vacuum gas oils</td>
<td>Ethylene feedstock</td>
<td>Aromatics</td>
</tr>
<tr>
<td></td>
<td>Kerosene/jet</td>
<td>S, aromatics</td>
</tr>
<tr>
<td></td>
<td>(S: 0.05 to 1.8 % w/w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diesel</td>
<td>S, aromatics</td>
</tr>
<tr>
<td></td>
<td>(S: 0.05 to 1.8 % w/w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FCC feed</td>
<td>S, N, metals</td>
</tr>
<tr>
<td></td>
<td>Low-sulphur fuel oil</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>Lube oil base stock</td>
<td>Aromatics</td>
</tr>
<tr>
<td>Atmospheric residue</td>
<td>FCC feedstock</td>
<td>S, N, CCR(asterisk), and metals</td>
</tr>
<tr>
<td></td>
<td>Low-sulphur fuel oil</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>Coker feedstock</td>
<td>S, CCR, and metals</td>
</tr>
<tr>
<td></td>
<td>RCC feedstock</td>
<td>CCR, and metals</td>
</tr>
</tbody>
</table>

(asterisk) NB: CCR=Conradson carbon residue.

### Hydrocracking

Hydrogen in substantial quantities is consumed in these processes, making the hydrogen manufacturing unit mandatory (Section 2.14) in these refineries that contain hydrocracking. In addition to the treated products, these processes produce a stream of light fuel gases containing hydrogen sulphide, ammonia and water.

As is reflected in Table 2.4, the main feed stream to a hydrocracker is the heavy vacuum distillate stream from the high vacuum distillation unit. These feedstocks are fractions which are very difficult to crack and cannot be cracked effectively in catalytic cracking units. Other process streams such as heavy cycle oil from the cat cracker unit, heavy gasoils from the coker or visbreaker unit, extracts from lube oil units, mid-distillates, residual fuel oils and reduced crudes may be blended to the main heavy vacuum distillate stream. The main products are LPG, gasoline, jet fuel and diesel fuel, all practically sulphur-free. The production of methane and ethane is very low, normally less than 1%.

### Table 2.4: Feedstocks and desired products of hydrocracking processes

<table>
<thead>
<tr>
<th>Feedstocks</th>
<th>Desired products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthas</td>
<td>LPG</td>
</tr>
<tr>
<td>Atmospheric gas oils</td>
<td>Naphtha</td>
</tr>
<tr>
<td>Atmospheric residue</td>
<td>LPG</td>
</tr>
<tr>
<td>Vacuum gas oils</td>
<td>Naphtha</td>
</tr>
<tr>
<td></td>
<td>Ethylene feedstock (LVOC)</td>
</tr>
<tr>
<td></td>
<td>Kerosene/jet</td>
</tr>
<tr>
<td></td>
<td>Diesel</td>
</tr>
<tr>
<td></td>
<td>Lube oil base stock</td>
</tr>
<tr>
<td>Vacuum residues</td>
<td>LPG</td>
</tr>
<tr>
<td>Tars and derived bitumens (metal content &lt;500 ppm)</td>
<td>Diesel</td>
</tr>
</tbody>
</table>
Chapter 2

Process description

Types of reactor technologies applied in hydroconversion and hydrotreatment

There are several residue hydrotreating and hydroconversion technologies in use today. They can be classified into four categories: fixed-bed; swing reactor; moving-bed and ebullated-bed. The selection of the type of process is predominantly determined by the metal content in the feed. Fixed-bed residue hydroconversion is applied for ‘low’ metal-containing feeds (100 ppm) and the required conversion is relatively low, moving bed or ebullated bed technology is used for ‘high’ metal-containing feeds. To overcome metal poisoning of the catalyst in fixed-beds and to maintain the concept, some licensors propose the swing reactor concept: one reactor is in operation whilst the other one is off-line for catalyst replacement. The concept and layout of the fixed-bed hydroconversion technology is identical to long residue hydrotreating. Moving bed technology or ebullated bed technology is selected when the metal content in the residue feed is typically above 100 ppm but below 500 ppm. Normally this concentration of metals in the feed is found in vacuum residue streams from heavier crudes, bitumen streams from tar sands and heavy atmospheric residue streams. Both technologies allow withdrawal and replacement of the catalyst during operation, the main difference is the reactor configuration.

Hydrotreating and hydroprocessing

Naphtha hydrotreater. Naphtha feed is mixed with a hydrogen-rich gas stream, heated and vaporised in the reactor feed/effluent exchanger and the furnace, and fed into the hydrotreater reactor with a fixed-bed cobalt/nickel/molybdenum catalyst. The reactor conditions can vary but are typically 30 to 40 bar and 320 to 380 °C. The reactor effluent is cooled in the feed/effluent exchanger and reactor cooler and flashed into the high-pressure separator. The flashed vapours, consisting mainly of unreacted hydrogen, are compressed and recycled to the reactor. The fractionation part is very similar to the one explained in the hydroconversion process. (See also hydrofining below in this section)

Catalytic distillation. (CD HDS)

This process aims to selectively desulphurise (ultra low sulphur) FCC gasoline with minimum octane loss. Hydrogen and full range FFC gasoline are fed to the reactive distillation column where light naphtha is distilled from the top. Bottoms containing the reacted mercaptans are fed to the CD HDS where heavy and mid naphtha are catalytically desulphurised. Catalytic distillation eliminates catalyst fouling because fractionation removes heavy coke precursors from the catalyst zone. Lifetime of CD HDS is similar to FCC (4-5 year cycles). Milder temperature and pressure diminishes octane losses.

Distillate hydrodesulphurisation

Figure 2.19 provides a simplified flow diagram of a typical distillate HDS unit. The distillate feed may range from kerosene up to long vacuum gas oil or mixtures thereof. The reactor system is in principle the same as for the naphtha hydrotreater. The main difference is that the feed does not fully vaporise and the reactor operating conditions are more severe, 40 – 70 barg and 330 – 390 °C. Furthermore, it is normal practice that wash water is injected into the reactor effluent stream when nitrogen-rich feedstocks are desulphurised.

Solid deposits like ammonium sulphides (NH₄)₂S and chlorides NH₄Cl are formed in the cooler parts of the unit and must be removed by water wash. The liquid from the low-pressure separator is fed to a stripper column to stabilise and strip off the light hydrocarbons and H₂S. The stripping steam and light hydrocarbons are taken overhead, condensed and separated into a sour water phase and a hydrocarbon phase. The water phase is sent to the sour water stripper, and the light hydrocarbon phase is normally recycled to the crude unit or naphtha hydrotreater distillation section for further fractionation. Any water dissolved and dispersed in the distillate should be removed to avoid the formation of haze and ice when stored.
The wet distillate is therefore either fed to a vacuum column, where the total water content is lowered to 50 ppm, or sometimes a combination of coalescer and molecular sieve beds is used, where water is selectively adsorbed on the bed.

Diesel oil deep desulphurisation (hydrofining).
Because this technique operates at low pressures, efficient hydrogen utilisation can be achieved within an overall refinery context. Very low sulphur contents can be achieved (8 ppm) in the raffinate. The unit usually operates at 45 bar and consumes very small amounts of hydrogen. Equivalent gasoline deep desulphurisation techniques for gasoline with a comparatively low hydrogen consumption are currently under development.

Research on this process has gained considerable importance in recent years (further information can be found in Sections 3.13, 4.13 and 6 of this document). Development is taking place both at the research and industrial levels to deliver a wider process option. Approaches can be grouped depending on whether the technique is applied before, after or during FCC; uses a large, a medium or no \( \text{H}_2 \) to remove sulphur species; targets solely reduction of sulphur content or combines other improvement processes; is a new process or an optimisation (revamping) of HDS design or conditions.

Lower sulphur content can be achieved by revamping existing HDS units by means of replacing catalyst type, increasing catalyst volume, enhancing operating severity (temperature and \( \text{H}_2 \) pressure), removing \( \text{H}_2 \text{S} \) from recycle gas and use high efficiency distribution trays. Commercially available catalyst are numerous and evolving, such as new catalyst preparation method that increases active Co-Mo-S phase.

The following tables show examples on revamping process data:

| Table 2.5 Revamping process examples from 500 ppm to 30 ppm sulphur |
|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                          | Current | UOP   | IFP   | Akzo | Criterion | Topsoe |
| LHSV(*)                 | 2       | 1.5   | 1.45  | 1.08 | 0.5       | 1     |
| Amine scrubber installed| no      | yes   | yes   | yes  | yes       | yes   |
| Mol % purity of \( \text{H}_2 \) | 75      | 90    | 91.3  | 75   | 75        | 75    |
| Ratio of circulating \( \text{H}_2 \) | 1       | 1.9   | 3.649 | 1    | 1.6       | 1.16  |
| Catalyst packing method  | Sock    | Dense | Sock  | Sock | Sock      | Sock  |

(*) Liquid Hourly Space Velocity

Source: [79, Fayruzov et al. 2009]
Table 2.6  Revamping process examples from 30 ppm to 10 ppm sulphur

<table>
<thead>
<tr>
<th>LHSV(*)</th>
<th>UOP</th>
<th>IFP</th>
<th>Akzo</th>
<th>Criterion</th>
<th>Topsoe</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHSV(*)</td>
<td>1.5 to 0.9</td>
<td>1.45 to 1</td>
<td>1.08 to 0.45</td>
<td>0.5 to 0.4</td>
<td>1 to 0.7</td>
</tr>
<tr>
<td>Ratio of circulating H2</td>
<td>1.9 to 2</td>
<td>3.649 to 2</td>
<td>1</td>
<td>1.6 to 1.85</td>
<td>1.16</td>
</tr>
<tr>
<td>Partial pressure (kg/cm2)</td>
<td>46</td>
<td>58</td>
<td>46</td>
<td>46</td>
<td>46</td>
</tr>
</tbody>
</table>

(*) Liquid Hourly Space Velocity

Source: [79, Fayruzov et al. 2009]

New deep HDS processes focus on process and reactor design configuration as well as addressing other steps. Some examples are octane recovery, cetane increases, dearomatization, eliminating Nitrogen compounds. These new techniques are based on other principles like reactive distillation, adsorption, reactive adsorption at high temperature or polar adsorption in counter current approach. Some of them might consume significant lower H2 like reactive adsorption.

There has been intensive development in non-H2 desulphurisation techniques. Most of them are mentioned in Chapter 6 of this document. Some oxidative desulphuration processes (like SulphCo) have reached commercialization with substantially lower operating costs.

Following Table 2.7 illustrates some process of deep desulphurisation of gasoil and naphtha:

Table 2.7  Examples of process for deep gasoil and naphtha desulphurisation

<table>
<thead>
<tr>
<th>Process</th>
<th>Key feature</th>
<th>Industrial application</th>
<th>H2-consumption</th>
<th>Octane loss</th>
<th>Name of process</th>
<th>Licensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha hydro-treating (NHT)</td>
<td>Conventional</td>
<td>yes</td>
<td>high</td>
<td>high</td>
<td>various</td>
<td>a number of firms</td>
</tr>
<tr>
<td>NHT+ octane increase</td>
<td>Zeolite + isomerisation</td>
<td>yes</td>
<td>high</td>
<td>low</td>
<td>Octgain, Isal</td>
<td>ExxonMobil, UOP</td>
</tr>
<tr>
<td>Selective NHT</td>
<td>RT-225</td>
<td>yes</td>
<td>medium</td>
<td>low</td>
<td>SCANfining</td>
<td>ExxonMobil</td>
</tr>
<tr>
<td>Dual catalyst</td>
<td>Catalytic distillation</td>
<td>yes</td>
<td>medium</td>
<td>low</td>
<td>Prime-G+</td>
<td>IFP</td>
</tr>
<tr>
<td>Selective NHT + octane increase</td>
<td>Combination</td>
<td>yes</td>
<td>medium</td>
<td>low</td>
<td>SCANfining II</td>
<td>ExxonMobil</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Zn adsorbent</td>
<td>yes</td>
<td>low</td>
<td>low</td>
<td>S Zorb</td>
<td>Philips</td>
</tr>
<tr>
<td>Alumina adsorbent</td>
<td>yes</td>
<td>low</td>
<td>low</td>
<td>Irvad</td>
<td>Alcoa</td>
<td></td>
</tr>
<tr>
<td>Extractive distillation</td>
<td>Selective solvent sys.</td>
<td>yes</td>
<td>none</td>
<td>low</td>
<td>GT-DeSulf</td>
<td>GTC</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Peroxyacid</td>
<td>yes</td>
<td>low</td>
<td>low</td>
<td>CED</td>
<td>Petrostar</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>pilot</td>
<td>none</td>
<td>low</td>
<td>SulphCo</td>
<td>Bechtel</td>
<td></td>
</tr>
<tr>
<td>Alkylation</td>
<td>Solid acid</td>
<td>yes</td>
<td>low</td>
<td>low</td>
<td>OATS</td>
<td>BP</td>
</tr>
<tr>
<td>Bio processing</td>
<td>Bio catalysis</td>
<td>yes</td>
<td>none</td>
<td>low</td>
<td>Enchira</td>
<td></td>
</tr>
</tbody>
</table>

Source: [80, Stanislaus et al. 2010]

Residue hydrotreating
The principle process scheme for residue hydrotreating is the same as normal distillate. The main difference is the reactor system which normally consist of two or three reactors in series. Removal of the metals from the residue feed normally occurs in the first reactor(s) and uses a low-activity coarser Co/Mo catalyst. Further hydrotreating and hydrogenation occur in the tail reactor(s), resulting in a higher hydrogen-to-carbon ratio and a lower Concarbon number of the residue. Since the catalysts operate in a H2S and NH3-rich environment the nickel/molybdenum
or nickel/tungsten catalysts are usually applied in the tail reactors. Table 2.8 shows the typical hydrotreatment operating conditions for the different feedstocks:

### Table 2.8: Typical hydrotreating operating conditions

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Naphtha</th>
<th>Mid distillate</th>
<th>Light gas oil</th>
<th>Heavy gas oil</th>
<th>Residuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid hourly space velocity</td>
<td>1.0 – 5.0</td>
<td>1.0 – 4.0</td>
<td>1.0 – 5.0</td>
<td>0.75 – 3.0</td>
<td>0.15 – 1</td>
</tr>
<tr>
<td>H₂/HC ratio, Nm³/m³</td>
<td>50</td>
<td>135</td>
<td>170</td>
<td>337</td>
<td>300</td>
</tr>
<tr>
<td>H₂ partial pressure, kg/cm²</td>
<td>14</td>
<td>28</td>
<td>35</td>
<td>55</td>
<td>55</td>
</tr>
</tbody>
</table>

Source: [166, Meyers, 1997]

Hydrogenation of light dienes
This process is a highly-selective catalytic process that can hydrogenate acetylenes and dienes to the corresponding monoolefin without affecting the valuable olefin content of the feedstock. In addition, this process can be designed to provide hydroisomerisation of some of the olefins (e.g. conversion of 1-butene to 2-butene). Hydrogenation takes place in a liquid-phase fixed-bed reactor. Unless the hydrogen purity is low, no separation step is required for the removal of the light ends from the product. Thus, reactor effluent can be charged directly to downstream units.

Saturation of aromatics
The use of highly-active noble-metal catalysts permits the reactions to take place under mild conditions. Because of the mild conditions and the very selective catalyst, the yields are high, and hydrogen consumption is largely limited to just the desired reactions. The process is carried out at moderate temperatures (205 – 370 ºC) and pressures (3,500 to 8,275 kPa) over a fixed catalyst bed in which aromatics are saturated and in which hydrogenation of olefins, naphthenic ring openings and the removal of sulphur and nitrogen occur.

Hydrocracking
Hydrocracking normally uses a fixed-bed catalytic reactor with cracking occurring under substantial pressure (35 to 200 kg/cm²) in the presence of hydrogen at temperatures between 280 and 475 ºC. This process also breaks the heavy, sulphur-, nitrogen- and oxygen-bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated and dewatered to remove impurities (H₂S, NH₃, H₂O) before being sent to the hydrocracker. If the hydrocracking feedstocks are first hydrotreated to remove impurities, sour water and sour gas streams will contain relatively low-levels of hydrogen sulphide and ammonia in the fractionator.

Depending on the products desired and the size of the unit, hydrocracking is conducted in either single-stage or multi-stage reactor processes. Hydrocrackers can be classified into three categories: single-stage once-through; single-stage recycle and two-stage recycle. These categories are described below:

Only fresh feed is processed in the single-stage once-through hydrocracker. The conversions achieved are around 80 – 90 % depending on catalyst and reactor conditions. The heavy residue is either sent to the fuel oil pool or further processed in a cat cracker or coking unit.

In the single-stage recycle configuration, the unconverted oil is recycled to the reactor for further conversion, increasing the overall conversion to around 97 – 98 %. A small bleed stream of about 2 – 3 % on fresh feed is required to avoid a buildup of polyaromatics (PAH) in the recycle loop. Figure 2.20 shows a simplified process flow diagram of the single-stage hydrocracker with recycle configuration. In the first reactor beds, conversion of N and S compounds, saturation of olefins and partial saturation of PAH takes place. In the subsequent beds, the actual cracking will take place. The vapour from the low-pressure (LP) separator is used as refinery fuel after amine treating. Many different fractionation section configurations
are found. A common fractionation section is illustrated in Figure 2.20. The product stream is fed to the debutaniser column to separate the LPG. The LPG stream is washed in an amine wash and then fractionated into a propane and a butane stream. The bottom stream from the debutaniser column is fed to the first fractionator. In this column, a light naphtha stream is taken as overhead product, heavy naphtha and kerosene are taken as side-streams and the bottom stream is fed to a second fractionator. In the second fractionator, operating at mild vacuum, the diesel product is taken as the overhead product and the bottom stream and the unconverted oil is recycled to the reactor section.

![Figure 2.20: Simplified process flow scheme for hydrocracker (single stage with recycling)](image)

In the two-stage recycle configuration, the first hydrocracker reactor operates in a once-through mode with a typical conversion of around 50%. The unconverted oil from the first hydrocracker reactor is fed to a second hydrocracker reactor for further conversion. The unconverted oil from the second stage hydrocracker is recycled to achieve an overall conversion of around 97 – 98%. A small bleed stream of about 2 – 3% on fresh feed is also required here. This concept is normally applied when a very heavy high refractory feedstock such as deasphalted oil is processed. Two-stage configurations are usually more cost effective for large capacity units, and more flexible and efficient for processing difficult feedstocks. By adjusting specific catalysts for each stage, most ammonia and hydrogen sulphide can be generated at the first stage, allowing to settle down a cleaner second stage reaction environment with improved middle distillate production yield and product quality. Table 2.9 shows the typical operating conditions of hydrocrackers.

**Table 2.9: Typical hydrocracker operating conditions**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>High-pressure hydrocracking</th>
<th>Moderate-pressure hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, % w/w</td>
<td>70 – 100</td>
<td>20 – 70</td>
</tr>
<tr>
<td>Pressure, barg</td>
<td>100 – 200</td>
<td>70 – 100</td>
</tr>
<tr>
<td>Liquid hourly space velocity</td>
<td>0.5 – 2.0</td>
<td>0.5 – 2.0</td>
</tr>
<tr>
<td>Average reactor temperature °C</td>
<td>340 – 425</td>
<td>340 – 425</td>
</tr>
<tr>
<td>Hydrogen circulation, Nm³/m³</td>
<td>650 – 1700</td>
<td>350 – 1200</td>
</tr>
</tbody>
</table>

*Source: [166, Meyers, 1997]*
Hydroconversion
In principle, three reactions are taking place: hydrodemetallisation, hydrotreating/hydrogenation and hydrocracking. Removal of the metals from the residue feed predominantly occurs in the first reactor(s) and uses a low activity cobalt and molybdenes (Co/Mo) catalyst. Hydrotreating, hydrogenation and hydrocracking occur in the following reactor(s) where the quality is mainly improved by increasing the hydrogen-to-carbon ratio. Conversion levels to products in a hydroconversion process are typically 50 – 70 % but depend significantly on the type of hydroconversion process and the quality of the feedstock.

Figure 2.21 shows a simplified process flow diagram of a moving bed process. The process comprises five reactors in series, catalyst handling facilities and a work-up section. The reactors operate at high pressure and relatively high temperatures.

The first three reactors are bunker hydrodemetallisation (HDM) reactors. The nickel-vanadium (Ni+V) conversion typically exceeds 60 % for the first 60 days of operation and then gradually trends towards the expected equilibrium conversion level, 50 to 70 %. This way, high-metal feeds can be treated.

The last two reactors are fixed-bed desulphurisation and conversion reactors. The moving bed technology employs a bunker flow/moving bed technology to replenish the HDM catalyst continuously. Catalysts are transported through a slurry transport system in which the rate of catalyst replenishment is controlled in accordance with the rate of metal deposition. The catalyst in the HDM reactors flows concurrently downward with the process fluids. Screens separate the catalysts from the process fluids before leaving the reactor. Sluice systems are present at the top and the bottom of the reactors to enable catalyst addition and withdrawal.

The following conversion section consists of two fixed-bed reactors in series, containing catalysts, that are highly active for sulphur removal and conversion. The ebullated bed reactor operates as a fluidised-bed three-phase system with back mixing of the unconverted liquid and the catalyst.

The concept of the fractionation section is also very licensor-dependent as it depends on the configuration of the separator system and the resulting temperatures. Typically it consists of a main fractionator, a vacuum distillation column and some form of a gas plant to fractionate and stabilise the lighter fractions. Products from the fractionation section are normally refinery fuel gas, LPG, naphtha, kerosene, light gasoil, vacuum distillate and a low-sulphur/metal vacuum residue (bottoms) stream. The refinery fuel gas and LPG streams are amine washed to remove H₂S. The naphtha product is normally fed to a naphtha hydrotreater for further processing identical to the straight run naphtha product. The kerosene and light gasoil products are normally fed to a hydrotreater for further purification. The vacuum distillate is converted further in a hydrocracker or FCC unit. The bottom stream is normally blended into the heavy fuel oil pool or used as delayed coker feedstock.
2.14 Hydrogen production

Purpose and principle
Oil refining activities face an increasing demand for hydrogen in order to meet their requirements and challenges as far as increasingly stringent regulations for site emissions in air, adaptation of conversion capacities to the European market and higher quality standards of final products are concerned.

There is an increasing demand for hydrogen in European refining, and this evolving demand product slate requires increased use of hydrocracking and hydrotreating. More hydrodesulphurisation is needed to achieve legislative requirements for lower sulphur content in fuels.

In such context, the purpose of a hydrogen plant is to produce hydrogen for use in hydrocracking and other hydrogen-consuming refinery process units (Sections 2.13 and 2.16). Many refineries with simplest configuration may still produce sufficient quantities of hydrogen at reforming operations (Section 2.6) for hydrotreating. Nowadays, however, more complex plants with extensive hydrotreating and/or hydrocracking operations typically require more hydrogen than is produced by their catalytic reforming units. This extra hydrogen can be provided by one of the following processes:

- reforming operations (Section 2.6) for hydrotreating (refineries with the simplest configuration may produce sufficient quantities);
- steam reforming of light ends or natural gas;
- partial oxidation (gasification) of heavy oil fractions (IGCC in Section 2.10) to produce syngas where hydrogen can be separated.

Complex plants with extensive hydrotreating and/or hydrocracking operations typically require more hydrogen than is produced by their catalytic reforming units. The reliable operation of a hydrogen plant is critical for the hydrogen-consuming processes. Reactions that may occur in these processes are listed in Table 2.10.

Feed and product streams
The feed of the hydrogen plant consists of hydrocarbons in the range from natural gas to heavy residue oils and coke. The conventional steam reforming process produces a hydrogen product of a maximum of 97 – 98 % v/v purity and higher if a purification process is applied.
The partial oxidation process requires oxygen if oxygen-blown gasification is used instead of air-blown gasification.

Table 2.10: Main chemical reactions occurring in hydrogen production processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Standard conditions (kJ/mol) at 15°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming process</td>
<td>C(_n)H(_m) + n H(_2)O \rightarrow n CO + (n+m/2)\frac{1}{2} H(_2)</td>
<td>Generic for steam reforming (endothermic)</td>
</tr>
<tr>
<td></td>
<td>CH(_4) + H(_2)O \rightarrow CO + 3 H(_2)</td>
<td>Steam methane reforming ((\Delta H = -206 \text{kJ/mol at 15°C}))</td>
</tr>
<tr>
<td></td>
<td>CO + H(_2)O \rightarrow CO(_2) + H(_2)</td>
<td>Shift (exothermic) ((\Delta H = +41.2 \text{kJ/mol at 15°C}))</td>
</tr>
<tr>
<td></td>
<td>CO + 3 H(_2) \rightarrow CH(_4) + H(_2)O</td>
<td>Methanation (exothermic)</td>
</tr>
<tr>
<td></td>
<td>CO(_2) + 4 H(_2) \rightarrow CH(_4) + 2 H(_2)O</td>
<td></td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>C(_n)H(_m) + n/2 O(_2) \rightarrow n CO + m/2 H(_2)</td>
<td>Generic for partial oxidation (endothermic)</td>
</tr>
<tr>
<td></td>
<td>CO + H(_2)O \rightarrow CO(_2) + H(_2)</td>
<td>Shift (exothermic) ((\Delta H = +41.2 \text{kJ/mol at 15°C}))</td>
</tr>
<tr>
<td>Gasification</td>
<td>C + H(_2)O \rightarrow CO + H(_2)</td>
<td>Coke gasification ((\Delta H = -XXX \text{kJ/mol at 15°C}))</td>
</tr>
<tr>
<td></td>
<td>CO + H(_2)O \rightarrow CO(_2) + H(_2)</td>
<td>Shift (exothermic) ((\Delta H = +41.2 \text{kJ/mol at 15°C}))</td>
</tr>
</tbody>
</table>

In steam reforming, only light hydrocarbons are reacted with steam to form hydrogen. However, all products of a refinery could be used for hydrogen production by partial oxidation. The most interesting option from the economic point of view is to use products with a low market value. In some refineries, heavy oil residues are transformed to petroleum coke and subsequently gasified (Section 0) to produce syngas.

**Hydrogen production strategy**

Both reforming and gasification can lead to a minimised environmental impact at overall site scale. The choice between these two approaches primarily depends on two factors:

- the availability and nature of excess hydrocarbon streams which may be used as feedstocks
- the quantity of hydrogen required.

The primary advantage of a gasification strategy is that several useful products are generated as raw synthesis gas containing carbon monoxide and hydrogen (see Table 2.11). It does so from heavier refinery hydrocarbon streams that would not otherwise have been used. Therefore, the implementation of gasification technology has an environmental and economic benefit on the overall refinery conversion performance. However, one clear limitation is that the hydrogen produced from gasification can only be considered a by-product. The heavier the feedstock, the lower the H\(_2\)/CO ratio: the most common solid and liquid refinery streams are going to yield a molar ratio less than 1 (see Figure 4.29 in Chapter 4.14.1). The economic and environmental viability of the gasification technology depends primarily on having a productive use of the resulting syngas/CO primary product. The second limitation arises from the availability of hydrogen within the refinery. More specifically, the heavier refinery hydrocarbon (waste) streams that would be gasified simply may not have enough hydrogen in them to produce the required quantity. In case of very large hydrogen requirement (as is often the case) then an additional hydrogen supply (usually by light hydrocarbon steam reforming) would be needed.
By using a steam reforming strategy, the yield is much higher relative quantity of hydrogen will be yielded. As such, hydrogen can be truly considered the primary product. However, the main limitation of this process is that it requires a light feedstock (natural gas, naphtha or other light hydrocarbon cuts) which is also a potential high value feedstock for other refinery or petrochemical applications, or a favourable fuel source for reducing the site PM, NOx and SOx emissions.

In all cases, hydrogen purification is necessary to meet the downstream desulphurisation process requirements. This is true for steam reforming, gasification, or any other already existing streams within the refinery.

**Process description**

*Steam reforming*

This is the most commonly used method for hydrogen production. The best feedstocks for steam reforming are light, saturated, and low in sulphur; this includes natural gas (the most common), refinery gas, LPG, and light naphtha. This is usually combined with a hydrogen purification process to produce very pure hydrogen (>99% v/v). In its simplest form, as shown in Figure 2.22, the steam methane reforming process for pure hydrogen production consists of four stages: a desulphurisation unit, a steam methane reformer, shift reactor(s), and finally pressure swing adsorption.

![Figure 2.22: The four main steps of H₂ production by steam methane reforming](source: [56, EIGA 2009])

A simplified scheme of a steam reforming process is shown in Figure 2.23. The reaction is typically carried out at 760 – 840°C and a pressure of 20 – 40 barg over a fixed catalyst bed. The process is carried out in the presence of a catalyst which is very sensitive to poisoning. Desulphurisation of the feedstock is required in order to protect the catalyst in the reformer furnace against poisoning and deactivation.
It is common practice to operate at excess steam-hydrocarbon ratios to prevent carbon formation. Heat for the endothermic reforming reaction is provided by the furnace burners. The reformed gas, a mixture of hydrogen, carbon dioxide, carbon monoxide, methane and steam, is cooled down to about 350 °C by rising steam. After reforming, the CO in the gas is reacted with steam to form additional hydrogen (shift reaction). The oxidation of the CO to CO$_2$ can be done in a one-step (low, medium or high temperature) converter or, as shown on Figure 2.23 here below, in a two-step high shift (high followed by low temperature) converter, reducing the CO content to less than 0.4 %. The product gas passes to a CO$_2$ absorber after being cooled, where the CO$_2$ concentration is reduced to 0.1 % v/v by a suitable regenerable liquid absorbent (e.g., MEA, hot potassium carbonate or sulfinol). The solvent, enriched with CO$_2$, is stripped in a solvent regenerator. Residual CO and CO$_2$ in the absorber overhead gas is methanated, reducing the CO and CO$_2$ content to about 5 – 10 ppm. Unlike CO, a small amount of CH$_4$ is usually not objectionable in hydrocracking units and other hydrotreating. More information can be found in the LVIC-AFF BREF.

**Gasification of coke**

The processes used for the gasification of petroleum coke are the same as these used in the gasification of coal and they are integrated in the Flexicoker (Section 0). In an oxygen-blown operating mode of a gasifier, the gas produced can be processed to recover hydrogen or synthesis gas, or can be used as a medium-calorific value fuel. The gasifier product gas (syngas, CO, H$_2$, CO$_2$, CH$_4$ and H$_2$O) after it has passed the cyclones, contains hydrogen sulphide (H$_2$S) and carbonyl sulphide (COS). With a sulphur adsorbent such as limestone (CaCO$_3$) or dolomite (Mg, CaCO$_3$) in the gasifier, the sulphur content of the gas can be drastically reduced. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. The particulates in product gas are removed in the barrier filter. Volatile metals and alkali tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burned and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas.
Table 2.11: Example of composition of petroleum coke used and the composition of the syngas produced in an oxygen-blown fluidised-bed gasification process

<table>
<thead>
<tr>
<th>Analysis of petroleum coke used in gasification</th>
<th>Composition of gas produced by gasification at 980 – 1135 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate analysis</td>
<td>% w/w</td>
</tr>
<tr>
<td>Carbon</td>
<td>87.1 – 90.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.8 – 4.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.1 – 2.3</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.6 – 2.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>Proximate analysis</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>80.4 – 89.2</td>
</tr>
<tr>
<td>Volatiles</td>
<td>9.0 – 9.7</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.9 – 10.2</td>
</tr>
<tr>
<td>Ash</td>
<td>0.2 – 0.4</td>
</tr>
</tbody>
</table>

*Source: [166, Meyers, 1997]*

Gasification of hydrocarbons (partial oxidation)

In partial oxidation, hydrocarbon feed reacts with oxygen at high temperatures to produce a mixture of hydrogen and carbon monoxide (also covered in IGCC in Section 2.10). Since the high temperature takes the place of a catalyst, partial oxidation is not limited to the light, clean feedstocks required for steam reforming.

Hydrogen processing in this system depends on how much of the gas is to be recovered as hydrogen, and how much is to be used as fuel. Where hydrogen production is a relatively small part of the total gas stream, a membrane is normally used to withdraw a hydrogen-rich stream. That stream is then refined in a purification unit.

Purification of hydrogen

A wide variety of processes are used to purify hydrogen streams. Since the streams are available at a wide variety of compositions, flows, and pressures, the method of purification will vary. They include wet scrubbing, membrane systems, cryogenic separation and pressure-swing adsorption (PSA). This last technique is the most commonly used. In the PSA plant, most impurities can be removed to any desired level. An adsorbent (molecular sieves) removes methane and nitrogen from the out-stream. Nitrogen is the most difficult to remove of the common impurities, and removing it completely requires additional adsorbent. Since nitrogen acts mainly as a diluent, it is usually left in the product if the hydrogen is not going to be used in a very high-pressure system such as a hydrocracker. Hydrogen purity is 99.9 – 99.999 % v/v after the PSA unit. The residual constituents of the product gas are mainly methane and less than 10 ppm CO. Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is normally accumulated in a vessel and used as fuel at a convenient location.

2.15 Integrated refinery management

Note for the TWG: See also extensive EMS section introduced in Chapter 4.

Refineries contain processes and activities that are integrated in different ways. Because of this integration, this section tries to analyse the following groups of activities:

- Process/activities that are so common in all parts of the refinery that has no sense to dealing with in each single process/activity section. Some of these issues are already treated in other sections, for example with energy issues (including management), cooling systems, storage and handling of materials and sulphur management (Section 4.23.5). So, no mention to these activities is made in this section.
- evaluates the implications for the environment of the process integration.
Chapter 2

All refinery process units, systems and activities are typically operated in an integrated way, aimed at optimising production in a way that is economic, sustainable and acceptable to society. This requires a concerted well-managed approach in the execution and planning of all activities likely to affect the environmental performance.

Sections 15 of Chapters 2, 3, 4 aim at describing general management activities related to environmental performance, with a focus on several aspects of housekeeping, soil and groundwater protection, and utility management which are particularly relevant to the refining sector. General techniques to prevent air emissions, such as fugitive emissions, odour and noise that are relevant to the whole refinery are included in Sections 23 of Chapters 2, 3, 4. Soil contamination prevention techniques are also included in Sections 25.

Sections 15 within Chapters 2 to 4 have been structured according to two categories.

- **Refinery management activities** including environmental management tools and good housekeeping techniques. Within this section activities such as maintenance, cleaning, good design, production planning (including start-ups and shutdowns), training, information system process supervision/control systems and safety systems have been included.
- **Utilities management** within a refinery not covered by other sections, such as water management, blowdown systems, compressed air generation and distribution and electricity distribution systems.

**Refinery management activities**

**Environmental management tools**

An environmental management system (EMS) is a system for managing all activities (including energy) in a refinery that presents the purpose of the refinery as a whole, the responsibilities of employees/management and procedures to be followed. An intrinsic aim of EMS is to achieve continuous improvement, with a refinery learning, in particular, from its own operational experience as well as that of others.

The development of Environmental Management Systems (EMS) started by building upon the experience gained with other business parameters. Quite often, management responsibility for safety, environmental protection, and sometimes quality. Environmental management is also named environmental care. In this section the importance of good housekeeping and management is highlighted. It is remarked that systems exist for improving performance in many fields such as safety, maintenance and product quality. Environmental Management Systems have also been developed for the improvement of refinery performance in environmental matters.

**Good housekeeping activities.**

Good housekeeping techniques refer to the proper handling of the day-to-day aspects of running a refinery. Numerous examples of this nature can be given for Many daily refinery activities undertaken in various domains like that have an impact on performance. Other activities that may have an impact on the environmental performance of a refinery can be the maintenance, cleaning, good design, new process and process modification development, good production planning (including start-ups, shutdowns), information systems process supervision/control systems, and training and safety systems that are likely to have an impact on its environmental performance and should be managed properly in that respect. Other European regulatory schemes like the Council Directive 96/82/EC on the control of major-accident hazards plays an important role in the safety management of refineries, underline the importance of proper housekeeping and the obligation to plan and control activities efficiently within the refinery EMS.

**Heat exchanger cleaning**
Heat exchangers are widely used throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream. The bundles are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Therefore, heat exchanger cleaning is one issue of particular importance to be addressed within refinery management activities.

Utilities management

Energy management including steam management and cooling are included in other Sections 8 and 10.

Water management

Water is used within a refinery as process water and cooling water. Rainwater (clean or contaminated) is another type of water that should be also considered. Sanitary waste water, ballast water and blowdown water are other sources of waste water. Water masterplans are normally applied to refineries in order to optimise the consumption of water. Water inventories are sometimes a great help in the management of water, matching the quantity and quality of the effluents. Water integration and management is dependent on the refinery configuration, the crude quality and the level of desalting required, the cost of potable water, the availability of rainwater and the quality of the cooling water. Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available as well as a number of standard possibilities for water reduction and reuse. In most refineries, a number of these options have already been implemented to some extent, either in the original design or by retrofit. Segregation of process water discharges and other types of water are also points to consider in the water management system. Sewage systems also play an important role in the water management system within refineries.

Ballast water is relevant to these refineries that have crude receipt facilities from ships or handle big product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and heavily polluted with oil. However, volumes of ballast water to be treated are declining with the gradual introduction of segregated ballast tankers.

Water and drainage applies to any industrial site. It entails the complete system of fresh water supply, rainwater, ballast water, process water, cooling water and groundwater as well as effluent collection, storage and the various (primary, secondary and tertiary) waste water treatment systems. The design is based on local factors (rainfall, receiving water bodies, etc.), effluent segregation, source reduction, first flush philosophies, flexible routing and reuse options.

Recirculated process water streams and cooling water streams are often manually purged to prevent the continued build-up of contaminants in the stream (blowdown system).

Purge/vents systems:
Most refinery process units and equipment are arranged into a collection unit called the purge/vent system. These systems provide for the safe handling and disposal of liquid and gases as well as for shutdown, cleaning and emergency situations. Purge/vent systems are either automatically vented from the process units through pressure relief valves, or are manually drawn from units. Part or all of the contents of equipment can also be purged prior to shutdown before normal or emergency shutdowns. Purge/vent systems use a series of flash drums and condensers to separate the blowdown into its vapour and liquid components.

Compressed air generation:
Compressed air is necessary as a utility within a refinery. It is normally generated by electric compressors and is distributed around the refinery.
Heating of pipes
Current practices are to apply steam heating (low-pressure steam), electric heating or hot oil heating of lines, if it is required. Electric heating normally generates less corrosion and consequently is easier to maintain compared with heating using steam. Hot oil heating is used when high temperatures are needed.

2.16 Isomerisation

Purpose and principle
Isomerisation is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, low-molecular-weight paraffins (C₄-C₆) are converted to isoparaffins having a much higher octane index. The isomerisation of olefins is also included in this section.

Feed and product streams
Typical feedstocks to isomerisation units are any butane, pentane or hexane-rich feedstream. These streams are hydrotreated naphtha, straight run light naphtha, light naphtha from hydrocrackers, light reformate, coker light naphtha and the light raffinate stream from an aromatic extraction unit. The feedstream to C₅/C₆ isomerisation unit is normally fractionated so that it includes as much of the C₅/C₆ as possible, while minimising heptanes and heavier compounds.

Process description
Figure 2.24 shows a simplified process flow diagram of a low-temperature isomerisation unit with hydrogen and hydrocarbon recycle. The isomerisation reactions occur in the presence of hydrogen and catalyst. The atmosphere of hydrogen is used to minimise carbon deposits on the catalyst, but with a low hydrogen consumption. The reactions normally take place in two reactors in a series. An advantage of the two-reactor scheme is that the first reactor may operate at higher temperatures to kinetically drive the reactions, while the tail reactor may be operated at lower temperatures to push the desired products closer to equilibrium conversion.

Figure 2.24: Simplified process flow scheme for an isomerisation unit
There are several isomerisation processes in use today, designs based on three isomerisation catalytic technologies that can be further designed to operate with or without hydrogen recycle and with or without hydrocarbon recycle. In general, they can be classified into two categories, ‘hydrocarbon once-through’ or ‘hydrocarbon recycled’.

- In ‘once-through’ isomerisation designs, only fresh feed is processed in the isomerisation unit. The octane number which can be achieved is only around 77 – 80 RON when using a zeolite-based catalyst and 82 – 85 RON using a chloride-promoted catalyst. Conversions of 80% can be expected.

- In hydrocarbon recycle isomerisation designs, the unconverted, lower octane paraffins are recycled for further conversion. Depending on the recycle option, the recycle may be normal paraffins or methylhexanes and n-hexane. The octane number obtained can be up to 92 RON, dependent on the feedstock composition, configuration and catalyst used. The yield in the isomerate is around 95 – 98% depending on the targeted octane number of the final stream.

There are three distinctly different types of catalysts currently in use: chloride-promoted, zeolitic, and sulphated-zirconia catalysts. The zeolite catalyst operates at significantly higher temperatures (250 – 275 °C and 28 barg) and is more tolerant to contaminants, though the resulting octane improvements are lower. The zeolite catalyst is mainly used when higher octane isomerate product does not justify the additional capital required to reduce feed contaminants for the chlorided alumina catalyst or is a better match for a retrofit unit. The highly active chloride-promoted catalyst operates at a relatively low temperature (190 – 210 °C and 20 barg) and gives the highest octane improvement. This type of catalyst requires the addition of small amounts of organic chlorides converted to hydrogen chloride in the reactor to maintain the high activity. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. Furthermore, this catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to less than 0.5 ppm is required. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to the desired isomers is enhanced at lower temperatures.

There are three distinctly different types of isomerisation catalysts currently in use:

- chloride-promoted
- zeolitic
- sulphated-zirconia catalysts.

The zeolite catalyst operates at significantly higher temperatures (250 - 280 °C and 15-25 barg) and is more tolerant to contaminants, though the resulting octane improvements are lower. The zeolite catalyst is mainly used when higher octane isomerate product does not justify the additional capital required to reduce feed contaminants for the chlorided-alumina catalyst or is a better match for a retrofit unit. The highly active chloride-promoted catalyst operates at a relatively low temperature (130-180 °C and 30 barg) and gives the highest octane improvement. This type of catalyst requires the addition of small amounts of organic chlorides which are converted to hydrogen chloride in the reactor to maintain the high activity. In such a reactor, the feed must be free of oxygen sources including water to avoid deactivation and corrosion problems. Furthermore, this catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to less than 0.5 ppm is required. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to the desired isomers is enhanced at lower temperatures.

After isomerisation, the light ends are stripped fractionated from the product stream leaving the reactor and are then sent to the sour gas treatment unit or refinery fuel gas or to the light ends recovery unit. In a hydrocarbon once-through isomerisation unit, the bottom stream from the stabiliser is, after product cooling, sent to the gasoline pool. In a hydrocarbon recycle stream isomerisation design, the bottom stream from the stabiliser is fed to a separation unit, which is either a deisohexaniser column or an adsorption system.
In the deisohexaniser column, a split can be made between the higher octane dimethylbutanes and the lower octane methylpentanes. The dimethylbutanes and lower boiling C\textsubscript{5} components (isomerate product) are taken overhead from the column and are sent to the gasoline pool. The methylpentanes and normal hexane are taken as a side-stream close to the bottom, and are recycled to the isomerisation reactor. The bottom stream from the deisohexaniser is a small quantity of heavy by-product which is sent with the isomerate product to the gasoline pool or to a catalytic reformer if the refinery recovers benzene as chemical feed. The principle of adsorption is that the unconverted normal paraffins are adsorbed on the molecular sieve whereas the isoparaffins pass the adsorbent. Desorption takes place with heated hydrogen-rich gas from the separator or a butane mixture. The desorbent is separated from the net hydrogen-rich recycle stream in a separator vessel and returned to the isomerisation reactor for further conversion.

2.17 Natural gas plants

Gas in Europe has been typically found in the North Sea. Natural gas is also obtained from a small number of on-shore oil fields, where it is co-produced with crude oil and separated at local facilities before being treated, brought up to specification and exported. The off-shore gas production consists of a number of central platforms with satellite platforms. The satellite platforms deliver gas to the central platform, where gas is dried (removal of water). Also condensates are partially removed, but these are reinjected again in the produced gas. Chemicals are added to the gas stream either at the well-head or prior to transmission to prevent solid hydrate formation and to limit corrosion in the underwater pipeline. Off-shore platforms are not included in the scope of this document. Subsequently, the central platforms deliver through one main gas pipeline to the on-shore natural gas plants for final treatment.

Purpose and principle
The overall objective of natural gas processing is to remove the treatment chemicals and to remove any contaminants from the well-head stream in order to produce a methane-rich gas which satisfies statutory and contractual specifications. The main contaminants to be removed fall into the following categories:

- **solids**: sands, clay, sometimes scale like carbonates and sulphates (including naturally-occurring radioactive metals (e.g. lead or radium), mercury
- **liquids**: water/brine, hydrocarbons, chemicals added at well-head
- **gases**: acid gases, carbon dioxide, hydrogen sulphide, nitrogen, mercury and other gases (e.g. mercaptans).

Feed and product streams
Feedstock is natural gas and the products that may be separated within the natural gas plants are methane rich gas, C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{4} fractions and condensates (C\textsubscript{5+}).

Process description
As shown in Figure 2.26, the purification plant consists of an acid gas treatment (sweetening plant) where acid gases as CO\textsubscript{2}, H\textsubscript{2}S, SO\textsubscript{2} are separated. Natural gas is considered ‘sour’ when contains significantly greater amounts of hydrogen sulphide than these quoted for pipeline quality or when it contains such amounts of SO\textsubscript{2} or CO\textsubscript{2} to make it impractical to use without purification. The H\textsubscript{2}S must be removed (called ‘sweetening’ the gas) before the gas can be utilised. If H\textsubscript{2}S is present, the gas is usually sweetened by absorption of the H\textsubscript{2}S in an amine solution. Amine processes are the most common process used in the United States and Europe.
Other methods, such as carbonate processes, solid bed absorbents, and physical absorption, are employed in the other sweetening plants. Natural gasoline, butane and propane are usually present in the gas, and gas processing plants are required for the recovery of these liquefiable constituents (see Figure 2.26). The type of processes found are very similar to those described in Section 2.12. As a summary, these processes are physical separations at very low temperatures (typically distillation). The following figures describe two of the main steps of the natural gas separation process.
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2.18 Polymerisation

This section covers the polymerisation, dimerisation and condensation of olefins.

Purpose and principle
Polymerisation is occasionally used to convert propene and butene to high octane gasoline blending components. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. Prevailing chemical reactions may vary according to olefin type and concentration but can be described in general terms shown below:

\[
\begin{align*}
2 \text{C}_3\text{H}_6 &\rightarrow \text{C}_6\text{H}_{12} \quad \text{(dimerisation)} \\
2 \text{C}_4\text{H}_8 &\rightarrow \text{C}_8\text{H}_{16} \quad \text{(dimerisation)} \\
\text{C}_3\text{H}_6 + \text{C}_4\text{H}_8 &\rightarrow \text{C}_7\text{H}_{14} \quad \text{(condensation)} \\
3 \text{C}_3\text{H}_6 &\rightarrow \text{C}_9\text{H}_{18} \quad \text{(polymerisation)}
\end{align*}
\]

Feed and product streams
Propene and butene contained in the LPG stream from the FCC are the most common feedstreams for this unit.

Process description
The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst adsorbed onto natural silica and extruded in pellets or in small cylinder forms. All reactions are exothermic, and therefore the process requires temperature control. The feed must be free of: sulphur, which poisons the catalyst; basic materials, which neutralise the catalyst and oxygen, which affects the reactions. The propene and butene feed is washed first with caustic to remove mercaptans, then with an amine solution to remove hydrogen sulphide, then with water to remove caustics and amines, and finally dried by passing through a silica gel or molecular sieve dryer. A simplified scheme of a polymerisation unit is shown in Figure 2.28.
When the polymerisation yield drops, the catalysts need to be replaced. After nitrogen purging, the polymerisation unit is opened and the catalyst removed by means of a high-pressure water jet. It can also be removed using steam (compression dumping). The phosphoric acid goes in the water medium, while the natural silica pellets break down to form a slurry, which is usually pumpable.

### 2.19 Primary distillation units

This section includes atmospheric and vacuum distillation. These two primary distillations are preceded by crude oil desalting and they are the first and fundamental separation processes in a refinery.

**Purpose and principle**

The Atmospheric Crude Oil Distillation Unit (CDU) is the first important processing step in a refinery. Crude oil is heated to elevated temperatures and then generally subjected to distillation under atmospheric pressure (or slightly higher) separating the various fractions according to their boiling range. Heavier fractions from the bottom of the CDU, which do not vaporise in this column, can be further separated later by vacuum distillation.

Increased demand for light products and a reduced demand for heavy fuel oil have resulted in refiners upgrading the atmospheric residue in more valuable lower boiling fractions such as naphtha, kerosene and middle distillates, mid-distillates. Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure to increase volatilisation and separation whilst avoiding thermal cracking. The high vacuum unit (HVU) is normally the first processing step in upgrading atmospheric residue followed by downstream refining units. HVU produces feedstocks for cracking units, coking, bitumen and base oil units. The contaminants from the crude oil stay predominantly in the vacuum residue.
Feed and product streams

The crude oil feed to the crude distillation unit is supplied from the crude oil storage tanks after desalting. Normally all crude oil entering a refinery passes through a crude distillation unit. In addition to that, it is common practice that off-specification product streams are reprocessed in the CDU. The products from the crude distillation unit, ranging from the lightest to the heaviest cut are; naphtha and light components (boiling <180 °C/C_1-C_{12} lights, naphtha and gasoline), kerosene (boiling range 180 – 240°C – C_8-C_{17}), light gasoil (boiling range approximately 240 - 300°C/C_8-C_{25}), heavy gasoil (boiling range approximately 300 – 360 °C/C_20 - C_{25}) and atmospheric residue (boiling >360 °C/>C_{22}). The overhead of this column is the light fraction, non-condensable refinery fuel gas (mainly methane and ethane). Typically this gas also contains hydrogen sulphide and ammonia gases. The mixture of these gases is known as ‘sour gas’ or ‘acid gas’. A certain amount of it passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide.

The main feed stream to the HVU is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue. In addition the bleed stream from the hydrocracker unit (if applicable) is normally sent to the HVU for further processing. The products from the HVU are light vacuum gasoil, heavy vacuum gasoil and vacuum residue. Light vacuum gasoil is normally routed to the gasoil hydrotreater(s), heavy gasoil is normally routed to a fluid cat cracker and/or hydrocracker unit. The vacuum residue can have many destinations such as visbreaking, flexicoking or delayed coking, residue hydproprocessing, residue gasification, bitumen blowing or it may go to the heavy fuel oil pool.

Process description

Atmospheric distillation

Distillation involves the heating, vaporisation, fractionation, condensation, and cooling of feedstocks. The desalted crude oil is heated to about 300 – 400 °C and fed to a vertical distillation column at atmospheric pressure where most of the feed is vaporised and separated into its various fractions by condensing on 30 to 50 fractionation trays, each corresponding to a different condensation temperature. The lighter fractions condense and are collected towards the top of the column.

The overhead hydrocarbon vapours are condensed and accumulated in the overhead reflux drum of the main fractionator. In this drum sour water, light fractions (about 0.5 % on crude charge) and stripping steam (1.5 % on crude) are separated from the hydrocarbon liquid. The overhead hydrocarbon liquid, so called the naphtha minus stream, is commonly fed directly to the downstream naphtha treater.

Within each atmospheric distillation tower, a number of side-streams of low-boiling point components are removed from different trays in the tower. These low-boiling point mixtures are in equilibrium with heavier components which must be removed. The side-streams are each sent to a different small stripping tower containing four to ten trays with steam injected injection under the bottom tray. The steam strips the light-end components from the heavier components and both the steam and light-ends are fed back to the atmospheric distillation tower above the corresponding side-stream draw tray.

Most of these fractions generated in the atmospheric distillation column can be sold as finished products after a hydrotreatment, or blended with products from downstream processes. In Figure 2.29 a simplified process flow diagram of a crude distillation unit is shown. Many refineries have more than one atmospheric distillation unit.
The operating conditions of the tower are based on the properties of the crude oil and the desired product yields and quality. To maximise the yield of distillates, the pressure is minimised, but the temperature is increased to the maximum. Every refinery has a crude distillation unit designed for a selected crude (mix). There are therefore many different crude distillation configurations with varying product cuts and heat integration.

Vacuum distillation
Figure 2.30 shows a simplified process flow diagram of the high vacuum unit. Atmospheric residue is heated up to 400 °C, partially vaporised (30 – 70 % by weight) and flashed into the base of the vacuum column at a pressure between 40 and 100 mbar (0.04 to 0.1 kg/cm²). The vacuum inside the fractionator is maintained with steam ejectors, vacuum pumps, barometric condensers or surface condensers. The injection of superheated steam at the base of the vacuum fractionator column further reduces the partial pressure of the hydrocarbons in the tower, facilitating vaporisation and separation.

The unvaporised part of the feed forms the bottom product and its temperature is controlled at about 355 °C to minimise coking. The flashed vapour rising through the column is contacted with wash oil (vacuum distillate) to wash out entrained liquid, coke and metals. The washed vapour is condensed in two or three main spray sections. In the lower sections of the column, the heavy vacuum distillate and optional medium vacuum gasoil are condensed. In the upper section of the vacuum column the light vacuum distillate is condensed. Light (non-condensable) components and steam from the top of the column are condensed and accumulated in an overhead drum for separating the light non-condensables, the heavier condensed gasoil and the water phase.

In the upper section of the vacuum column the light vacuum distillate is condensed. Light (non-condensable) components and steam from the top of the column are condensed and accumulated in an overhead drum for separating the light non-condensables, the heavier condensed gasoil and the water phase.

The most important operational aspect of a vacuum unit is the quality of the heavy vacuum gasoil, especially when this is fed to a hydrocracker unit. The Concarbon level and/or metal content is very critical for a hydrocracker unit and depends on the operation and performance of especially the wash oil section in the vacuum distillation unit as well as the desalter in the crude distillation unit.
Figure 2.30: Simplified process flow scheme for high vacuum distillation unit
2.20 Product treatments

The treatments used in a refinery to achieve certain product specifications are included in this section, in which two types of processes can be identified.

The first group of processes corresponds to extraction or removal techniques where the component to treat is removed from the stream to be treated. Under this category, mention can be made of molecular sieve extraction for the removal of carbon dioxide, water, hydrogen sulphide or mercaptans (Section 4.25.5.3), amine scrubbing for the removal of hydrogen sulphide (included in Section 4.23.5.1) or caustic washing for the removal of acids or mercaptans.

The second group is composed of these systems where the chemical to be treated is not removed from the stream to be treated.

**Extraction**

**Purpose and principle**

In petroleum refining, chemical treatment is used to remove or change the undesirable properties associated with sulphur, nitrogen, or oxygen compound contaminants in petroleum products. Some of these systems (so called i.e. ‘mercaptan oxidation’) are designed to reduce the mercaptan content (organic sulphur compounds) of hydrocarbon streams to improve product odour and to reduce corrosivity. These treatments are accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. The extraction process removes the mercaptans by caustic extraction, resulting in a lower sulphur content. The following reaction takes place at low temperatures:

\[
\text{R-SH} + \text{NaOH} \rightleftharpoons \text{NaSR} + \text{H}_2\text{O}
\]

Mercaptan oxidation-sweetening is another version of the mercaptan oxidation process in which the mercaptans in the hydrocarbon products are converted to less odorous and less corrosive disulphides which remain in the product. The reaction is:

\[
\text{NaSR} + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \frac{1}{2} \text{RSSR}
\]

As a result no reduction in the total sulphur content takes place during sweetening and consequently it is only applied to these streams where sulphur content is not a problem.

**Feed and product streams**

The mercaptan oxidation-extraction process entails the removal of mercaptans from LPG, naphtha and gasoline and kerosene streams. Oxidation or ‘sweetening’ is used on gasoline and distillate fractions. It should be stressed that mercaptans are also removed by hydrotreatment (Section 2.13).

**Process description**

Mercaptans are removed from light hydrocarbon streams by a concentrated alkaline wash in an extraction column under elevated pressure (5 barg). If H₂S or acids are present a caustic prewash is required. The treated and odour-free hydrocarbon stream leaves the reactor as an overhead stream.

The aqueous bottom phase is heated to 50 °C, mixed with air and fed to the oxidation reactor. The dissolved NaSR is now converted into disulphides (which are insoluble in caustic soda water solution) at 4.5 barg. By using an excess of air and adding catalyst, a high rate of reaction is maintained. In this way the alkaline solution is regenerated. The liquid from the reactor is routed to a vessel where spent air, the disulphide fraction insoluble in the caustic solution and the caustic solution are separated. The spent air is routed to an incinerator or process furnace, the disulphides are usually recycled to the crude and the regenerated caustic is circulated to the...
Chapter 2

extraction column. Figure 2.31 shows a simplified process flow diagram of an extraction process.

Another oxidation process is also a mercaptan oxidation process that uses a solid catalyst bed. Air and a minimum amount of alkaline caustic (‘mini-alky’ operation) are injected into the hydrocarbon stream and the caustic cannot regenerate. As the hydrocarbon passes through the mercaptan oxidation catalyst bed, sulphur mercaptans are oxidised to disulphide.

![Simplified process flow diagram of the mercaptan oxidation extraction process](image)

Figure 2.31: Simplified process flow diagram of the mercaptan oxidation extraction process

Both processes can be integrated in a so-called caustic cascading system to achieve the desired product quality improvements at minimum caustic make-up and spent caustic disposal costs.

Figure 2.32 shows a simplified process flow diagram of the mercaptan oxidation extraction process.

**Catalytic dewaxing**

Another process that can be found in refineries is the selective hydrocracking (hydrofiner), where one or two zeolite catalysts are used to selectively crack the wax paraffins (n- and near-to-n-paraffins). This technique can be used for the dewaxing of middle mid-distillate components that may be blended into products for extreme winter conditions. A variation of this is the use of isodewaxing catalyst that isomerises the n-paraffin wax to desirable isoparaffin lube molecules, while co-producing low-quality middle mid-distillate transportation fuels. The design and operation of this unit is similar to that of a normal hydrotreater unit (Section 2.13).
storage and handling of refinery materials

Storage and handling of refinery materials are not covered exhaustively in this document, because the storage and handling of oil products are within the scope of the horizontal BREF on storage, to which reference will be made as appropriate. This section also covers activities related to feed and product blending, piping and other small techniques used for the handling of materials. Storage of specific products, such as base oils, bitumen and petroleum coke, is included in the respective production sections.

Purpose and principle
Crude oil, petroleum intermediates and final products are transferred to, in and from refineries through marine terminals via pipeline or rail/road vehicles. Between these movements, the products are stored in tanks. Storage tanks or caverns are used throughout the refining process to store crude oil, other raw materials and intermediate process feeds. Finished petroleum products are also kept in storage tanks before transport off site. Tanks are also needed to accommodate the blocked-out operation of processing units and to link continuous refinery processes with discontinuous ones. Consequently, storage is an essential part of a refinery. Blending systems are also used in refineries to prepare feed streams to individual refinery units and to produce finished products to be sold.

Feed blending may be applied to prepare the optimum feed stream to a refinery unit, thereby ensuring the optimum performance of the refinery unit. For example, a refiner processes a mixture of four different low-sulphur crudes in an atmospheric distillation unit. The feed blend is selected so that the throughput in the distillation unit and further downstream units are optimised/maximised with the objective of maximising overall profit. Alternatively, it also
happens that the different quality crudes are processed separately for a short period (a few days) in ‘blocked-out’ operations.

Product blending is applied to produce the optimum mix of finished refinery products. The majority of the product streams as produced in different refinery units, normally identified as an intermediate product stream, can be blended into more than one finished product stream. For example (hydrotreated) kerosene product is normally blended into diesel oil, light heating oil and even heavy fuel oil, with the remainder blended into the jet fuel oil. The amount of kerosene allocated to the different products is selected so that product demands and specifications are met with the objective of maximising overall profit. Blending products involves mixing the products in various proportions to meet specifications such as vapour pressure, specific gravity, sulphur content, viscosity, octane number, cetane index, initial boiling point and pour point and to add distinctive smells (LPG).

Process description
The crude oil storage systems can be located either at a separate oil terminal or within the refinery complex. More than 50% of the refinery area is occupied by oil movement facilities. Storage tanks can be divided into four main types: pressure vessels, fixed roof tanks, fixed roof tanks with floating covers and floating roof tanks. Figure 2.33 shows a drawing of the different types of storage systems found in a refinery.

Pressure vessels are normally used to store gases at high pressures material (>91 kPa) most typically LPG. Fixed-roof tanks can hold a wide range of materials. For very low vapour pressure liquids they can be open to the atmosphere. They can also be designed to hold volatile liquids with several classes of permitted pressure build-up, as a pressure tank, with several classes of allowed pressure buildup, from 20 mbarg (low pressure) to 60 mbarg (high pressure). In these situations measures to prevent vapour loss and the occurrence of flammable atmospheres such as inerting and/or vapour recovery are required. Such pressure tanks are necessarily provided with pressure/vacuum relief valves. To prevent explosions and implosions, the vacuum setting being 6 mbarg. Floating roof tanks are constructed in such a way that the roof floats on the liquid and moves with the liquid level (>14 kPa to ≤91 kPa). Fixed roof tanks may also be fitted with internal floating covers. Floating covers float upon and move with the liquid and act as a barrier to evaporation. External floating roof tanks are generally larger and are extensively used for crude oil and product storage.

Above-ground storage tanks (ASTs) are used at refineries for holding either the raw feedstock (crude oil) or end-products generated by the refinery processes (gasoline, diesel, fuel oils, etc.). Underground storage tanks are used much less frequently (if at all) at refineries—primarily for

Figure 2.33: Examples of some types of storage tanks
storing fuel for onsite boilers and vehicles, or for capturing liquids at low-level drain points. The storage of crude oil and products in caverns is also applicable in some European countries.

Blending can be carried out in-line or in batch blending tanks. An in-line blending system consists of a manifold where individual streams are blended on flow control, and the blend ratio is normally controlled and optimised by a computer. When a certain volume of a given quality product is specified, the computer uses linear programming models to optimise the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost. To ensure that the blended streams meet the desired specifications, in-line stream analysers for flash point, RVP, boiling point, specific gravity, research and motor octane number (RON and MON), sulphur, viscosity, cloud point and others are inserted to provide feedback to the computer, which in turn corrects blending ratios where necessary.

Batch blending involves mixing the feed streams in a blend tank, from where the relevant process units are fed. The same applies to intermediate product streams, which are first sent to intermediate storage tanks, where they are batch blended into the final product tanks.

Additives and odorants. The odorant is stored as a liquid, normally in fixed tanks. The odorant is not added to the gas stream prior to liquefaction but is usually added to the LPG whilst the LPG is being loaded into the delivery tankers, although in-tank odorising is also carried out. Allowance may be made for any residual mercaptans already present in the LPG. The pump addition rate is carefully controlled. In the case of liquid propane, methanol may be added with the odorising agent in order to prevent hydrate icing in propane evaporators.

Text moved from section 4.21.21

The design and operation of odorising facilities should be to a very high standard which minimises the risk of odorant leaks or spillages. To an extent, the operational aspects of this are facilitated by the ease of detection of even the smallest odorant release, but this needs to be used as an aid to vigilance, not as a reason for lax control.

Odorising plants should be designed to minimise the potential for leaks, e.g. by having the minimum number of pumps/valves/filters/tank connections, etc, by using welded, not flanged, connections wherever possible and by protecting the plant from possible impact damage. All such items used need to be designed to a very high standard of sealing efficiency. Devices such as automatic self-sealing couplings for loading lines are preferred.

Plants should be designed to deal with the high vapour pressure of odorants and should use inert or pressure controlled natural gas blanketing of the vapour spaces above stored odorant. During deliveries into tanks any displaced vapour needs to be returned to the delivery vehicle, adsorbed on activated carbon or incinerated. The use of demountable semi-bulk containers avoids the generation of displaced vapours and is preferred where appropriate.

Achieved environmental benefits

In view of the nature and power of the odorants used, there should be no normal release of odorant to any environmental medium.

Reference literature
[18a, Irish EPA, 1992]

Pipes, valves and auxiliary systems, such as vacuum recovery units are found throughout a refinery. Gases, liquids and even solids are transferred from unit operation to unit operation by pipes. Process pipes are normally above ground but some pipes are underground.
2.22 Visbreaking and other thermal conversions

2.22.1 Visbreaking

Purpose and principle
Visbreaking is a well-established non-catalytic thermal process that converts atmospheric or vacuum residues to gas, naphtha, distillates and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules.

When vacuum residue is directly blended with the heavy fuel oil pool, significant quantities of cutter stock (normally high-value gasoil) need to be blended to the residue to meet the viscosity specifications of the heavy fuel oil. By thermally cracking the vacuum residue at relatively mild conditions, about 10 – 15 % of the feed is cracked to lighter fractions and, more importantly, the viscosity of the vacuum residue is reduced significantly. For this reason, the thermal cracker unit is normally called the ‘visbreaker’ gasoil unit.

Feed and product streams
The atmospheric residue from the crude distillation unit, the vacuum residue from the high vacuum unit, heavy gas oils or vacuum gasoils or mixtures are typically the feedstocks. In this process, only part of the feedstock is converted and a large amount of residue remains unconverted. As no catalyst is involved in the thermal cracking process, the quality of the feedstock in terms of metals and sulphur is not critical. A significant quantity of gas is produced and all distillate products need further treatment and upgrading prior to running them to storage.

Process description
Thermal cracking is one of the oldest conversion processes to upgrade heavy oil fractions. At present it is mainly used to upgrade vacuum residue. Figure 2.34 shows a simplified process flow diagram of the visbreaker unit. The most important factor in controlling the cracking severity should always be the stability and viscosity of the visbroken residue fed to the fuel oil pool. In general, an increase in the temperature or residence time results in an increase in severity. Increased severity produces higher gas-plus-gasoline yield and at the same time a cracked residue (fuel oil) of lower viscosity. Excessive cracking, however, leads to an unstable fuel oil, resulting in sludge and sediment formation during storage. Thermal cracking converts maximum 20 % of the feed. Thermal cracking units to upgrade atmospheric residue have conversion levels significantly higher (35 – 45 %) and the viscosity of the atmospheric residue is reduced.
The feedstock is heated above 500 °C and then fed to a reaction chamber which is kept at a pressure of about 9.65 barg. Following the reactor step, the process stream is mixed with a cooler recycle stream, which stops the cracking reactions. The product is then fed to a flasher chamber, where pressure is reduced and lighter products vaporise and are drawn off. The lighter products are fed to a fractionating tower, where the various fractions are separated. The bottoms consist of heavy residue, part of which is recycled to cool the process stream leaving the reaction chamber; the remaining bottoms are usually blended into residual fuel.

There are two types of visbreaker operations, ‘coil or furnace cracking’ and ‘soaker cracking’. Coil cracking uses higher furnace outlet temperatures (470 – 500 °C) and reaction times from one to three minutes, while soaker cracking uses lower furnace outlet temperatures (430 - 440 °C) and longer reaction times. The product yields and properties are similar. Run times of three – six months are common for furnace visbreakers and six – 18 months for soaker visbreakers.

2.22.2 Thermal gasoil unit

The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gasoil and naphtha cuts produced. As shown in Figure 2.35, after a first thermal cracking, the resulting products are separated in a cyclone. The gaseous phase is introduced in the flash zone of the main distillation column and separated according to desired boiling intervals. The heavy gas oil (HVGO) and the vacuum gas oil from the flash column (LVGO) are treated in a second thermal cracker and reintroduced into the column.
The resulting vacuum flashed cracked residue (VFCR) has a high sulphur content and can only be used as fuel in the refinery power plant if equipped with an efficient and appropriately sized flue-gas cleaning system.

### 2.23 New high conversion techniques

Residue upgrading has great importance among refiners due to a continued decrease in demand for high sulphur fuel oil (HSFO) and a great demand for higher volumes and quality of middle distillates. In addition, the price differential between light/sweet and heavy/sour crudes is driving the operators to process larger volumes of heavy crudes.

Refiners and engineering firms aim to minimise fuel oil production at minimum investment and operating cost. The technology options available for residue upgrading depend on the difficulty of the feed to be processed, whether it is atmospheric (AR) or vacuum residue (VR), the metal contents and the level of conversion desired.

There has not been any technology breakthrough, only marginal improvements on proven technologies. Final results will depend on how the integration within units is done.

The following table summarises these processes that have experienced recent improvements regarding residue conversion and, or valorisation:

<table>
<thead>
<tr>
<th>Feed</th>
<th>Carbon rejection</th>
<th>H2 addition</th>
<th>Partial Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum GO</td>
<td>FCC</td>
<td>H2Cracking</td>
<td></td>
</tr>
<tr>
<td>Vacuum Residue</td>
<td>Coking VisbreakingSDA RXFCC</td>
<td>ARDS/VRDS H-Oil HCK HDHplus</td>
<td>Gasification</td>
</tr>
</tbody>
</table>
Table 2.13 Examples of recent improvements made by several conversion techniques

<table>
<thead>
<tr>
<th>BREF Section</th>
<th>Technique names</th>
<th>Technical description</th>
<th>Advantage</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Solvent Deasphalting</td>
<td>Separates by molecular weight</td>
<td>Separates residue from deasphalted oil</td>
<td>High post treatment</td>
</tr>
<tr>
<td>5</td>
<td>F.C.C. upgrade</td>
<td>Better catalysts enable heavier/wider feedstocks</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Residue FCC/Deep C.C</td>
<td>Fluidised process, 2 stage regenerator</td>
<td>Cost effective</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Delayed Cocker</td>
<td>Low pressure low recycling, low coke</td>
<td>High flexibility and high conversion to lighter</td>
<td>Uses much water; Harder to sell coke at fair price and high capital cost</td>
</tr>
<tr>
<td>10</td>
<td>IGCC/Gasification</td>
<td>Valorisation of waste to Syngas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Circulating Fluid Bed Boiler (CFB)</td>
<td>Coke valorisation at low emission</td>
<td>Cogen possible</td>
<td>Solid handling</td>
</tr>
<tr>
<td>13</td>
<td>Atmospheric residue DS</td>
<td>Optimised catalyst combination</td>
<td>High investment and Ops cost</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Vacuum residue DS</td>
<td>Higher pH2</td>
<td>High investment and Ops cost</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Slurry H.C.</td>
<td>Disperse phase catalyst and elevated temp</td>
<td>Selective conversion, min residue</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Residue H.C./ebullated bed H.C.</td>
<td>Fixed bed+HT catalysts</td>
<td>Reduces metals, sulphur, CCR, produces high distillates</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Visbreaking</td>
<td>Rapid heat in furnace and cracked for a specific residence time in a soaking zone</td>
<td>Reduce viscosity, low cap cost</td>
<td>High post treatment, low conversion to light</td>
</tr>
<tr>
<td>22</td>
<td>Thermal GO/deep thermal conversion</td>
<td>Lower temp, special internal for backmixing</td>
<td>Selective cracking, lower investment cost</td>
<td></td>
</tr>
</tbody>
</table>

Source: EIPPCB review

2.24 Techniques for the elimination/valorisation of external waste used as secondary raw material

There is an increasing role played by the refineries in recycling waste oil, not only managing their own residues but also valorising external waste.

The following wastes are partly use as feedstock in the EU refineries:

- Re-refining of waste oil:

  Used oil from different application is first collected and then part of it is send back to refineries.
  In 2006 in the EU this recycle effort represented only a 0.1% of the crude oil feedstock, however this initiative is growing.
  The largest group of end users that are recycling are hotel and restaurant kitchens as well as auto repair shops.
  The following table shows the order of magnitude on this quantities by country.

- Recycle of waste rubber in asphalt grades

  There is a large volume of spent tyres in EU. In some processes, tyres are converted into powder and then mixed with asphalt grades.

- Waste oil hydrogenated in refineries:
Chapter 2

For more in depth description, see Chapter 6 on emerging techniques, (hydro)isomerization. There are some examples of the recycling of animal and vegetable oil (waste) by using retrofitted desulphurisation unit: e.g. Cepsa (Spain) started in 2011 and plan a 100,000 m³/year production. Oil is hydrogenated and then mixed in diesel gasoline grades.

Table 2.14 Re-refining waste oil in Europe

<table>
<thead>
<tr>
<th>Member state</th>
<th>Collected waste oil in 2006 (tonnes)</th>
<th>Distillation of waste oil (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re-fin (base oil)</td>
<td>Burning (replacing coal)</td>
</tr>
<tr>
<td>Austria</td>
<td>39,596</td>
<td>12,396</td>
</tr>
<tr>
<td>Belgium</td>
<td>60,000</td>
<td>15,000</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>17,000</td>
<td></td>
</tr>
<tr>
<td>Cyprus</td>
<td>4,300</td>
<td></td>
</tr>
<tr>
<td>Czech Republic</td>
<td>32,867</td>
<td>986</td>
</tr>
<tr>
<td>Denmark</td>
<td>20,000</td>
<td>15,500</td>
</tr>
<tr>
<td>Estonia</td>
<td>5,400</td>
<td>11,250</td>
</tr>
<tr>
<td>Finland</td>
<td>22,500</td>
<td>39,150</td>
</tr>
<tr>
<td>France</td>
<td>224,759</td>
<td>99,403</td>
</tr>
<tr>
<td>Germany</td>
<td>525,000</td>
<td>135,000</td>
</tr>
<tr>
<td>Greece</td>
<td>36,000</td>
<td>36,000</td>
</tr>
<tr>
<td>Hungary</td>
<td>27,823</td>
<td></td>
</tr>
<tr>
<td>Ireland</td>
<td>20,000</td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td>216,300</td>
<td>172,600</td>
</tr>
<tr>
<td>Latvia</td>
<td>11,000</td>
<td></td>
</tr>
<tr>
<td>Lithuania</td>
<td>14,000</td>
<td></td>
</tr>
<tr>
<td>Luxembourg</td>
<td>5,364</td>
<td>5,364</td>
</tr>
<tr>
<td>Malta</td>
<td>1,200</td>
<td></td>
</tr>
<tr>
<td>Netherlands</td>
<td>50,000</td>
<td>18,000</td>
</tr>
<tr>
<td>Poland</td>
<td>76,500</td>
<td>63,500</td>
</tr>
<tr>
<td>Portugal</td>
<td>28,700</td>
<td>6,800</td>
</tr>
<tr>
<td>Romania</td>
<td>27,663</td>
<td>9,500</td>
</tr>
<tr>
<td>Slovenia</td>
<td>3,967</td>
<td></td>
</tr>
<tr>
<td>Slovakia</td>
<td>15,000</td>
<td>6,000</td>
</tr>
<tr>
<td>Spain</td>
<td>216,045</td>
<td>140,084</td>
</tr>
<tr>
<td>Sweden</td>
<td>45,000</td>
<td>8,000</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>353,000</td>
<td></td>
</tr>
<tr>
<td>Total:</td>
<td>2,095,984</td>
<td>728,633</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>100 %</td>
<td>35 %</td>
</tr>
</tbody>
</table>

( ) Includind direct burning and simple treatment

Source: GEIR 2008 quoted by Oköpol - 2008

2.25 Techniques for the abatement of emissions

There are many non-production techniques in use in a refinery. In particular, relevant for this document are the techniques used to control and abate emissions to air, water and soil. Descriptions of many of these techniques can be found in the CWW BREF [6, EC 2003] and in Chapter 4 (Section 4.25 to 4.27). These techniques are not described in this chapter because they are typically techniques that might be considered in the determination of BAT and consequently are extensively described and analysed in Chapter 4, Sections 4.25 and 4.26.

Even if some preventive techniques or primary measures can also be implemented, pollutants such as NOx, particulates, H2S, SO2, other sulphur compounds and VOC, among others, are typically abated by end-of-pipe techniques. One of the largest systems within a refinery is the abatement of H2S produced on-site. These systems typically contain an amine scrubbing system.
and a sulphur-recovery unit to convert $\text{H}_2\text{S}$ into sulphur, a by-product produced within refineries.

Flares are another technique used within the refinery for safety and environmental reasons. Techniques for the abatement of odour and noise are also relevant for refineries. Specific information on flare systems can be found in Section 3.5.2.6 of the CWW BREF [6, EC 2003].

Refineries also contain waste water plants with different unit operations. Oil separators, flotation, flocculation and biological treatment are typical within refineries. Biological treatment is required when biodegradation of some organic chemicals that may be present within the waste water stream is necessary. Final water cleaning systems can also be present.

Most refineries treat waste water on-site using end-of-pipe waste water treatment facilities prior to discharge. However, several refineries utilise off-site waste water treatment services. The on-site and off-site waste water treatment facilities reduce the amounts of pollutants.

Refineries also generate solid wastes. Some of them are recycled within the refinery; others (e.g. catalysts) are recycled by specialist companies and others are disposed of. Soil contamination prevention techniques are also relevant to the whole refinery.
3 CURRENT EMISSION AND CONSUMPTION LEVELS

This chapter provides data and information about current emission and consumption levels in existing installations at the time of writing (2009 – 2010). Because it covers many types and sizes of refineries, the data are very wide-ranging. The goal of the chapter is to bring together, the emission and consumption levels of the refinery as a whole and for each specific process. The data cited will, in most cases, enable an estimate of the concentration and load of emissions, in turn enabling a competent authority issuing a permit to verify the information provided in the permit application.

Section 3.1 gives an overview of the main emissions and consumptions of European refineries as a whole. It is not a simple aggregation of the emissions and consumptions in the other sections: most of them cannot be aggregated because of the integration of processes in refineries.

Sections 3.2 to 3.22 cover the emissions and consumptions from the various processes/activities covered by this document. Sections 3.23 to 3.25 cover the emissions generated by the techniques used to abate emissions, including the emissions from sulphur recovery units. The chapter ends with a section on monitoring, which covers the monitoring systems typically applied in refineries and provides some discussion on their application.

3.1 Current emission and consumption levels in refineries as a whole

Refineries are industrial sites that manage huge amounts of raw materials and products and are also intensive consumers of energy and water. From storage and the refining process they generate emissions to the atmosphere, to water and they may potentially pollute the soil.

This chapter addresses these three media in turn, and the pollutants that affect them, and is a summary of the emissions from all refinery processes. The main environmental problems were mentioned in Chapter 1 (Section 1.4), but without figures. This section aims to quantify refinery emissions.

Although the principal raw material input to petroleum refineries is crude oil, refineries use and generate an enormous large number of chemicals, some of which leave the facilities as discharges of air emissions, waste water or solid waste. Pollutants generated typically include ammonia (NH₃), carbon dioxide (CO₂), carbon monoxide (CO), hydrogen sulphide (H₂S), metals, nitrogen oxides (NOₓ), particulates, spent acids (e.g. HF, H₂SO₄), sulphur oxides (SOₓ), volatile organic compounds (VOC) and numerous other organic compounds (some very toxic).

Figure 3.1 shows a simplified example of what is consumed and emitted by a refinery. This figure shows only focuses on the main typical pollutants, among more than 90 specific compounds that have already been identified as these likely to be generated by refining processes and activities [108, USAEPA, 1995]. The great majority are pollutants to air. In this figure, low values in the ranges normally correspond to refineries with abatement techniques and good environmental performance and practises, whereas high values typically correspond to refineries without abatement techniques.

Table 3.1 shows the environmental account of refinery processes, Next table shows and provides a summary of the impact on the different media from the different activities found within refineries.
### Table 3.1: Environmental account of refinery processes

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fundamental processes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delivery</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Loading</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Storage</td>
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<td></td>
<td>X</td>
<td></td>
<td>0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Process furnaces</td>
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<td>0</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>Separation processes</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude oil atmospheric distillation unit</td>
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<td>X</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>X</td>
</tr>
<tr>
<td>Vacuum distillation unit</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>X</td>
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<tr>
<td>Gas separation unit</td>
<td>X</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>Conversion processes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal cracking, visbreaking</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>X</td>
</tr>
<tr>
<td>Delayed coking</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Catalytic cracking</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>Hydrocracking</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Bitumen blowing</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0</td>
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<td>MTBE production</td>
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<td>Hydrodesulphurisation</td>
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<td>Sweetening</td>
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<td>Gas washing</td>
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<td>Lubricating oil production</td>
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<td>X</td>
<td>X</td>
<td>0</td>
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<tr>
<td>- with solvents</td>
<td>X</td>
<td>0</td>
<td>0</td>
<td>X</td>
<td>0</td>
<td>—</td>
<td>X</td>
</tr>
<tr>
<td>- with molecular sieves</td>
<td>X</td>
<td>—</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>—</td>
<td>X</td>
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<td>0</td>
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<td>X</td>
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<td>X</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>Waste water treatment</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>—</td>
<td>0</td>
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<tr>
<td>Blending units</td>
<td>X</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>—</td>
<td>X</td>
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<tr>
<td>Off-gas clean up (Exhaust gas recovery unit)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>X</td>
</tr>
</tbody>
</table>

**NB:** X: high impact; 0: small impact; —: very small or no impact

Source: [302, UBA Germany, 2000]

### 3.1.1 Present consumption levels in refineries

#### 3.1.1.1 Energy

**General aspects information**

Petroleum refining is one of the most energy-intensive manufacturing industries. In a country like the US, refining activities account for 28% of the energy consumed by industry.

The capacity of the combustion plants in a refinery varies widely from less than 10 to up to 200 megawatts thermal input (MWth). The total installed capacity ranges from several hundred to more than 1500 MWhth in the largest refineries (which equals 1.7 to 5.4 GJ per tonne crude processed). This capacity is equal to an overall power installation from of 20 to 1000 MW. These ranges depend strongly on the degree of energy integration of the refinery, its complexity, and the integration of units such as cogeneration, petrochemicals and lubricant oil plant.

Energy is required by the combustion systems and process units. The largest energy use is by internal or external fuels in a combustion plant which can reach up to 200 MW thermal input in size. Some refineries use Combined Heat and Power (CHP) units to raise some of their steam and electricity. Such units may be operated by third parties and export some of their energy, and
may use commercial rather than internal refinery fuels. Processes such as catalytic cracking can provide energy from the burn off of coke, usually supplemented by internal fuel for efficient heat recovery. Sulphur removal from products is energy intensive as it requires hydrogen production.

Source: TWG data collection questionnaires – 2008

Figure 3.1: Example of specific emissions and consumptions in European refineries

Actual specific consumption of 48 European refineries for recent years are displayed shown in Table 3.2. Most of them (90% of data – From 5th to 95th percentiles) ranged from 1.67 to 3.73 million GJ/t feedstock processed. It ranged from 1.5 - 4.0 GJ/t of crude with an average of 2.75. A large part of this energy is traditionally provided by the refinery’s own consumption of various internal fuels and residues generated by the crude oil processing. Around 6 - 9 % of the crude feedstock received is actually burnt in the refinery. Obviously, as shown on Figure 3.3, the site’s overall CO2 emissions are rather narrowly correlated to specific consumption.

Growing impact of desulphurisation processes

Processes that have the greatest throughput dominate energy consumption: atmospheric distillation and, to a lesser extent, vacuum distillation units represent together 35 to 40 % of the total process energy consumed in a refinery. However, it can be noted from Figure 3.4 that energy consumption is also clearly correlated to the part of sulphur input that has been recovered from the overall refinery feedstock, linked to the fact that, on average, another 20 – 25 % of this energy is spent in hydrotreating.

It is also clearly illustrated in Figure 3.2 which gives the distribution of energy consumption for each main process typically operated in US refineries, calculated as an average from the 146 refineries that were operated in 2001 [68, Worrell et al. 2005]. In this graphic, all data are expressed in primary energy (see the graphic footnotes).
Impact of site complexity
It is interesting to notice on Figure 3.3 that, despite quite a large dispersion of values, there is also a clear general trend for most complex sites to be associated with highest specific energy consumptions.

Use of natural gas
A growing part of necessary energy comes from the supply of external fuels, especially natural gas which is used in 31 out of these 48 refineries (64.5 % of the sample). Natural gas represents in average 17 %, and up to 82 % of the overall consumption of the sites concerned. As shown in Figure 3.4, there is no obvious correlation between the part of total gaseous fuels (RFG + eventual external supply of natural gas) and the specific energy consumption. However, refineries where natural gas is the most intensively used are usually operating recent CHP power plants for their steam delivery: it is then not surprising that the largest natural gas use is rather well correlated with the best specific energy consumptions.
Table 3.2: Specific energy consumption and other relevant data for a selection of EU refineries

<table>
<thead>
<tr>
<th>Questionnaire label</th>
<th>Nelson index</th>
<th>Total feedstock refined</th>
<th>Net thermal energy used</th>
<th>Specific energy consumption</th>
<th>Specific CO₂ emission</th>
<th>Natural gas/total energy</th>
<th>Total gaseous fuels/total energy</th>
<th>Semirefined (SE) input (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N°</td>
<td>8.2</td>
<td>9 096</td>
<td>42.04</td>
<td>0.31</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1</td>
<td>11.2</td>
<td>606</td>
<td>NA</td>
<td>0.28</td>
<td>1%</td>
<td>6%</td>
<td>3.8%</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>13.5</td>
<td>12 400</td>
<td>43.26</td>
<td>0.24</td>
<td>82%</td>
<td>89%</td>
<td>2.2%</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6.4</td>
<td>3 268</td>
<td>7.05</td>
<td>0.15</td>
<td>10%</td>
<td>96%</td>
<td>5.9%</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.2</td>
<td>9 350</td>
<td>20.41</td>
<td>0.16</td>
<td>8%</td>
<td>67%</td>
<td>4.9%</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.8</td>
<td>8 852</td>
<td>22.13</td>
<td>0.16</td>
<td>8%</td>
<td>67%</td>
<td>7.5%</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>6.2</td>
<td>9 350</td>
<td>20.41</td>
<td>0.16</td>
<td>8%</td>
<td>67%</td>
<td>4.9%</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>13.5</td>
<td>12 400</td>
<td>43.26</td>
<td>0.24</td>
<td>82%</td>
<td>89%</td>
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<tr>
<td>7</td>
<td>6.4</td>
<td>3 268</td>
<td>7.05</td>
<td>0.15</td>
<td>10%</td>
<td>96%</td>
<td>5.9%</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6.2</td>
<td>9 350</td>
<td>20.41</td>
<td>0.16</td>
<td>8%</td>
<td>67%</td>
<td>4.9%</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.8</td>
<td>8 852</td>
<td>22.13</td>
<td>0.16</td>
<td>8%</td>
<td>67%</td>
<td>7.5%</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>6.2</td>
<td>9 350</td>
<td>20.41</td>
<td>0.16</td>
<td>8%</td>
<td>67%</td>
<td>4.9%</td>
<td></td>
</tr>
</tbody>
</table>

No of values: 56
### Table 3.1: Energy and Emissions for EU Refineries

<table>
<thead>
<tr>
<th></th>
<th>Total feedstock refined</th>
<th>Net thermal energy used</th>
<th>Specific energy consumption</th>
<th>Specific CO₂ emission</th>
<th>Natural gas/total energy</th>
<th>Total gaseous fuels/total energy</th>
<th>Emitted/S input (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>606 kt</td>
<td>106 GJ</td>
<td>0.67 GJ/t</td>
<td>0.10 %</td>
<td>0.0 %</td>
<td>0.9 %</td>
<td>0.2 %</td>
</tr>
<tr>
<td>Maximum</td>
<td>19151 kt</td>
<td>69 GJ</td>
<td>7.65 GJ/t</td>
<td>0.69 %</td>
<td>82.3 %</td>
<td>100 %</td>
<td>18.9 %</td>
</tr>
<tr>
<td>Average</td>
<td>7436 kt</td>
<td>22 GJ</td>
<td>2.75 GJ/t</td>
<td>0.22 %</td>
<td>9.8 %</td>
<td>70.5 %</td>
<td>5.1 %</td>
</tr>
<tr>
<td>Sum</td>
<td>401544 kt</td>
<td>1075 GJ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5th Percentile</td>
<td></td>
<td></td>
<td>1.67 GJ/t</td>
<td>0.106 %</td>
<td>0.0 %</td>
<td>27.4 %</td>
<td>0.6 %</td>
</tr>
<tr>
<td>95th Percentile</td>
<td></td>
<td></td>
<td>3.73 GJ/t</td>
<td>0.395 %</td>
<td>37.1 %</td>
<td>100 %</td>
<td>12.5 %</td>
</tr>
</tbody>
</table>

*NB: NA: these data have not been made available to the TWG*

---

**Figure 3.3:** Specific energy consumption compared to CO₂ emissions and site complexity for a sample of EU refineries

**Figure 3.4:** Use of gaseous fuels and emitted part of sulphur input for a sample of EU refineries sorted by ascending order of specific energy consumption
3.1.1.2 Water

Water and steam are mainly used:

- in the various refinery processes, e.g. to assist the distillation process or the cracking of hydrocarbons, in overhead systems, and in for washing, scrubbing, quenching or (steam) stripping. Petroleum refineries use relatively large volumes of water in the processes. The desalter is the biggest user, and therefore also the main producer of waste water in oil refineries (with the exception of base oil refineries);
- for tank and flare seal drains;
- for cleaning operations;
- in for steam generation as a feedstock for boilers and CHPs;
- and especially, in for cooling systems.

Wash water is used in a number of processes, of which Wash water is also used in the overhead systems of many processes. Tank and flare seal drains and cleaning water all contribute to the amount and quality of process water streams. From a qualitative point of view, the first three categories of use generate the main part of the organic load which must be abated in the WWTP, since the water has been in direct contact with hydrocarbons and is usually heavily contaminated. On the other hand, from a quantitative point of view, the amount of water consumed used depends primarily on the type of refinery and, especially, on the cooling systems used: closed or open (once-through). It ranges from 0.01 up to 5 tonnes per tonne of crude oil processed.

Actual specific consumptions usage of water of 58 European refineries are displayed in Table 3.3. Most of them (90% of the data - from the 5th to 95th percentiles) ranged between 0.2 and 25 m3/t of feedstock refined. The largest part of it (more than 50% on average) is still used for cooling. As well shown in Figure 3.5, the highest specific consumptions usage (above 1 m3/t) reached at the site level are always determined by the highest cooling consumptions usage. They relate to sites where the greatest proportion of fully open once-through cooling circuits are still used.

Potable water from public supply represents, on average, 23% of the overall consumptions usage of these refineries, but its use varies greatly. Some sites do not use any potable water, while other sites fully rely upon it, including for purposes other than sanitary use.

![Figure 3.5: Specific water consumption usage data for a selection of European refineri](image-url)
### Table 3.3: Water consumption data for a set of 53 European refineries

<table>
<thead>
<tr>
<th>Site label</th>
<th>Nelson Index</th>
<th>Total water consumed Mm³/yr</th>
<th>Specific water consumption m³/t</th>
<th>Water for industrial processes</th>
<th>Water for boilers feed</th>
<th>Water for cooling systems</th>
<th>Proportion of use of potable water consumption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2</td>
<td>13.50</td>
<td>1.48</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>2</td>
<td>11.2</td>
<td>0.74</td>
<td>1.22</td>
<td>31000 42.9 %</td>
<td>0.05</td>
<td>3600000 49 %</td>
<td>0.59</td>
</tr>
<tr>
<td>3</td>
<td>5.7</td>
<td>0.50</td>
<td>0.14</td>
<td>15000 3.0 %</td>
<td>0.04</td>
<td>4120000 83 %</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>3.1</td>
<td>4.42</td>
<td>0.90</td>
<td>117000 2.6 %</td>
<td>0.02</td>
<td>5000000 11 %</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>6.8</td>
<td>0.74</td>
<td>0.27</td>
<td>204000 27.5 %</td>
<td>0.07</td>
<td>4320000 58 %</td>
<td>0.16</td>
</tr>
<tr>
<td>6</td>
<td>6.2</td>
<td>6.94</td>
<td>1.62</td>
<td>7010000 87.0 %</td>
<td>0.57</td>
<td>713456000 97.54</td>
<td>0.28</td>
</tr>
<tr>
<td>7</td>
<td>6.4</td>
<td>13.65</td>
<td>4.18</td>
<td>1802816 13.2 %</td>
<td>0.55</td>
<td>1180517 86 %</td>
<td>3.61</td>
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<tr>
<td>8</td>
<td>NA</td>
<td>35.81</td>
<td>37.56</td>
<td>79504 0.2 %</td>
<td>0.08</td>
<td>383091 1 %</td>
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<tr>
<td>9</td>
<td>6.6</td>
<td>5.79</td>
<td>0.10</td>
<td>873560 15.1 %</td>
<td>0.15</td>
<td>1581200 27 %</td>
<td>0.28</td>
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<td>10</td>
<td>6.8</td>
<td>9.20</td>
<td>0.04</td>
<td>477856 5.2 %</td>
<td>0.05</td>
<td>2030890 22 %</td>
<td>0.23</td>
</tr>
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<td>6.2</td>
<td>3.77</td>
<td>0.40</td>
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<td>0.54</td>
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<td>NA</td>
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<td>NA</td>
</tr>
<tr>
<td>13</td>
<td>6.0</td>
<td>6.58</td>
<td>1.24</td>
<td>5384185 81.8 %</td>
<td>1.02</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>14</td>
<td>9.3</td>
<td>42.47</td>
<td>2.57</td>
<td>4351435 10.2 %</td>
<td>0.26</td>
<td>4457867 10 %</td>
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<tr>
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</tr>
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<td>NA</td>
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<td>NA</td>
</tr>
<tr>
<td>18</td>
<td>12.9</td>
<td>11.90</td>
<td>1.44</td>
<td>5306385 44.6 %</td>
<td>0.64</td>
<td>3297800 28 %</td>
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</tr>
<tr>
<td>19</td>
<td>12.9</td>
<td>11.02</td>
<td>1.19</td>
<td>574218 5.2 %</td>
<td>0.06</td>
<td>3232352 29 %</td>
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</tr>
<tr>
<td>20</td>
<td>13.1</td>
<td>842.09</td>
<td>149.65</td>
<td>497281 0.1 %</td>
<td>0.09</td>
<td>9447040 1 %</td>
<td>1.68</td>
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<tr>
<td>21</td>
<td>7.2</td>
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<td>1.00</td>
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<td>NA</td>
<td>NA</td>
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<td>22</td>
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<td>17.97</td>
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<td>NA</td>
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<td>NA</td>
</tr>
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<td>23</td>
<td>4.9</td>
<td>266.18</td>
<td>30.76</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>24</td>
<td>9.7</td>
<td>1.40</td>
<td>0.39</td>
<td>547000 39.0 %</td>
<td>0.15</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>25</td>
<td>10.8</td>
<td>7.19</td>
<td>0.71</td>
<td>623664 8.7 %</td>
<td>0.06</td>
<td>3162240 44 %</td>
<td>0.31</td>
</tr>
<tr>
<td>26</td>
<td>10.8</td>
<td>388.84</td>
<td>20.30</td>
<td>11028626 2.8 %</td>
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<tr>
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<td>7.38</td>
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<td>3510671 48 %</td>
<td>0.25</td>
<td>3722846 50 %</td>
</tr>
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<td>6.3</td>
<td>5.54</td>
<td>0.53</td>
<td>1358440 24.5 %</td>
<td>0.13</td>
<td>1824770 33 %</td>
<td>0.17</td>
</tr>
</tbody>
</table>

March 2012 PB/EIPPCB/REF_Draft 2
6.7

8.35

0.69

2 595 498

31.1 %

0.21

3 604 606

43 %

0.30

2144738

26 %

0.18

32

11.4

3.51

0.60

799 098

22.8 %

0.14

1 158 205

33 %

0.20

1509710

43 %

0.26

33

4.6

2.56

0.55

NA

NA

34

8.6

6.90

0.66

NA

441 049

6%

0.04

NA

35

5.7

2.15

0.59

NA

451 435

21 %

0.12

600219

36

10.1

NA

NA

NA

37

9.5

7.14

0.98

1 952 263

27.3 %

0.27

1 760 370

25 %

0.24

3415251

38

7.3

3.46

0.42

17 000

0.5 %

0.002

NA

NA

39

8.2

1.75

0.17

NA

NA

NA

40

6.2

0.72

0.13

NA

NA

41

6.5

12.41

3.15

NA

NA

42

12.0

5.41

0.50

NA

NA

43

8.7

148.39

9.59

NA

8 201 500

44

1.6

0.85

0.19

NA

45

8.4

24.87

2.47

530 000

2.1 %

0.05

4 016 000

46

6.2

2.69

0.28

25 2957

9.4 %

0.03

2 200 270

47

11.6

5.52

0.46

43 1427

7.8 %

0.04

4 076 298

48

8.4

14.85

2.15

3 861 846

26.0 %

0.56

49

5.7

3.70

0.25

1 795 317

48.5 %

0.12

50

10.5

3.10

0.67

859 919

27.7 %

51

8.4

4.50

1.02

1 402 658

31.2 %

52

10.9

1.48

0.30

NA

53

3.8

0.96

NA

557 000

54

5.4

NA

NA

NA

55

5.1

NA

NA

1400000

56

12.4

2.70

0.43

57

8.2

68.84

11.91

G

R
ES
S

31

58

10.2

12.15

57

53
0.23
842
39
0.73
196

W

95th Percentile

O

Average:
5th Percentile

PB/EIPPCB/REF_Draft 2

0.00
0.32

100 %

0.66

551 648

25.6 %

0.15

0.47

4 799 449

67.2 %

0.66

142 000

4.1 %

0.02

0

0.0 %

0.00

NA

721 000

100 %

0.13

NA

1 171 395

9.4 %

0.30

G

NA

O

48 %

NA

125 681

2.3 %

0.01

NA

450 000

0.3 %

0.03

NA

16 %

0.40

20260000

82 %

0.23

74 %

0.34

4 214 512

28 %

1 909 028

52 %

AF
T

0.0 %
57.3 %

6 902 700

28 %

PR

0.53

0

1 465 000

14 100

1.6 %

0.00

35 000

0.1 %

0.00

0.02

59 697

2.2 %

0.01

0.06

262 800

4.8 %

0.02

0.89

8 713 325

58.7 %

1.26

3 704 345

100 %

0.25

81 %

2.02

175800

7%

748275

14 %

0.61

6140076

41 %

0.13

NA

0.19

984 095

32 %

0.21

934425

30 %

0.20

0

0.0 %

0.00

0.32

1 837 388

41 %

0.42

1074965

24 %

0.24

2 337 675

52.0 %

0.53

NA

34 124

2.3 %

0.01

42 %

NA

NA

450 000

47.0 %

NA

NA

1.49

R

D

58.2 %

6%

0.02

0.17

NA

IN

NA

NA

1.49

NA
400 000
NA

NA

NA

10200000

NA
10.85

1400000

680 236

25.2 %

0.11

768 017

28 %

0.12

928026

34 %

0.15

0

0.0 %

0.00

4.5 %

0.54

2 073 024

3%

0.36

63572370

92 %

11.00

84 802

0.1 %

0.01

3 613 982

30 %

0.32

8284316

68 %

0.72

248 923

2.0 %

0.02

31

30

31

31

30

30

30

30

52

52

50

KI
N

Minimum:
Maximum:

NA

3.4 %

3 109 536

1.06

NA

51

31

0.13

15 000

0.06 %

0.002

360 000

1%

0.04

54 000

7%

0.02

0

0.0 %

0.00

149.65

11 028 626

81.8 %

1.02

9 447 040

83 %

1.68

831 672 535

99 %

147.80

11 294 307

100 %

1.26

R

Nbr of values:

NA

28 1000

Chapter 3

5.89

1 681 185

19.7 %

0.22

2 462 633

32 %

0.33

47 760 617

51 %

7.69

1 140 267

23.3 %

0.16

0.18

24 000

0.36 %

0.013

391 546

2%

0.110

109 360

9%

0.019

0

0.0 %

0.000

25.53

5 345 285

53.3 %

0.612

6 329 684

78 %

0.603

236 255 396

97 %

28.97

7 033 828

100 %

0.659

March 2012

123


Figure 3.6 shows in some more details, and with a linear scale instead of the logarithmic one used in Figure 3.5 a breakdown of the main water sources of consumption usage for the sub-sample of European refineries for which this information was fully available. What appears notably is the rather constant consumption water use related to the boiler feed water used in all of these sites, regardless of their very increasing total site consumption usage. Furthermore, this figure displays clearly the beneficial effect of cooling water recycling on the site’s overall specific consumption usage.

![Figure 3.6: Water specific consumption breakdown for a sample of European refineries](image)

3.1.1.3 Chemicals

The amount of chemicals used in a refinery is around 300 tonnes per each million of tonnes of crude oil processed.

Note for TWG: this is a very vague information: if no more updating data is made available it would be suggest to delete it.

3.1.2 Emissions to air

The main air emissions from a refinery are CO₂, SO₂, NOₓ, VOC and particulates (dust, soot and associated heavy metals (mainly V and Ni)). However, noise, odour, H₂S, NH₃, CO, CS₂, benzene, toluene, dioxins, HF and HCl also contribute to the air emissions. They emerge typically from sources such as stacks of process furnaces and boilers, regenerators (FCC), individual items such as valves and pump seals and to a lesser extent from flares and incinerator stacks. Some documents have already been published that establish emissions factors for the calculation of air emissions from refineries [208, USAEPA, 1996] [136, MRI, 1997]. The E-PRTR regulation [74, EC 2010] requires refineries to make inventories of a a large number of air emissions data since 2007.
3.1.2.1 Carbon dioxide emissions

Almost all of the carbon present in crude oil, once produced from the oil well, will be converted into \( \text{CO}_2 \) sooner or later. A small portion (<3 – 10\%) of the \( \text{CO}_2 \) will be converted in the refinery during the processing of crude oil into marketable products. The remainder will be converted into \( \text{CO}_2 \) once the refined oil products are sold and subsequently consumed by the various sectors of industry and private consumers.

In 2007, oil refineries in the EU-27 (Romania and Bulgaria excluded) emitted around 135 Mt of \( \text{CO}_2 \), 89\% of it coming from the combustion of liquid fuels. In 1990 these figures were respectively 115 Mt of \( \text{CO}_2 \) and 91\%. The 15\% increase of \( \text{CO}_2 \) emissions between 1990 and 2007 is mainly linked to the increasing average site growing complexity, the diversification of refining processes and the significant increase of hydrotreatment capacities for deeper product desulphurisation and conversion.

The share of \( \text{CO}_2 \) emissions from oil refining in the total greenhouse gas emissions was, in 2007, around 3\% at EU-15 level. At the individual Member State level, it ranged from around 0.5\% (for Ireland) to 5\% (for the Netherlands).

Actual specific emissions of 53 European refineries for recent years are displayed in Table 3.2 in Section 3.1.1.1. The largest part - 90\% of them from the 5th to 95th percentiles - have range within 0.11 – 0.39 t/t of feedstock processed, with an average of 0.22. As shown in Figure 3.3, highest values are often associated with the most complex sites.

At the individual site level, \( \text{CO}_2 \) emissions by themselves ranged from 0.168 to 5.547 million tonnes per year. However, it could be interesting to note that \( \text{the} \) lowest and highest emissions are originate from two refineries which show with nearly the same \( \text{CO}_2 \) specific emissions (0.28 – 0.29 t/t), which is close to the European average.

The main emission sources for \( \text{CO}_2 \) are the process furnaces and boilers, gas turbines, FCC regenerators, flare systems and incinerators. The range of \( \text{CO}_2 \) emissions is very wide (28500 - 1120000 t/yr for a single refinery) and specific emissions range from 0.02 to 0.82 tonnes of \( \text{CO}_2 \) per tonne of crude processed. Next figure gives the plot of the specific \( \text{CO}_2 \) emissions from some European refineries as a function of the Nelson complexity index. As it can be seen, the figure shows that specific emissions of \( \text{CO}_2 \) depend on the refinery complexity. More complex refineries tend to consume more energy and consequently emit more \( \text{CO}_2 \).

3.1.2.2 Nitrogen oxides emissions

The term \( \text{NO}_x \), by convention, only refers to \( \text{NO} \) (nitric oxide) and \( \text{NO}_2 \) (nitrogen dioxide). \( \text{N}_2\text{O} \) can be also found in flue-gases from FCCs and some SCR. In most combustion processes \( \text{NO} \) contributes to over 90\% of the total \( \text{NO}_x \). However, as it is rapidly oxidised to \( \text{NO}_2 \) in the atmosphere, \( \text{NO}_x \) emissions of \( \text{NO} \) are expressed as \( \text{NO}_2 \).

Main Contributing processes and units

Combustion processes are the main source of \( \text{NO}_x \). Based on the information gathered by the TWG, the following Figure 3.7 and Figure 3.8 display site-level data on the \( \text{NO}_x \) specific emissions and the main \( \text{NO}_x \) contributing units and processes within a sample of 58 European sites. The main emission sources for \( \text{NO}_x \) are combustion processes, i.e.: process furnaces and boilers, CHP and gas turbines, FCC regenerators, and to a lesser extent, eventual waste gas incinerators, gas turbine and the flare system. Roughly 60 – 70\% of the \( \text{NO}_x \) of a refinery derives from the use of fuels in furnaces, boilers and gas turbines, 16\% relates to the FCC, 11\% to engines and the rest to gas turbines and combined cycle systems. However, the respective \( \text{NO}_x \) weight of these units in the overall site emissions are highly variable, as the tendency is shown based on the data gathered in the same tables.
Chapter 3

In the case of refineries without an FCC unit, the major NOx contribution obviously comes from furnaces and boilers, which account most often for about 60 – 90 % of emissions, as shown in Figure 3.7. Gas turbines and CHP, when they are operated on such plants, are responsible for a significant part (30 – 50 %) of NOx emissions, and seem to be associated with the highest specific emissions at the site level. SRU and flare systems usually account for less than 5 – 10 %.

In the case of a refinery configuration including an FCC unit, furnaces and boilers remain the major NOx contributors and generate most often 50 – 80 % of site emissions, while the FCC by itself may only represent 15 – 25 % of them. As displayed in Figure 3.8, most of the remainder is emitted by CHP and gas turbines which, as stated above, are clearly related to highest specific emissions reported.

When operating a coker, coking emissions can also represent a very significant contribution (up to 40 %) which appear here in the ‘Other’ category.

Figure 3.7:  Respective weight of main NOx-contributing processes for 12 European refineries not operating an FCC unit as a function of their specific emissions (g/t of feed)

Figure 3.8:  Respective weight of main NOx-contributing processes for 24 European refineries operating an FCC unit as a function of their specific emissions (g/t of feed)
Influence of the overall configuration site

The range of NO\textsubscript{x} emissions is reported for the site sample displayed in Figure 3.9 within the period 2007 – 2008, where it is from 50 to 5000 tonnes per year. The specific emission range of NO\textsubscript{x} varies from 60 to 5000, with most of these refineries emitting within the range of 100 – 450 g/t. The average specific emissions obtained within the particular subgroup of refineries without an FCC is 258 g/t processed. This average only increases up to 269 g/t processed (+4 %) for the subgroup operating an FCC. Therefore, it seems that FCC configurations should not necessarily be considered intrinsically generating a degradation of NO\textsubscript{x} emissions at the site level.

Figure 3.9 displays the distribution of the Nelson index and the specific energy consumption for these two subgroups of European refineries, each of them ordered by ascending specific NO\textsubscript{x} emission. It is seen that no obvious correlation can be remarked as far as the Nelson index is concerned, and that the specific NO\textsubscript{x} emissions of non-FCC sites and FCC sites evolve basically in the same range of 60 – 600 g/t of feedstock processed. And once again, for both categories of refineries, the highest specific NO\textsubscript{x} emissions are clearly associated with the highest specific energy consumptions.

[101, World Bank, 1998]. Next figure gives the plot of the specific NO\textsubscript{x} emissions from some European refineries as a function of the Nelson complexity index. As it can be seen, the figure does not show that specific emissions of NO\textsubscript{x} depend on the refinery complexity.

![Figure 3.9: Influence of the configuration, complexity and specific energy consumption on NO\textsubscript{x} emissions](image)

Influence of the refinery fuel mix

NO\textsubscript{x} emissions from refineries depend on the fuel type, fuel nitrogen or hydrogen content, combustor equipment design, and operating conditions. In the particular case of FCC regenerator flue-gas, NO\textsubscript{x} are mostly in general not thermal NO\textsubscript{x} produced by the interference of air-contained nitrogen in high temperature combustion, but are directly linked to the nitrogen content in the feedstock. Accordingly, large differences in the NO\textsubscript{x} emission levels can be expected between refineries and even between different combustion installations at the same refinery at different times. Nevertheless, over long periods, general trends can be observed showing a rather clear correlation between NO\textsubscript{x} emissions and the use of gaseous fuels for energy system firing. As shown in Figure 3.10, the highest values of NO\textsubscript{x} specific emissions recorded within a sample of 51 European refineries are mostly associated with the lowest percentages of energy coming from gaseous fuels in the fuel mix used at these sites (whatever the part taken by the eventual natural gas external supply in these gaseous fuels).
Figure 3.10: Influence of the gaseous fuels used for energy supply on the site NO\textsubscript{x} emissions

Table 3.4: NO\textsubscript{x} emissions and main contributing unit data for 58 European refineries

<table>
<thead>
<tr>
<th>Questionnaire</th>
<th>Nelson Index</th>
<th>FCC (yes=1)?</th>
<th>Year</th>
<th>Total NO\textsubscript{x}</th>
<th>NO\textsubscript{x} specific emission</th>
<th>Furnace + boilers</th>
<th>CHP + stand-alone gas turbines</th>
<th>FCC</th>
<th>SRU</th>
<th>Flares</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>t/yr</td>
<td>g/t</td>
<td>t/yr</td>
<td>%</td>
<td>t/yr</td>
<td>%</td>
<td>t/yr</td>
<td>%</td>
<td>t/yr</td>
<td>%</td>
<td>t/yr</td>
<td>%</td>
</tr>
<tr>
<td>40 6.2</td>
<td>0</td>
<td>2008</td>
<td>337</td>
<td>59</td>
<td>328</td>
<td>97 %</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.7</td>
<td>2.3 %</td>
</tr>
<tr>
<td>53 3.8</td>
<td>0</td>
<td>2008</td>
<td>380</td>
<td>69</td>
<td>375</td>
<td>99 %</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>0.8 %</td>
</tr>
<tr>
<td>25 9.7</td>
<td>0</td>
<td>2007</td>
<td>294</td>
<td>81</td>
<td>270</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>24.2</td>
<td>8.2 %</td>
</tr>
<tr>
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<td>2008</td>
<td>329</td>
<td>83</td>
<td>323</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>0.6 %</td>
</tr>
<tr>
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<td>89</td>
<td>536</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>NA</td>
<td>-</td>
<td>-</td>
<td>NA</td>
<td>-</td>
</tr>
<tr>
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<td>272</td>
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<td>-</td>
<td>NA</td>
<td>-</td>
<td>-</td>
<td>NA</td>
<td>-</td>
</tr>
<tr>
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<td>2008</td>
<td>1384</td>
<td>277</td>
<td>NA</td>
<td>-</td>
<td>NA</td>
<td>-</td>
<td>-</td>
<td>NA</td>
<td>-</td>
</tr>
<tr>
<td>33 4.6</td>
<td>0</td>
<td>2008</td>
<td>1725</td>
<td>357</td>
<td>887</td>
<td>51 %</td>
<td>814</td>
<td>47 %</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>0</td>
<td>2008</td>
<td>3208</td>
<td>392</td>
<td>2316</td>
<td>72 %</td>
<td>870</td>
<td>27 %</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>35 5.7</td>
<td>0</td>
<td>2008</td>
<td>1535</td>
<td>424</td>
<td>927</td>
<td>60 %</td>
<td>609</td>
<td>40 %</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>8 NA</td>
<td>0</td>
<td>2008</td>
<td>477</td>
<td>500</td>
<td>476</td>
<td>100 %</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>46 4.9</td>
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<td>2007</td>
<td>2337</td>
<td>612</td>
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<td>-</td>
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<td>-</td>
</tr>
<tr>
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<td>2007</td>
<td>1030</td>
<td>173</td>
<td>136</td>
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<td>318</td>
<td>69 %</td>
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<td>-</td>
<td>9</td>
</tr>
<tr>
<td>23 8.4</td>
<td>0</td>
<td>2007</td>
<td>1030</td>
<td>173</td>
<td>136</td>
<td>29 %</td>
<td>318</td>
<td>69 %</td>
<td>-</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>39 8.2</td>
<td>1</td>
<td>2008</td>
<td>687</td>
<td>68</td>
<td>620</td>
<td>90 %</td>
<td>-</td>
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<td>48</td>
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<td>1400</td>
<td>93</td>
<td>760</td>
<td>54 %</td>
<td>300</td>
<td>21 %</td>
<td>300</td>
<td>21 %</td>
<td>20</td>
</tr>
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<td>3 6.8</td>
<td>1</td>
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<td>343</td>
<td>124</td>
<td>NA</td>
<td>-</td>
<td>NA</td>
<td>-</td>
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<tr>
<td>1 6.2</td>
<td>1</td>
<td>2008</td>
<td>1203</td>
<td>132</td>
<td>NA</td>
<td>-</td>
<td>564</td>
<td>47 %</td>
<td>53</td>
<td>4 %</td>
<td>NA</td>
</tr>
<tr>
<td>18 12.9</td>
<td>1</td>
<td>2007</td>
<td>1144</td>
<td>138</td>
<td>959</td>
<td>84 %</td>
<td>-</td>
<td>-</td>
<td>127</td>
<td>11 %</td>
<td>20.7</td>
</tr>
<tr>
<td>16 8.7</td>
<td>1</td>
<td>2008</td>
<td>1064</td>
<td>149</td>
<td>340</td>
<td>32 %</td>
<td>-</td>
<td>-</td>
<td>702</td>
<td>66 %</td>
<td>0</td>
</tr>
<tr>
<td>11 6.2</td>
<td>1</td>
<td>2008</td>
<td>1512</td>
<td>162</td>
<td>NA</td>
<td>-</td>
<td>NA</td>
<td>-</td>
<td>-</td>
<td>NA</td>
<td>-</td>
</tr>
<tr>
<td>46 6.2</td>
<td>1</td>
<td>2008</td>
<td>1685</td>
<td>173</td>
<td>1322</td>
<td>78 %</td>
<td>101</td>
<td>6 %</td>
<td>187</td>
<td>11 %</td>
<td>-</td>
</tr>
</tbody>
</table>
As it has been mentioned above, FCC generates NO\textsubscript{x} emissions and they represent around 16 % of the NO\textsubscript{x} emissions in refineries. As consequence, it is possible that FCC refineries may emit more NO\textsubscript{x} than the ones that they do not have. In the graph, refineries with FCC have been plotted with red points. As it can be seen, the figure does not show that specific emissions of NO\textsubscript{x} depends on having or not having a FCC.

Specific emissions may be transformed to concentrations if a factor is calculated. Data from some European refineries have been compiled with the idea to analyse the factor between specific emission with concentration values. The data compiled is summarised in the next table:
Chapter 3

<table>
<thead>
<tr>
<th>Refinery capacity (Mt)</th>
<th>Total flue-gas volume (10^9 Nm^3/yr)</th>
<th>Specific volume of flue-gas (10^9 Nm^3/yr per Mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>22.173</td>
<td>1.48</td>
</tr>
<tr>
<td>12.4</td>
<td>10.214</td>
<td>0.82</td>
</tr>
<tr>
<td>10</td>
<td>11.9</td>
<td>0.84 Gas-fired refineries</td>
</tr>
<tr>
<td>0.62</td>
<td>2.2</td>
<td>1.55 More-liquid-fuel</td>
</tr>
<tr>
<td>0.62</td>
<td>6.6</td>
<td>1.46</td>
</tr>
<tr>
<td>0.62</td>
<td>7.4</td>
<td>1.36</td>
</tr>
<tr>
<td>0.62</td>
<td>9.6</td>
<td>0.95 Less-liquid-fuel</td>
</tr>
<tr>
<td>9</td>
<td>22.2</td>
<td>0.92</td>
</tr>
<tr>
<td>9</td>
<td>22.2</td>
<td>0.92</td>
</tr>
<tr>
<td>5</td>
<td>5.92</td>
<td>1.65</td>
</tr>
<tr>
<td>4.5</td>
<td>5.545</td>
<td>1.25</td>
</tr>
<tr>
<td>4.2</td>
<td>1.906</td>
<td>0.48</td>
</tr>
<tr>
<td>2.5</td>
<td>0.866</td>
<td>0.35</td>
</tr>
<tr>
<td>1.2</td>
<td>0.388</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Range in a EU+ country

1 – 1.5

*Values that correspond to the same refinery but for different years. The proportion of RFG increases as you go down in the table.

Table 3.5: Volume of flue-gas generated by EU refineries
Source: [268, TWG, 2001]

As it can be shown in this table, the specific volume of flue-gas is very variable. However, it has been found a correlation that specially refineries (last two rows in the table) tend to give lower values. The average for other nine refineries is around 1 and it varies between 0.48 and 1.55. This factor depends on fuel distribution (gas/liquid ratio as shown in the asterisk example within the table); fuel composition, oxygen content of the flue-gas, etc. and consequently the range is wide. However, it may be calculated, considering these values, that a refinery emitting 200 tonnes of NOx/Mt of crude processes may emit flue-gases with a NOx concentration of 130-420 mg/Nm^3 (average: 200 mg/Nm^3). Note for TWG: this information is updated and translated to Section 4.15.9.3.

3.1.2.3 Particulate emissions

The concern with particulate emissions (including heavy metals) stems from health effects. The main emission sources are process furnaces/boilers (mainly these fired with (liquid) heavy fuel oil), catalytic cracker regenerators, coke plants, incinerators, decoking and sootblowing of furnaces and the flare. As shown, the range of emissions found in most European refineries (5th to 95th percentiles within a sample of 43 plants) is approximately from 100 to 2000 tonnes of particulates emitted per year, which correspond with a specific emission range found is from 40 to 75 tonnes of particulates per million tonnes of crude oil processed. The lower emission value can be achieved in simple refineries burning substantial amounts of gas or when effective dedusting devices (ESP, bag filters) are installed.

Table 3.6: Specific emission ranges of PM, PM10 and PM2.5 for 43 European refineries

<table>
<thead>
<tr>
<th>Type of particulates</th>
<th>Unit</th>
<th>Specific load</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5th – 95th percentile</td>
<td>50th percentile</td>
</tr>
<tr>
<td>PM (total)</td>
<td>g/t</td>
<td>24 – 62675</td>
<td>181</td>
</tr>
<tr>
<td>PM10</td>
<td>g/t</td>
<td>0.1 – 45</td>
<td>15</td>
</tr>
<tr>
<td>PM2.5</td>
<td>g/t</td>
<td>0.01 – 12</td>
<td>4</td>
</tr>
</tbody>
</table>

Important heavy metals in crude oils are arsenic, mercury, nickel and vanadium. Nickel and vanadium are enriched in the residues during distillation (see Table 3.64 in Section 3.10.2) and are removed with the particulate matter by ESP or fabric filters after combustion in the furnaces.
or after the regeneration of catalysts by burning off. Table 3.7 shows data on air emissions of nickel and vanadium from two EU+ refineries. More data on metal emissions are available in Table 3.16 (see Section 3.1.2.6).

### Table 3.7: Nickel and vanadium emissions from two specific refineries

<table>
<thead>
<tr>
<th>Refinery capacity (Mt)</th>
<th>Nickel</th>
<th>Vanadium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific load (t/Mt)</td>
<td>Range of concentration (mg/Nm³)</td>
</tr>
<tr>
<td>15.3</td>
<td>0.196</td>
<td>0.2 – 1.2</td>
</tr>
<tr>
<td>12.3</td>
<td>0.772</td>
<td>0.02 – 2.35</td>
</tr>
</tbody>
</table>

#### 3.1.2.4 Sulphur oxides emissions

Sulphur emissions to the atmosphere have long been an issue for refineries. All crude oils contain sulphur compounds. Consequently, when firing non- or partially desulphurised refinery fuels, SO₂ and SO₃ will be emitted. There is a direct relation between the sulphur content of the fuel and the amount of SOₓ emitted (for example, a fuel with 1% sulphur generates a flue-gas with around 1700 mg/Nm³). The sulphur, which is not extracted from the products in the refinery, will remain in the various products and will be burnt to SOₓ by the various end-users. The refinery, as a consumer of fuel for its energy use, similarly emits SOₓ. However, natural gas, as a growing external energy supply in oil refining, normally contains only traces of sulphur compounds.

**Sulphur input/output mass balance**

The sulphur output distribution can vary greatly depending on FCC unit, furnace and boiler operation modes, SRU and hydrotreater performances and the overall share of products not for combustion.

According to a 2006 investigation by CONCAWE based on 67 European sites (accounting for 68% of the crude and intermediate feedstock refined in OECD), 156 kt of sulphur have been emitted to air (i.e. 312 kt of SO₂ after oxidation) out of a 4183 kt total sulphur intake, representing 3.73% as shown in Figure 3.11.

Moreover, based on the information gathered by the TWG, the following Table 3.8 displays site-level data on the sulphur input, specific emissions and the fuels used in a set of 49 European sites. Within this sample, the median percentage of sulphur emitted in the air and recovered by the SRUs (respectively 4.4% and 44.7% of the refinery sulphur input) are very close to the ratios displayed in Figure 3.11. It means that this TWG European sample is representative of the European global situation as reflected in the CONCAWE survey.
Chapter 3

Sulphur in crude
(%)

Sulphur in
intermediate
products (%)

Sulphur input in
feedstock (t) (3)

Sulphur input in
external fuels (t)

Total Sulphur
input (t)

Sulphur in RFG
(ppm)

Sulphur in liquid
fuel (%)

RFG/total fuel
burnt (%)

Natural gas/Total
fuel burnt (%)

Total gas/Total fuel
burnt (%)

Sulphur emitted in
air/input (%)

12
29
34
79
161
225
254
259
266
268
304
322
428
435
441
466
502
514
518
540
639
667
678
724
741
777
789
870
908
960
966
980
999
1037
1045
1062
1117
1119
1162
1183
1210
1242
1271
1370
1443
1530
1589
2417
2564

0.22
0.24
1.10
0.50
1.22
2.16
0.62
0.25
2.00
0.25
1.30
0.50
1.00
1.30
0.50
0.40
0.30
1.30
0.85
0.90
0.70
0.30
1.30
0.61
0.74
0.80
0.32
1.68
1.10
0.46
0.86
1.36
0.80
0.47
1.00
1.15
0.30
1.40
0.74
0.80
1.65
1.91
0.30
0.67
1.04
1.99
1.09
3.10
1.05

NA
NA
0.05
0.50
0.13
0.30
0.80
0.20
0.30
1.20
0.50
NA
1.50
0.45
2.50
0.60
2.00
2.00
0.50
0.03
1.70
1.50
0.10
0.05
0.70
0.50
1.85
NA
NA
2.30
NA

8672
12984
106458
24500
86856
75685
40517
11025
18800
8816
132506
75000
118020
89700
23480
41086
13200
36036
39185
77715
32940
14946
184874
19935
43262
74800
40390
331841
59569
54408
153941
161135
57226
24497
97730
125595
29650
8484
113959
69905
82303
139304
30474
4878
37551
208188
88233
157588
35244

0
0
0
0
0
0
0
0
0
0
3522
0
19
0
0
0
0
0
0
0
0
0
1
0
0
0
0
0
0
0
0
0
0
0
0
0
0
327
0
0
0
0
0
0
0
0
0
34220
0

8672
12984
106458
24500
86857
75685
40517
11025
18800
8816
136027
75000
118039
89700
23480
41086
13200
36036
39185
77715
32940
14946
184874
19935
43262
74800
40390
331841
59569
54408
153941
161135
57226
24497
97730
125595
29650
8811
113959
69905
82303
139304
30474
4878
37551
208188
88233
191807
35244

15
19
24
100
647
3200
288
6
NA
168
516
950
20
20
400
87
20
500
1300
100
500
500
10
5
44
100
47
652
1177
49
800
800
2000
393
10
0
350
1000
2123
NA
0.76
49
50
16300
0
50
4900
380
0

0.68
0.40
0.002
0.09
1.87
0.81
0.49
0.35
0.40
0.80
NA
0.10
NA
1.00
0.67
1.60
0.96
0.37
1.08
0.63
1.60
1.12
0.8
1.28
1.80
0.96
1.28
0.86
1.00
0.69
0.87
1.50
1.2
1.00
1.79
1.90
1.0
1.46
1.30
1.12
1.71
1.95
1.40
1.26
2.28

100
82
99
100
72
63
54
1
25
92
81
75
6
44
86
97
89
100
46
85
95
73
13
96
83
58
76
49
45
62
44
64
69
70
58
48
59
5
48
60
46
50
61
63
25
51
55
29
41

0
7
0
0
28
34
0
0
0
0
2
25
82
0
3
3
6
0
0
4
0
0
41
0
3
10
0
29
29
20
41
0
9
3
13
2
0
1
22
8
0
17
0
0
27
7
4
1
0

100
89
99
100
100
97
54
1
25
92
84
100
89
44
89
100
95
100
46
89
95
73
54
96
86
68
76
78
74
82
85
64
78
74
71
50
59
6
70
67
46
67
61
63
51
58
59
29
41

0.3
0.6
0.2
0.8
0.8
0.5
2.7
5.2
0.7
5.3
1.1
3.2
2.2
1.7
4.7
6.2
8.4
2.0
3.0
3.0
4.5
10.8
2.6
5.9
4.9
4.9
11.6
2.5
4.5
8.6
5.2
3.7
6.2
11.2
4.9
4.4
18.9
3.8
7.9
7.5
4.1
3.3
13.4
10.2
7.0
3.8
7.4
3.5
13.9

March 2012

G

O

PR

IN

AF
T

R

D

G

N

KI

R

132

R
ES
S

Specific SO2
(g/t crude treated)
(2)

41
40
39
4
18
25
24
44
55
3
26
49
6
48
52
42
51
5
33
22
50
15
28
7
9
11
47
27
32
46
14
31
16
13
20
30
45
2
43
10
36
37
12
17
35
34
38
21
29

O
W

Sulphur balance and specific emissions to air for a sample of 49 European sites

Questionnaire (1)

Table 3.8:

PB/EIPPCB/REF_Draft 2


Main contributing processes and units

There are both continuous and non-continuous sources of SO\textsubscript{x} emissions. The number of sources may vary from refinery to refinery. The main emission sources of SO\textsubscript{x} are the process furnaces/boilers, gas turbines, sulphur recovery units, FCC regenerators, flare system, waste water stripping and incondensable off-gas incinerators, decocking operations and coke calcination, and the treating units. CONCAWE [49a, CONCAWE, 1998] The CONCAWE 2006 investigation already referred to in this section gives an average distribution of the SO\textsubscript{x} emissions of some 70 from the 67 refineries studied, as shown in Table 3.9. Mainly as a result of the use of liquid refinery fuels in boilers and furnaces, 59.4% of refinery SO\textsubscript{x} emissions stem from combustion processes. FCC units account for 13.5%, sulphur recovery units for 10.7% and other miscellaneous sources for 11.4%. Next table shows the ranges found for these refineries.

Note for TWG: the original Table 3.5 is now replaced by the following one.

Table 3.9: SO\textsubscript{2} breakdown by main contributing units as an average from a sample of 67 European refineries

<table>
<thead>
<tr>
<th>SO\textsubscript{2} emitted by:</th>
<th>Percentage of the sulphur refinery intake</th>
<th>Approximate percentage of refinery SO\textsubscript{2} emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel fired in furnaces/boilers</td>
<td>1.8%</td>
<td>48%</td>
</tr>
<tr>
<td>FCC units</td>
<td>0.4%</td>
<td>11%</td>
</tr>
<tr>
<td>Sulphur recovery units</td>
<td>0.6%</td>
<td>16%</td>
</tr>
<tr>
<td>Flares</td>
<td>0.7%</td>
<td>20%</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>0.2%</td>
<td>5%</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>3.7%</strong></td>
<td><strong>100%</strong></td>
</tr>
</tbody>
</table>

The same report mentioned above shows that, in 1995 the average SO\textsubscript{2} concentration in European refineries amounted to 1350 mg/Nm\textsuperscript{3}; concentrations ranged from 226 – 2064 mg/Nm\textsuperscript{3} flue gas. Some data on average bubble calculations have been included in Section 3.15. The range of annual emissions is from 49 to 10000 tonnes per year and specific emissions range from 30 – 6000 tonnes of SO\textsubscript{2} per million of tonne of crude processed. That report also shows that, despite similar sulphur levels in the crude oil, major differences exist between average refinery SO\textsubscript{x} emissions. In order to complement this information the next three figures relating SO\textsubscript{x} emissions from EU1 refineries are plot. Next figure gives the plot of the SO\textsubscript{x} emissions...
from some European refineries as a function of the crude capacity. Figure shows that bigger refineries tend to emit more $\text{SO}_2$.

Note for TWG: Original Figure 3.4 ‘$\text{SO}_2$ emissions from some European refineries as function of the crude capacity’ Source: [268, TWG, 2001] deleted and replaced

However, if the emissions of $\text{SO}_2$ are divided by the capacity of the refinery, the figure does not show that specific emissions of $\text{SO}_2$ depends on the crude capacity. The following figure shows the results for the same refineries of the picture above.

Note for TWG: Original Figure 3.5 Specific $\text{SO}_2$ emissions from some European refineries as function of the crude capacity - Source: [268, TWG, 2001] deleted and replaced

No correlation is also found when the specific $\text{SO}_2$ emissions are plotted against Nelson complexity index. As it can be seen, the figure does not show that specific emissions of $\text{SO}_2$ depend on the refinery complexity.

Note for TWG: Original Figure 3.6 Specific $\text{SO}_2$ emissions from some European refineries against the Nelson complexity index - Source: [268, TWG, 2001] deleted and replaced

For further details, site-level individual data collected through TWG questionnaires have been summarised in Table 3.10 for 57 European sites. The first part of the table corresponds to the group of sites which do not operate an FCC unit, while FCC sites are gathered in the second part of this table (next page). These data show the distribution of $\text{SO}_2$ emissions according to main contributing units or processes.

Table 3.10: $\text{SO}_2$ emissions and main contributing units for a sample of 57 European sites

<table>
<thead>
<tr>
<th>Site label</th>
<th>Nelson Index</th>
<th>FCC (yes=1)</th>
<th>Year</th>
<th>Total $\text{SO}_2$ (t/yr)</th>
<th>$\text{S}$ emitted/$\text{S}$ input (%)</th>
<th>Furnaces + boilers</th>
<th>CHPs + standalone gas turbines</th>
<th>FCC</th>
<th>SRU</th>
<th>Flares</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\text{t/yr}$</td>
<td>$%$</td>
<td>$\text{t/yr}$</td>
<td>$%$</td>
<td>$\text{t/yr}$</td>
<td>$%$</td>
<td>$\text{t/yr}$</td>
<td>$%$</td>
</tr>
<tr>
<td>41</td>
<td>6.5</td>
<td>2008</td>
<td>49</td>
<td>0.3%</td>
<td>5</td>
<td>10%</td>
<td></td>
<td></td>
<td></td>
<td>36</td>
<td>73%</td>
</tr>
<tr>
<td>25</td>
<td>9.7</td>
<td>2007</td>
<td>812</td>
<td>0.5%</td>
<td>568</td>
<td>70%</td>
<td></td>
<td></td>
<td></td>
<td>244</td>
<td>30%</td>
</tr>
<tr>
<td>40</td>
<td>6.2</td>
<td>2008</td>
<td>162</td>
<td>0.6%</td>
<td>158</td>
<td>98%</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>2%</td>
</tr>
<tr>
<td>55</td>
<td>5.1</td>
<td>2008</td>
<td>250</td>
<td>0.7%</td>
<td>111</td>
<td>44%</td>
<td></td>
<td></td>
<td></td>
<td>142</td>
<td>57%</td>
</tr>
<tr>
<td>4</td>
<td>3.1</td>
<td>2008</td>
<td>386</td>
<td>0.8%</td>
<td>76</td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>26</td>
<td>10.8</td>
<td>2008</td>
<td>101</td>
<td>1.1%</td>
<td>2639</td>
<td>85%</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>0.2%</td>
</tr>
<tr>
<td>48</td>
<td>8.4</td>
<td>2007</td>
<td>3000</td>
<td>1.7%</td>
<td>NA</td>
<td>NA</td>
<td></td>
<td></td>
<td></td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>56</td>
<td>12.4</td>
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## Chapter 3

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**Table Notes:**
- FCC emissions have been initially included in furnace and boilers emissions.
- ( - ) Not applicable
- NB: NA These data have not been made available to TWG.
- Source: TWG data collection questionnaires.

**Comments:**
- FCC emissions have been initially included in furnace and boilers emissions.
- ( - ) Not applicable
- NB: NA These data have not been made available to TWG.
- Source: TWG data collection questionnaires.
As shown in Figure 3.12 and Figure 3.13, no obvious correlation can be graphically observed, neither for the first group of sites (non-FCC operated) nor for the second one (including FCC), between the sulphur emitted/input ratio calculated for these refineries and the respective weight of their different main contributing units or processes. In both cases, furnaces and boilers appear most often as the main contributors, which confirms the trend shown in Table 3.9. It is even truer if emissions from all the entire energy system, including eventual CHPs and standalone, gas turbines are considered.

For the selected refineries operating an FCC, this unit generates a rather stable past proportion, most often within 15 – 30 %, of the SO$_2$ site emissions. It should also be noted the important role played, by sources involved in the ‘Other’ category, when they exist. Even if their average weight reported to the overall European refining emissions is low (around 5 %, as shown in Table 3.9), they most often represent a major part of the individual site-level SO$_2$ emissions for the refineries concerned. These emissions come in particular from:

- the incineration of waste water stripping and/or process incondensable off-gases, when they are eventually still not recycled into the RFG treating system;
- the eventual coke plants, and especially the green coke calcination;
- the contribution of flares, which can be very significant, notably for refineries experiencing abnormal operating conditions like technical difficulties or major start-up/shutdown episodes.

Influence of crude sulphur content and the site refining overall configuration

An overview of the historic development of the distribution of sulphur output in European refineries is given in Table 3.11. It also presents the average sulphur recovery percentage in the western European refineries that has grown from about 10 % in the late 70s to more than 36 - 45 % now. This table shows that the reductions of sulphur content achieved in the oil products destined to combustion (so called S in fuels) sold to customers. It can be noted that these reductions were achieved while are not mirrored in direct sulphur emissions from the refineries, which have remained static and have recently shown a significant decrease since 1995.

![Figure 3.12](image_url)  
Figure 3.12: Respective weight of main SO$_2$ contributing processes for 12 European refineries not operating a FCC unit as a function of their sulphur emitted/input ratio
Figure 3.13: Respective weight of main SO₂ contributing processes for 24 European refineries operating an FCC as a function of their sulphur emitted/input ratio

Table 3.11: Trends of sulphur distribution in western European refineries (data in kt/yr)

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(1). For all OECD Europe
(2). From the CONCAWE refinery site sample covered by the annual survey
Source: [49a, CONCAWE, 1998] [ 63, CONCAWE 2010]

Figure 3.14 shows, for 51 European refineries, the interaction between various parameters related to the crude quality (% of sulphur), the site complexity (measured with the Nelson Index), and the specific emissions reported to the amount of feedstock treated (SO₂ g/t) and to the sulphur total intake (% of sulphur emitted/input ratio). Available data is displayed for two site groups according to the presence of an FCC unit (34 sites) or not (17 sites).

Figure 3.14: Influence of the configuration, complexity and crude quality on SO₂ emissions
Several comments points can be derived from this graphic.

- The highest SO$_2$ specific emissions are not necessarily associated with the most complex sites.

- As it was mentioned in the beginning of this section, FCC units contribute between 7 to 14 to around 11 % of the SO$_2$ European refining emissions, and represent on average 20 % (up to 66 %) of the individual emissions of the sites concerned. Within a refinery, then possibly. However, as shown on Figure 3.14, refineries with FCC may not tend to emit more SO$_2$ than refineries without FCC. However, red points in the above graph do not show that refineries with FCC tend to emit more SO$_2$.

- Another important variable that is typically referred to for explaining the behaviour of SO$_2$ emissions in refineries is the content of sulphur in the crude oil processed. However, once again, Figures data displayed in the above figure Figure 3.14 show that, within this site sample, refineries with similar sulphur content in the treated crude oil that they process (e.g. 0.8 %) can have very high differences in specific emissions, and many sites achieving very high specific emissions are actually these treating the most favourable crudes. Moreover, it is shown in the figure that no correlation is demonstrated with this figure. This also reinforces the conclusion of the Concawe report that shows that, despite similar sulphur levels in the crude oil, major differences exist between average refinery SO$_2$ emissions.

Table 3.12 shows that since 1985 the sulphur recovered in refineries has increased, which reflects the steady increase in sulphur recovery capacity of European refineries. This is also demonstrated in the decrease in the sulphur content of the oil products leaving the refineries. However, Table 3.12 also shows that since 1985 direct SO$_2$ emissions from European refineries have been stable. It demonstrates that on average the reductions in SO$_2$ emissions have clearly lagged behind the sulphur reductions achieved in the oil products sold to the customers of the refineries.

<table>
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<th></th>
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<th></th>
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<td>S in fuel oil</td>
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<td>75.7</td>
<td>69.1</td>
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<td>59.0</td>
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<td>11.9</td>
<td>13.2</td>
<td>13.5</td>
<td>14.6</td>
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<tr>
<td>S fixed in special products</td>
<td>10</td>
<td>11.9</td>
<td>39.0</td>
<td>26.9</td>
<td>27.1</td>
<td>36.3</td>
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<tr>
<td>S recovered</td>
<td>40</td>
<td>44.7</td>
<td>49.0</td>
<td>26.9</td>
<td>27.1</td>
<td>36.3</td>
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<td>30.9</td>
<td>40.1</td>
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<td>100.0</td>
<td>100.0</td>
<td>99.6</td>
<td>99.6</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Notes: (w/w of total)
1): Figures for the year 1979 from the first CONCAWE report (1979) are not accurate
2): Chemical feedstock (naphtha), bitumen, coke, lube oil
Total sulphur intake in 1995 was 6.56 Mt.

Table 3.12: Historical trend sulphur output distribution European refining industry Source: [115, CONCAWE, 1999]

Table 3.12 depicts the development of the sulphur balance in European refineries from 1979 to 1995. It shows that in 1995 36.3 % of the 6.56 million tonnes of sulphur intake is recovered as elementary sulphur and 8.6 % is emitted as SO$_2$ by the refinery. About 50 % w/w is emitted as SO$_2$ via the combustion of the oil products, while 14.6 % w/w is accumulated in non-fuel products, such as bitumen, lube oils, coke and chemical feed stocks. These last compounds may
be burnt to some extent or can finish their life as solid or liquid waste and consequently might contribute to emissions to the air, water and soil. The historic trend is clearly one of a steady decrease in the sulphur levels in oil products and an equally steady increase in the sulphur recovered in the refinery. The decrease of sulphur levels in oil products is partly the result of tighter European and national legislation, especially with respect to middle distillates. A major part of the decrease is the result of changes in the demand for fuel oil.

**Influence of the refinery fuel mix**

Another parameter which could be expected to strongly influence the refinery SO$_2$ emissions would be the part taken by the ratio of gaseous fuels (including the eventual supply of external natural gas) and residual liquid fuels in the site energy supply.. As shown in Figure 3.15, there is a quite clear correlation within this site sample between the SO$_2$ specific emissions and the weight of residual fuel oils in the site fuel mix, even if some sites burning with very high liquid fuel ratios can achieve very good SO$_2$ performance.

![Figure 3.15: Influence of the gaseous fuels used for energy supply on the site SO$_2$ emissions](image)

Note to TWG: figure has been updated
Chapter 3

3.1.2.5 Volatile organic compounds emissions

Volatile organic compounds (VOC) is the generic term applied to all compounds containing organic carbon, which evaporate at ambient temperature and contribute to the formation of odour nuisance, ‘summer smog’ and, with sufficient sunshine, tropospheric ozone and odour nuisance. VOC losses can be calculated following through various methods based on emission factors or directly measured (discrepancies in the emission numbers from both methods are found in many cases. Extensive information on this issue can be found in Section 3.28.1.4 related specifically to VOC monitoring.

The main sources of VOCs from refineries are vents, flares, air blowing, blowdown systems, fugitive emissions from piping systems, waste water systems, fixed roof storage tanks (tank breathing), loading and unloading systems, other storage, handling and blowdown systems. Diffuse (Fugitive VOC emission sources such as (single) seals from pumps, compressors, valves and flanges and leaks in pipelines and equipment may contribute significantly 20 – 50 % to the total VOC emissions. The range of emissions found in Most of the European refineries (from 5th to 95th percentiles based on the 53 sites gathered by the TWG) (including storage farms) is from 600 to 10000 150 to 6500 tonnes of VOC emitted per year; the related specific emission range is from 50 to 1000 50 to 6000 tonnes of VOC per million tonnes of crude oil total feed processed. Almost all of these results have been achieved using emission factor estimates. However, this range is lower than but consistent with the order of magnitude given by around 30 overall site measurements already realised with airborne optical methods (e.g. DIAL, SOF) at 0.05 – 0.07 % of the concerned site throughputs. All available data are displayed in Table 3.13. For more details on the item of diffuse VOC monitoring see Section 3.28.1.4.

Figure 3.16 has been constructed from the 39 refineries in this sample for which the full distribution of VOC (Total VOC or NM-VOCs) per contributing processes has been made available.

<table>
<thead>
<tr>
<th>Site label</th>
<th>Nelson index</th>
<th>Total VOCs</th>
<th>NM- VOCs</th>
<th>Diffuse VOCs</th>
<th>Benzene</th>
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<td>392 50</td>
<td>134 13</td>
<td>1430 0.2</td>
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<tr>
<td>50th perc.</td>
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<td>1291 194</td>
<td>1292 193</td>
<td>15413 2.6</td>
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</tr>
<tr>
<td>95th perc.</td>
<td>6421 1095</td>
<td>5029 590</td>
<td>4353 570</td>
<td>54129 8.0</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.16: VOC specific emission range and breakdown for 39 European refineries
As it appears in Figure 3.16, the highest specific VOC emissions at the site level are mainly driven by fugitive emissions (leakages from units and pipes) and storage emissions. For the lowest ones, the waste water treatment takes a more significant part. It could reflect the actual stage in the technical progression which might be usually followed by refineries in dealing with the VOC emissions: at first the priority is given to storage and fugitive emissions, then the other types of emissions are treated.

Some accidental spillages can be of a continuous nature, such as leaking pump seals, leaking valve glands and leaks from pipework. Others which are of a one-off nature, can occur from sources such as equipment failures, overfilling of tanks and overfilling of road and rail cars. As shown in Figure 3.16, from the TWG 2008 data collection, the fugitive emissions from process equipment are one of the largest single sources of VOCs emitted to the atmosphere in a refinery and can account for 50% of the total emissions. Fugitive emissions include the emissions that occur from items such as valves, pump and compressor seals, flanges, vents and open ends. Valves are considered to account for approximately 50 - 60% of fugitive emissions. Furthermore, a major portion of fugitive emissions comes from only a small fraction of the sources (e.g. less than 1% of valves in gas/vapour service can account for over 70% of the fugitive emissions of a refinery). Some valves are more likely to leak than others, e.g.:

- valves that are operated frequently, such as control valves, may wear down more quickly and allow emission paths to develop. However, newer, low-leak control valves provide good fugitive emissions control performance.
- valves with rising stems (gate valves, globe valves) are likely to leak more frequently than quarter-turn type valves such as ball and plug valves.

Factors driving these releases of hydrocarbons are equipment design, quality of the sealing system, maintenance programme and properties of the line contents. Poor designs (with wider tolerances), poor sealing systems (e.g. leak-prone valve packings) and limited maintenance will lead to higher emissions. These emissions can be estimated using the factors in Table 3.14.

For example emission factors can be estimated, using the USAEPA stratified method as presented in Table 3.15 taking into account they are derived from short term measurements, that a pump for light liquid that has an emission measured in the range of 1001 - 10,000 ppm, has an emission factor of 33.5 g/h. Other methods have been applied to calculate the fugitive emissions from refineries. They are the adsorption method and DIAL method (see Section 3.28). Emission factors measured with the latest method are presented in Table 3.15.

Table 3.14: Emission factors according to stratified USAEPA-method for the assessment of fugitive emissions

<table>
<thead>
<tr>
<th>Emission source</th>
<th>Emission factor in (g/(h.source)) for measured values in ppm v/v in the following three ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission range (ppm v/v)</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>Valves for gas or vapour</td>
<td>0.14</td>
</tr>
<tr>
<td>Valves for liquids with Vp&gt;0.3 kPa (light liquid)</td>
<td>0.28</td>
</tr>
<tr>
<td>Valves for liquids with Vp&lt;0.3 kPa (heavy liquid)</td>
<td>0.23</td>
</tr>
<tr>
<td>Pumps for light liquids</td>
<td>1.98</td>
</tr>
<tr>
<td>Pumps for heavy liquids</td>
<td>3.80</td>
</tr>
<tr>
<td>Compressors</td>
<td>11.32</td>
</tr>
<tr>
<td>Safety valves for gases</td>
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</tr>
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<td>Flanges</td>
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</tr>
<tr>
<td>Open-end valves</td>
<td>0.13</td>
</tr>
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</table>

Source: [107, Janson, 1999] [77, REF TWG 2010]
Table 3.15  Examples of VOC emissions from two refineries with a capacity of 10Mt/yr

<table>
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<th>VOC emissions (t/yr) Ref 2 - capacity of 9.6 Mt/yr</th>
</tr>
</thead>
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<td>(NA)</td>
</tr>
<tr>
<td>Waste water treatment plant</td>
<td>400</td>
<td>(NA)</td>
</tr>
<tr>
<td>Product harbour</td>
<td>815</td>
<td>(NA)</td>
</tr>
<tr>
<td>Process area</td>
<td>1000</td>
<td>(NA)</td>
</tr>
<tr>
<td>Tank area</td>
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<td>320</td>
</tr>
<tr>
<td>TOTAL</td>
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<td>508</td>
</tr>
</tbody>
</table>

3.1.2.6  Other air emissions

Other pollutants considered are carbon monoxide (process furnaces/boilers, gas turbines, catalytic cracker regenerators, flare system, incinerators, cold vents), methane (storage and handling (loading), cold vents and leaks) and halon from firefighting equipment. Noise, H$_2$S, NH$_3$, CS$_2$, dioxins and HF also contribute to the air emissions from a refinery.

Mercury and components of arsenic are volatile and are emitted to some extent with the clean gas. A part of these compounds react with plant material or deposit on the catalysts in the reactors of the conversion plants. Therefore protective layers are used for the interception of the catalyst poisons.

Flares, compressors, pumps, turbines and air coolers require particular attention as regards sources of noise.

Finally, odours in a refinery are mainly created by sulphur compounds as H$_2$S, mercaptanes but also by some hydrocarbons (e.g. aromatics). The main sources of odour in refineries are storage (e.g. sour crudes), bitumen production, desalter water, sewers, dissolved air flotation and biotreatment and flaring.

Table 3.16 gathers a set of data illustrating the performance of European refineries, made available from the 61 site-level questionnaires provided by the TWG in charge of the revision of the present document.
Table 3.16: Specific air emission ranges for various substances from European refineries

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific load (g/t of feed)</th>
<th>No of values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5th – 95th percentile</td>
<td>50th percentile</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>10 – 415</td>
<td>53</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1 – 22</td>
<td>1.1</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>0.15 – 1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Hydrofluoric acid (1)</td>
<td>0.01 – 1.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.18 – 8</td>
<td>2.5</td>
</tr>
<tr>
<td>BTEX</td>
<td>1 – 70</td>
<td>17</td>
</tr>
<tr>
<td>PAH-16</td>
<td>0.001 – 0.4</td>
<td>0.005</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.001 – 0.014</td>
<td>0.002</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.001 – 0.034</td>
<td>0.002</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.001 – 0.18</td>
<td>0.007</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.001 – 0.07</td>
<td>0.009</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.0001 – 0.038</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn (1)</td>
<td>0.002 – 0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>Ni</td>
<td>0.002 – 1.3</td>
<td>0.16</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001 – 0.1</td>
<td>0.009</td>
</tr>
<tr>
<td>Se (2)</td>
<td>0.002 – 0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>V</td>
<td>0.001 – 1.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.001 – 0.62</td>
<td>0.04</td>
</tr>
<tr>
<td>Heavy metals (2)</td>
<td>0.01 – 3.4</td>
<td>0.38</td>
</tr>
</tbody>
</table>

(1) For these parameters, only min, max and average are provided given the limited number of available values
(2) Sum of individual percentile data for the following metals: Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, Zn.

3.1.2.7 Expression of full or partial site air emissions using ‘bubbles’

Note to TWG: According to the conclusions of subgroup meeting (23-24 May 2011) the relevant parts of the ‘bubble approach’ description have been moved to Chapter 4 (Section 4.15.9.3), and a proposal for an harmonized methodology is provided in Annex 9.9.

The ‘bubble’ approach for the evaluation and monitoring of refinery air emissions

The ‘bubble’ approach is a generic tool for expressing and comparing the level of performance achieved or expected at refinery site level, from a clearly identified set of combustion and process units, and for a given substance or parameter. As represented in Figure 3.17, this approach consists of considering all concerned emissions together, as emitted through a single virtual single stack.

![Image of a bubble representing a single virtual chimney stack](image)

Figure 3.17: The single ‘virtual chimney stack’ of a bubble approach

This approach is considered as especially suitable to oil refining, where some flexibility is needed for expressing or evaluating the environmental performance at site level. This flexibility is notably justified by the following factors:
Chapter 3

- the recognised complexity of refining sites, with multiplicity of combustion and process units, often interlinked for their feedstock and energy supply

- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received

- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements

- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls have been duly justified as not being possible and have to be compensated elsewhere.

Moreover, as shown on various graphics presented in this BREF document (see in particular Figure 3.10 and Figure 3.20 in this Section) best performing sites do not seem to be necessarily only those where main contributing units are operated at the best individual level of performance or equipped with the most complete combination of reducing techniques, but also those where the overall performance is best optimised. In such context, the bubble tool is a good support for promoting and monitoring an actual site level performance optimisation.

A methodology for the bubble calculation is provided in Annex XX. If needed, full or partial site level AELs can be calculated using this methodology, by introducing in the calculation individual BAT AELs that are already provided in this BREF.

**Bubble perimeter**

The exact bubble perimeter to be considered for a given site will depend on the purpose the bubble tool is used for. In the purpose of this BREF, the generic methodology provided in Annex XX is designed to cover, as necessary, all sources of permanent emissions of a refinery (i.e. combustion plants, cat crackers, sulphur recovery units, coke calciners and other processes where appropriate).

**Bubble substances or parameters**

As far as refinery air emissions are concerned, some Countries have considered it could be helpful to cover simultaneously all usual main parameters (CO, PM, NO\textsubscript{X}, SO\textsubscript{2} and eventually VOC) in a bubble approach, with the aim to address site energy consumption and air emissions in a more consistent way, and to introduce the same site-level flexibility for all these parameters which are very often interdependent.

However, in the context of the work undertaken in 2009–2010 for the revision of this BREF document, SO\textsubscript{2} and NO\textsubscript{X} have been recognised as the two parameters which deserve in priority a BREF common methodology for a site level bubble expressed AEL calculation, and for which enough supporting information and data have been provided.

**Bubble averaging period**

The averaging period to be considered will depend on the purpose the bubble tool is used for. In the particular context of this document, the methodology proposed has been based primarily on a yearly average, since a long term period has been considered as the most appropriate for reflecting best performances achievable in normal operating conditions, and giving enough time and flexibility in order to integrate necessary feedstock, process and fuel adjustments. However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter term bubble can be easily derived from the long term bubble using monitoring results. For a given site, or set of contributing units on a given site, it is possible to develop a sound shorter term bubble calculation on the basis of a complete set of short term average values (e.g. the 365 daily averages of a current 1 year long period). Highest values should be eliminated as necessary in order to ensure that normal operating conditions are still reflected. Then a short term (e.g daily) bubble expressed level of performance can be derived from the monitoring report by selecting the appropriate deviation expected above and below the strict yearly average basis (e.g. the t/yr strictly divided by 365).
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Bubble development and calculation

The site-level bubble is a sum of two terms:

- a first term related to the energy system, including at least all furnaces, standalone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable AEL concentration ranges expected on each category of installations.

- a second term related to the process units (including at least FCC UNIT if any, and SRU). This term should be driven by suitable AEL concentration or specific emission ranges expected on each of them when BAT is applied.

In the context of this BREF and for the purpose of expressing meaningful AELs at site or partial site level, the bubble determination should always be based on concentration and specific emission ranges expected at all concerned installations when BAT is applied, and should involve the following steps (regardless of their order):

1. exhaustive identification and geographical mapping of all included sources;
2. determination of the off-gas volumetric contributions expected from all included sources;
3. determination of the mass contributions expected from all included sources;
4. determination of the bubble-associated monitoring regime.

The actual details of the calculation and additional information on each of these steps are given in Annex 9.9. More details on this approach are available in section 4.15.9.3.

The total emissions of one substance released by all the stacks on site can therefore be expressed as a single value using this approach based on available data provided through TWG data collection.

Actual NO\textsubscript{x} emissions from European refineries: bubble-expressed examples

Site individual sets of NO\textsubscript{x} data collected by the TWG for each site have been gathered in Table 3.17. These data have been processed in order to calculate the annual average equivalent concentration of NO\textsubscript{x} in the sum of flue-gases emitted by the four categories of contributing units as listed below. These calculations are based on actual emissions reported for the year 2007 or 2008. Two examples of bubble-expressed emission levels, which correspond respectively to Figure 3.18 and Figure 3.19, are presented for the set of sites concerned.

In the first case displayed as shown in Figure 3.18, which corresponds to column (e) in Table 3.17, the full selection list of contributors has been used, which includes:

- furnaces and boilers
- CHPs and gas turbines
- FCC units
- sulphur recovery units.

Mass and volumetric contribution terms from each of these four categories were fully available for a sample of 24 sites, among which seven were non-FCC sites and 17 were FCC sites; Figure 3.18 shows the range of equivalent concentrations obtained. The contributing unit for which less data was available, in particular as far as volumetric contributions are concerned, is SRU and is mainly responsible for the limited size of this refinery set.
In the second case, illustrated by Figure 3.19, the small NO\textsubscript{x} contribution of sulphur recovery units have not been taken into account, and the selection of contributors only include:

- Furnaces and boilers,
- CHPs and gas turbines,
- FCC units.

Mass and volumetric contribution terms from each of these three categories were fully available for a total of 30 sites, among which 10 were non-FCC sites and 20 were FCC sites. The results obtained for the whole group of refineries are very close to the results obtained in the first case.

In both cases, as shown in Figure 3.18 and Figure 3.19, an information summary is provided for each refinery on the part taken by the refinery fuel gas and an eventual additional natural gas supply in the refinery energy mix, together with the main NO\textsubscript{x} abatement techniques implemented on the FCC unit and the energy system.
Table 3.17: Equivalent concentrations of NOx emissions for a sample of European refineries

<table>
<thead>
<tr>
<th>Questionnaire</th>
<th>Configuration with FCC</th>
<th>Specific NO, emission</th>
<th>Furnace + boilers</th>
<th>CHP + gas turbines</th>
<th>FCC</th>
<th>SRU</th>
<th>Bubble CP (a)</th>
<th>Bubble CP+CHP (b)</th>
<th>Bubble CP+SRU (c)</th>
<th>Bubble FCC (d)</th>
<th>Full bubble (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>1</td>
<td>68</td>
<td>620</td>
<td>6.03</td>
<td>0.00</td>
<td>48</td>
<td>0.73</td>
<td>0.19</td>
<td>103</td>
<td>103</td>
<td>100</td>
</tr>
<tr>
<td>1(f)</td>
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<td>92</td>
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<td>88</td>
<td>0.76</td>
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<td>NA</td>
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<td>1</td>
<td>93</td>
<td>365</td>
<td>5.60</td>
<td>0.60</td>
<td>300</td>
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<td>136</td>
<td>171</td>
<td>172</td>
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<td>138</td>
<td>959</td>
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<td>154</td>
<td>155</td>
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<td>NA</td>
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<td>324</td>
<td>1.70</td>
<td>0.03</td>
<td>246</td>
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<td>381</td>
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<td>1</td>
<td>249</td>
<td>1056</td>
<td>4.74</td>
<td>0.56</td>
<td>178</td>
<td>1.13</td>
<td>21</td>
<td>223</td>
<td>255</td>
<td>256</td>
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<td>1</td>
<td>254</td>
<td>783</td>
<td>3.13</td>
<td>1.10</td>
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<td>0.74</td>
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<td>742</td>
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<td>177</td>
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<td>22</td>
<td>0.05</td>
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</tr>
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<td>318</td>
<td>1589</td>
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<td>607</td>
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<td>766</td>
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<td>248</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>339</td>
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<td>561</td>
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<td>320</td>
<td>320</td>
<td>317</td>
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<td>3339</td>
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<td>2.51</td>
<td>0.10</td>
<td>464</td>
<td>533</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>394</td>
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<td>2.62</td>
<td>252</td>
<td>1.40</td>
<td>0</td>
<td>NA</td>
<td>158</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>406</td>
<td>1419</td>
<td>3.39</td>
<td>0.00</td>
<td>618</td>
<td>1.24</td>
<td>0.08</td>
<td>408</td>
<td>418</td>
<td>408</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>431</td>
<td>968</td>
<td>5.45</td>
<td>11.58</td>
<td>626</td>
<td>0.85</td>
<td>30</td>
<td>0.34</td>
<td>372</td>
<td>321</td>
</tr>
<tr>
<td>45</td>
<td>1</td>
<td>453</td>
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<td>3.68</td>
<td>0.00</td>
<td>1125</td>
<td>1.90</td>
<td>10</td>
<td>0.05</td>
<td>364</td>
<td>463</td>
</tr>
<tr>
<td>37</td>
<td>1</td>
<td>575</td>
<td>1728</td>
<td>4.85</td>
<td>1792</td>
<td>1.79</td>
<td>381</td>
<td>1.25</td>
<td>1.2</td>
<td>0.08</td>
<td>356</td>
</tr>
</tbody>
</table>

No of values 32 32 32 32 31 22 22 25 26 31 30 25 21 25

Average 263 1191 5 559 1.84 434 1.38 12 0 281 306 307 331 305

Minimal 59 221 0.88 0.00 48 0.38 0.00 0.00 87 94 94 66 94

5th percentile 69 302 1.65 0.00 127 0.70 0.00 0.02 99 110 103 110 101

50th perc. 252 964 4.49 0.63 357 1.25 0.10 0.09 250 256 256 290 247

95th perc. 474 2907 9.09 2.52 1125 2.51 0.37 0.30 602 622 574 618 618

Maximal 575 3608 11.91 11.58 1396 3.95 0.65 0.65 529 757 656 735 656

(a) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers
(b) Equivalent concentration calculated for off-gases emitted by all furnaces, boilers, and CHP and standalone gas turbines if any
(c) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers, CHP and standalone gas turbines if any, and SRUs
(d) Equivalent concentration corresponding to the FCC alone
(e) Equivalent concentration corresponding to the sum of (c) and off-gases emitted by the FCC UNITS if any
(f) NB: Site 1 data made available for 2009 emissions tail gas of SRU treated in SNOx of CHP plant

NB: NA This data has not been made available to the TWG
**Figure 3.18:** Equivalent concentration of the NO\(_X\) emissions from the whole energy system, FCC and SRU units of 24 European refineries

**NO\(_X\) : Emissions from furnaces and boilers + CHP + SRU**

**Figure 3.19:** Equivalent concentration of the NO\(_X\) emissions from the whole energy system and the FCC unit of 30 European refineries

**Actual SO\(_2\) emissions from European refineries: a bubble-expressed example**

Similar to what has been presented above for the NO\(_X\) emissions, individual site sets of SO\(_2\) data collected by the TWG have been gathered in Table 3.18. These data have been processed in order to calculate the annual average equivalent concentration of SO\(_2\) in the sum of the flue-
gases emitted by the four categories of contributing units as listed below. These calculations are based on actual emissions reported for the year 2007 or 2008.

An example of bubble-expressed emission levels is displayed in Figure 3.20, which corresponds to Column (e) in Table 3.18. The full selection of contributors has been used, which includes:

- Furnaces and boilers
- CHPs and gas turbines
- FCC units
- Sulphur recovery units.

Massic and volumetric contribution terms from each of these four categories were fully available for a sample of 29 sites, among which 10 were non-FCC sites and 19 were FCC sites, and Figure 3.20 shows the range of equivalent concentrations obtained. The contributing unit category for which the data was available, in particular as far as volumetric contributions were concerned, was once again SRUs, mainly responsible for the limitation of this refinery data set.

As shown in Figure 3.20, an information summary is provided for each refinery on the part taken by the refinery fuel gas and an eventual additional natural gas supply in the refinery energy mix, together with the main NOx abatement techniques implemented on the FCC unit and the energy system.

**Figure 3.20:** Equivalent concentration of the SO2 emissions from the whole energy system and the FCC and SRU unit of 30 European refineries
<table>
<thead>
<tr>
<th>Questionnaire</th>
<th>Configuration with FCC?</th>
<th>Furnaces+boilers</th>
<th>CHP-gas turbines</th>
<th>FCC</th>
<th>SRU</th>
<th>Bubble CP (a)</th>
<th>Bubble CP+CHP+SRU (b)</th>
<th>Bubble CP+CHP+SRU+FCC if any (c)</th>
<th>Bubble CP+CHP+SRU enriched (d)</th>
<th>Bubble CP+CHP+FC enriched (e)</th>
<th>No of values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>0</td>
<td>50</td>
<td>2.09</td>
<td>0.00</td>
<td>0.00</td>
<td>575</td>
<td>24</td>
<td>24</td>
<td>296</td>
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<td>35</td>
</tr>
<tr>
<td>No</td>
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<td>23</td>
<td>3.03</td>
<td>454</td>
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<td>62</td>
<td>0.76</td>
<td>NA</td>
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</tr>
<tr>
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<td>2</td>
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<td>5.61</td>
<td>970</td>
<td>1.13</td>
<td>1535</td>
<td>0.06</td>
<td>24</td>
<td>35</td>
</tr>
<tr>
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<td>3</td>
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<td>18044</td>
<td>11.58</td>
<td>640</td>
<td>0.85</td>
<td>1498</td>
<td>0.34</td>
<td>47</td>
<td>32</td>
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<td>4</td>
<td>304</td>
<td>6.20</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.84</td>
<td>941</td>
<td>0.11</td>
<td>49</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1400</td>
<td>5.60</td>
<td>0.60</td>
<td>3200</td>
<td>2.00</td>
<td>0.08</td>
<td>250</td>
<td>226</td>
<td>580</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1110</td>
<td>3.68</td>
<td>5800</td>
<td>3.71</td>
<td>3600</td>
<td>3.95</td>
<td>760</td>
<td>0.05</td>
<td>302</td>
<td>24</td>
</tr>
<tr>
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<td>241</td>
<td>2.62</td>
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<td>2018</td>
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<td>421</td>
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<td>5710</td>
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<td>0.94</td>
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<td>936</td>
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<td>4706</td>
<td>4.85</td>
<td>0.00</td>
<td>1.79</td>
<td>303</td>
<td>1.25</td>
<td>3430</td>
<td>0.08</td>
<td>970</td>
<td>35</td>
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<td>19</td>
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<td>0.00</td>
<td>0.00</td>
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<td>0.05</td>
<td>1174</td>
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<td>20</td>
<td>9218</td>
<td>7.20</td>
<td>194</td>
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<td>3779</td>
<td>2.51</td>
<td>4632</td>
<td>0.10</td>
<td>1280</td>
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<td></td>
<td>21</td>
<td>6193</td>
<td>3.13</td>
<td>3</td>
<td>1.15</td>
<td>708</td>
<td>0.71</td>
<td>340</td>
<td>NA</td>
<td>1340</td>
<td>34</td>
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<td></td>
<td>22</td>
<td>1328</td>
<td>0.75</td>
<td>0.00</td>
<td>0.00</td>
<td>543</td>
<td>1.21</td>
<td>583</td>
<td>0.06</td>
<td>1760</td>
<td>34</td>
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</tbody>
</table>

Table 3.18: Equivalent concentrations of SO2 emissions for a sample of European refineries

(a) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers
(b) Equivalent concentration calculated for off-gases emitted by all furnaces, boilers, and CHP and standalone gas turbines if any
(c) Equivalent concentration calculated for off-gases emitted by all furnaces and boilers, CHP and standalone gas turbines if any, and SRUs
(d) Equivalent concentration corresponding to the sum of (c) and off-gases emitted by the FCC UNITs if any
(e) Equivalent concentration calculated as for (c) and (d) but neglecting the volumetric contribution from SRUs
(f) NB: Site 1 data made available for 2009 emissions- tail gas of SRU treated in SNOX of CHP plant - NA data not available to the TWG
(1) These values are calculated only for the FCC-refinery sample.
Chapter 3

However, flue-gases emitted by sulphur recovery units are typically highly concentrated, representing, at the site level, small volumetric contributions which are rarely measured and often estimated with rather significant uncertainty. As an alternative - which corresponds to Column (f) in Table 3.18 - these small volumetric contributions could been neglected. The equivalent concentration would then be calculated with the mass contributions from the four categories of sources above mentioned, but only divided into the volumetric contributions from:

- furnaces and boilers
- CHPs and gas turbines
- and FCC units.

With this option, data necessary for the calculation are available for a wider sample of 32 sites, among which 10 are non-FCC sites and 22 are FCC sites. The site equivalent concentrations obtained for the whole group of refineries are, on average, slightly higher than these obtained in the first case, due to their artificial ‘enrichment’ related to the decrease of the overall flue-gas volume.

3.1.3 Emissions to water

Waste waters consist of cooling water, process water, sanitary sewerage water and storm water. The quantity of waste waters generated and their characteristics depend on the process configuration. This can vary over time and can vary from one refinery site to another, depending on refinery complexities, variability of feed stocks, integration with petrochemical facilities, techniques, etc. Waste waters are generally treated in on-site waste water treatment facilities and then discharged. The water and blowdown streams from refinery operations can become contaminated with dissolved gases, dissolved and suspended solids and hydrocarbons. Water can also become contaminated with dissolved gases in the process, compounds that could be toxic and/or could give to water an unpleasant smell. Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia, hydrogen sulphide and hydrocarbons). Sour water needs stripping prior to further treatment or reuse as wash water. Generated off-gases containing pollutants should be properly routed and treated before release (see 4.26.4).

Depending on the prevailing climate, storm or rainwater can also generate a significant effluent stream in refineries. Rainwater may come into contact with potentially oil-polluted surfaces (‘surface water run-off’). The effect of rainwater on both the amount and the quality of the effluent water and the problems that the water discharges to either fresh continental waters or to the sea are issues to consider. Occasionally, ballast water from crude carriers and from other seagoing vessels or barges transporting oil products is also treated in refineries. Furthermore, sanitary waste water and firefighting water are waste water sources which all need attention and quality control prior to deciding on treatment, direct discharge and/or potential reuse.

Some water emission parameters that should be considered relevant for refining activities are the pH, dissolved solids, total suspended solids (TSS), total organic carbon (TOC), total nitrogen and its various forms (organic R-NH₂, ammonium NH₄+, reduced or Kjeldahl NTK, nitrite NO₂, and nitrate NO₃), total phosphorous, COD, BOD, H₂S, NH₃, oil, aromatics (BTEX), phenols, salt, AOX, mercaptans, cyanides, MTBE and ETBE, fluoride, PAH, heavy metals, temperature, conductivity, bacteria and fish toxicity. Based on data collected (see Section 3.1.1.2), as a general guide, approximately 0.05 – 1 an average of 5 – 6 m³ is used m³ of waste water (process waste water, cooling water and sanitary waste water) per tonne of crude feed. This value is strongly dependent on the type of cooling system in use on site, driving the level of water recycling. Water from processes account for around 0.1 – 1.6 m³/tonne of feed (see Section 3.26).
The resulting discharge of the aforementioned substances depends on the ‘in-process’ preventive measures (good housekeeping, reuse) and the presence and technical standards of waste water treatment facilities. The typical process water pollutants and/or waste water parameters relevant to the overall refining process and prior to any purification steps are as stated in Table 3.19.

Table 3.19: Representative concentrations of pollutants in typical refinery effluents before treatment

<table>
<thead>
<tr>
<th>Source</th>
<th>Oil</th>
<th>H₂S (RSH)</th>
<th>NH₃ (NH₄⁺)</th>
<th>Phenols</th>
<th>BOD COD</th>
<th>TOC</th>
<th>CN⁻ (CNS⁻)</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation Units</td>
<td>XX</td>
<td>XX</td>
<td>XX</td>
<td>X</td>
<td>XX</td>
<td></td>
<td>-</td>
<td>XX</td>
</tr>
<tr>
<td>Hydrotreatment</td>
<td>XX</td>
<td>XX(X)</td>
<td>XX</td>
<td>-</td>
<td>X(X)</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Visbreaker</td>
<td>XX</td>
<td>XX</td>
<td>XX</td>
<td>XX</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Catalytic Cracking</td>
<td>XX</td>
<td>XXX</td>
<td>XX</td>
<td>XX</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>XX</td>
<td>XXX</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lube oil</td>
<td>XX</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>XX</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spent caustic</td>
<td>XX</td>
<td>XX</td>
<td>-</td>
<td>XXX</td>
<td>XXX</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Ballast water</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td></td>
<td>-</td>
<td>X</td>
</tr>
<tr>
<td>Utilities (Rain)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td></td>
<td>-</td>
<td>X</td>
</tr>
<tr>
<td>Sanitary/Domestic</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td></td>
<td>-</td>
<td>XX</td>
</tr>
</tbody>
</table>

Key: X = <50 mg/l, XX = 50 – 500 mg/l, XXX = >500 mg/l

Source: [115, CONCAWE, 1999]

Table 3.20 shows summarises the annual average composition range and annual averages of the water effluents from European refineries. Most data have been gathered in 2009 – 2010 by the Technical Working Group set up for the revision of the present BREF document, and relate to a sample of 44 sites, all equipped with a dedicated WWTP. These data reflect a annual period of continuous emissions between years 2006 – 2008.

The details on the various steps of treatment in operation at the refinery sites are shown in section 4.26

More detailed data on main parameters used for characterising organic and nitrogen compounds are shown in Table 3.21 and Table 3.22. The actual range and distribution shape of annual average concentrations and their eventual correlation with related specific emissions are displayed in following Figure 3.21 to Figure 3.26, respectively for parameters TOC, COD, BOD₅, TSS and Total Nitrogen. These particular figures only concern data relating to refineries where aqueous effluents are treated in a single dedicated waste water treatment plant.

The amount of oil discharged is usually expressed in grams of Total Hydrocarbon Content (THC) per tonne of refinery throughput. According to CONCAWE, nearly 90 % of the European refineries already meet the standard of the Oslo/Paris Commission of 3 grams of THC/tonne of refinery throughput.
Table 3.20: Typical refinery influent/effluent annual average composition and load

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Composition after pretreatment by API, CPI and SWS</th>
<th>Annual effluent composition downstream WWTP</th>
<th>Specific load (g/t feedstock)</th>
<th>No. ((^2))</th>
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</thead>
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<tr>
<td>pH (pH unit)</td>
<td>7</td>
<td>10</td>
<td>6 – 9</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>45</td>
<td>10 – 35</td>
<td></td>
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<tr>
<td>TOC</td>
<td>100</td>
<td>250</td>
<td>4 – 50</td>
<td>14</td>
</tr>
<tr>
<td>COD</td>
<td>300 – 500</td>
<td>1000</td>
<td>19 – 125</td>
<td>66</td>
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<td>BOD5</td>
<td>80 – 150</td>
<td>300</td>
<td>2 – 30</td>
<td>10</td>
</tr>
<tr>
<td>NH3-THC (^1)</td>
<td>40 – 50</td>
<td>100</td>
<td>0.05 – 6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>THC (^1)</td>
<td>NA</td>
<td>NA</td>
<td>0.3 – 5</td>
<td>1.2</td>
</tr>
<tr>
<td>TSS</td>
<td>20 – 60</td>
<td>200</td>
<td>4 – 35</td>
<td>15</td>
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<tr>
<td>AOX (^1)</td>
<td>NA</td>
<td>NA</td>
<td>0 – 6</td>
<td>0.2</td>
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<tr>
<td>Ammonium-N</td>
<td>12 – 15</td>
<td>30</td>
<td>0.3 – 15</td>
<td>2.7</td>
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<tr>
<td>Nitrites-N</td>
<td>NA</td>
<td>NA</td>
<td>0.03 – 1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Nitrates-N</td>
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<td>NA</td>
<td>0.4 – 12</td>
<td>1.7</td>
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<td>Kjeldahl nitrogen</td>
<td>25</td>
<td>50</td>
<td>2 – 20</td>
<td>5.4</td>
</tr>
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<td>Total Nitrogen</td>
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<td>50</td>
<td>3 – 22</td>
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<td>20</td>
<td>0.1 – 1.5</td>
<td>0.3</td>
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<td>25</td>
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<td>0.1</td>
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<td>MTBE (^1)</td>
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<td>0.003 – 0.1</td>
<td>0.02</td>
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<td>60</td>
<td>0.2 – 3</td>
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<td>NA</td>
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<td>0.003</td>
</tr>
<tr>
<td>Ethylbenzene</td>
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<td>NA</td>
<td>&lt;0.001 – 0.005</td>
<td>0.001</td>
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<tr>
<td>Xylenes</td>
<td>NA</td>
<td>NA</td>
<td>&lt;0.001 – 0.2</td>
<td>0.001</td>
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<td>5</td>
<td>10</td>
<td>&lt;0.001 – 1</td>
<td>0.005</td>
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<td>PAH-16 (homolog)</td>
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<td>0.5</td>
<td>&lt;0.0001 – 0.01</td>
<td>0.0007</td>
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<td>&lt;0.001 – 0.02</td>
<td>0.003</td>
</tr>
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<td>NA</td>
<td>NA</td>
<td>0.2 – 0.6</td>
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<td>&lt;0.001 – 0.05</td>
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<td>&lt;0.001 – 0.05</td>
<td>0.003</td>
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<td>NA</td>
<td>&lt;0.001 – 0.02</td>
<td>0.002</td>
</tr>
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<td>&lt;0.001 – 0.003</td>
<td>0.001</td>
</tr>
<tr>
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<td>NA</td>
<td>0.01 – 0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron-Fe</td>
<td>NA</td>
<td>NA</td>
<td>0.15 – 3</td>
<td>0.4</td>
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<td>&lt;0.002 – 0.1</td>
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<td>&lt;0.0001 – 0.01</td>
<td>0.001</td>
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<td>0.003 – 0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Stain-Sh</td>
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<td>NA</td>
<td>&lt;0.001 – 0.02</td>
<td>0.01</td>
</tr>
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<td>Vanadium-V</td>
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<td>NA</td>
<td>0.005 – 0.1</td>
<td>0.02</td>
</tr>
<tr>
<td>Zinc-Zn</td>
<td>NA</td>
<td>NA</td>
<td>0.005 – 0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Heavy metals (^2)</td>
<td>1</td>
<td>2</td>
<td>0.05 – 1.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^1\) dependent on whether or not relevant units are part of the refinery 
\(^2\) Number of available site yearly concentration values provided to the TWG 
\(^3\) Measured according to method EN 9377-1 
\(^4\) Measured according to method EN 9377-2:2000 (GC-FID) 
\(^5\) Sum of individual percentile data for the following metals: Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn; V, Zn. 
\(-^\) Not appropriate 
Source: Questionnaires no 1 – 61

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<tr>
<th>Site label</th>
<th>Total feed refined</th>
<th>Dedicated WWTP</th>
<th>TOC</th>
<th>BODs</th>
<th>COD</th>
<th>TSS</th>
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<td>38</td>
<td>8.183</td>
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<td>5.4</td>
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<td>60</td>
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</tr>
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This table includes data on emissions of main organic pollutants and suspended solids from a sample of 48 European sites, with values normalized for TOC (mg/l), BODs (mg/l), COD (mg/l), and TSS (g/t). The data is specific to sites with a dedicated WWTP and is presented in a tabular format for easy comparison.
Chapter 3

W

R

No 51
Average (3)

kg/yr mg/l

g/t

kg/yr mg/l

g/t

kg/yr

mg/l

Total nitrogen
(as N)

g/t kg/yr (2)

mg/l

0.9

10.70

7.3
12.0

12.52 127639 9.80 4.63 47170 27
1.60
11.00
13.00
71.00
16.80
16.00 1.71 14000
24.00

2.64 31950
1.34 11000

0.34 1655
21
0.34

320

1.40

1.95

1858

3.40

4.56 4343

kg/yr

6.51 80721
17.15 174808

11.71
4.67
2.58
54.93
21.02
17.62
1.23
1.84
4.50 18.67
4.90 6.84
3.57 4.58

122856
56400
21100
378998
92483
201442
6030
5100
61017
6521
26248

O

0.20

g/t

G

0.60

4

16.8

15

2.7
2.7

5

0.5
2.5

23

0.4
4.2

1.10
2.28
1.37
2.75
0.41

9096 0.09
7669
11838 0.05
9945 0.08
5805
0.00
5.36 31530
1.66 17371
0.17 615

0.14
0.58
0.46
0.10
1.25

32
2

8
12

0.73

7.00
1597 3.77

6.31 10192

13.00

0.11

910

0.60

0.71

0.04
0.06

349
220

2.40
0.34
0.80
1.70

1.91 16536
0.24 854
0.38 5438

23.18
8.10
21 17.00
11.20

82859
79500
19960
29215
2930
13563

5.40

4.35 37601

IN

0.9
14.8
1.7
4.2
0.

0.60
0.58

5846

AF
T

7

6.19

9
4.30

15.62
4.80
4.11
4.08
4.02
1.42 1.64

2.20 1.09 15541
6.60 3.27 12494
18.90 6.03 35472
49.24 227000

2.60 27239 5.20

R

11

PR

30.00 6.99 61877
0.98 9158
5.40 2.28 14590

10794
6276
5778
3513

48
7579

g/t

Nitrogen
Kjeldahl

R
ES
S

mg/l

Nitrates
(NO3 - N)

2.39

1400
3300
1800
1037
12108

8

400

1.24

4900

19
0.12
2.24

0.07
3.13

1060 0.49 0.16 2467 16.70 5.59 83823
4402 5.95 11.80 12261 5.21 2.25 10385

2.7
0.04
7.5

50
2.87 30991

4.58
1.45
8.95

5.59 32318
0.75 2635 0.51
2995 0.12
94475 0.88

0.08 291.7 20.51 3.36 11789 8.12 1.33 4666
238.5 5.44
11275 2.98
6171
9277 1.00
10508 13.04
624.5

22
4.71

19
22
13
1.64 14617 0.47

8
0.23

11
15
1733 4.60

13
15
13
2.37 17520 9.86

8660

3.50 25508
0.45 4500
1.01 5700
2.82 11100
43 19.50 5.04 55000

D

9096
12 400
10 193
19151
10490
12087
8183
6900
4400
11430
4900
2772
3268
953
5727
8852
9350
6412
5303
16552
4858
7153
728
8272
3359
8635
3613
14251
3817
5886
4610
10462
3624
5622
7293
10098
5668
3942
10916
9712
11871
15000
4620
4990

(2)

Nitrites
(NO2 - N)

G

0
0
0
0
0
0
0
0
0
0
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1

Ammonium
(NH4 - N)

N

kt

Emissions of nitrogen compounds from a sample of 51 European sites

KI

Total
feed

(1)

O

1
6
26
27
30
31
38
48
51
58
4
5
7
8
9
10
11
12
13
14
15
16
17
18
19
22
25
28
29
32
33
34
35
36
37
39
40
41
42
46
47
49
50
52
53
54
56
57
59
60
61

WWTP

Site label

Table 3.22:

9.80
1.60
4.00

5.00
18.32
13.42
6.00
40 15.00
9.10
4.00

0.98
5.47
5.51
2.00

3.51
0.45
5.88
27.96 4.80
8.13
13.87

11596
82064
25452
10000
18000
37851
2837
33955
16856
16944
146349

8
10
8
31
38
41
3.57 24281 23.5 12.84 8.19 56152

5th Perc. (3) 2499
2 0.36 0.13 587 0.03 0.05 229 0.43 0.20 1456 3.19 1.08 2112 8.24 1.75 0.69 3872
50th Perc.(3) 5753
9 2.70 1.10 6737 0.16 0.10 400 1.70 1.42 10192 5.40 2.28 9158 21.2 8.12 4.05 18000
95th Perc.(3) 14363 29 15.00 5.40 35426 1.49 0.74 6840 12.40 3.00 20817 20.35 6.57 75045 42.1 22.26 17.30 108255
(1): 0 = collective, 1 = dedicated
(2): intermediate concentration (in mg/l) after API, CPI and SWS
(3): only for dedicated WWTP

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March 2012

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Figure 3.21: Distribution of COD emissions for a sample of 36 European refineries

Figure 3.22: Distribution of BOD5 emissions for a sample of 29 European refineries

Figure 3.23: Distribution of TOC emissions for a sample of 21 European refineries
Figure 3.24: Distribution of suspended solid emissions for a sample of 34 European refineries

Figure 3.25: Distribution of annual average concentrations of nitrogen compound discharges for a sample of 26 European refineries
3.1.4 Waste generation

To avoid duplication, all data about waste generation are gathered in Section 3.27. Refineries also generate solid wastes and sludges with a range of 0.01–2 kg per tonne of crude processed (before waste treatment). According to the World Bank, 80% of these solid wastes may be considered hazardous because of the presence of toxic organics and heavy metals [101, World Bank, 1998].

The refinery waste generation was covered in a report [82, CONCAWE, 1995] representing the 1993 European refinery waste situation (see Table 3.23). A summary of the waste generated in a refinery is 45% sludge, 35% non-refining wastes, and 20% other refining wastes. From the one million tonnes of wastes identified in Europe in 1993, 39.9% was placed in landfills, 21.4% was recycled or reused, 14.9% was incinerated with energy recovery, 8.4% was incinerated without energy recovery, 10% was landfarmed, 1.7% was used as alternative fuel and the rest (0.6%) was sent to unidentified disposal routes [82, CONCAWE, 1995].

Table 3.23 shows the percentage of wastes categorized in for each group.

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<td></td>
<td>Spent caustic</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>Spent caustic</td>
<td>6.0</td>
</tr>
<tr>
<td>16 08/16 08 07</td>
<td>Other catalysts</td>
<td>4.7</td>
</tr>
<tr>
<td>16 08/16 08 07</td>
<td>Desulfurisation catalyst</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Spent caustic</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Sludges originate from various sources such as crude and product tanks bottoms, dealkalizers, alkylation units, boiler feed water preparation, biotreaters, the cleaning of heat exchanger bundles and equipment, oil spills and soil remediation. In terms of volume, oily sludges represent the largest waste category from refineries. Partly this is due to the presence of basic sediment and water in the crude, which can vary from crude to crude. Biosludge production takes place only if a refinery operates a biotreater.

Other wastes are generated from many of the refining processes, petroleum handling operations and waste water treatment. Both hazardous and non-hazardous wastes are generated. Spent catalysts originate from reformers, catalytic crackers, hydrocrackers, hydrometallisation, hydrodesulphurisation and hydrotreating units. The regeneration of catalysts is a well-established technique.

<table>
<thead>
<tr>
<th>Type of Waste</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tank scales</td>
<td>2.4</td>
</tr>
<tr>
<td>Sorbents</td>
<td>1.9</td>
</tr>
<tr>
<td>Flue-gas desulphurisation</td>
<td>1.3</td>
</tr>
<tr>
<td>Spent chemicals</td>
<td>1.2</td>
</tr>
<tr>
<td>Reformer catalyst</td>
<td>0.4</td>
</tr>
<tr>
<td>Acid tar</td>
<td>0.2</td>
</tr>
<tr>
<td>Non-refining wastes (construction/demolition and domestic waste)</td>
<td></td>
</tr>
<tr>
<td>Domestic</td>
<td>43.8</td>
</tr>
<tr>
<td>Rubble</td>
<td>41.9</td>
</tr>
<tr>
<td>Scrap metal</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Table 3.23: Percentage of each type of waste in a refinery

Source: CONCAWE
3.2 Alkylation

This section contains data on consumption and emissions generated by alkylation processes.

Consumptions

Table 3.24 gives a summary of the utility and chemical consumptions in the two techniques currently used in the alkylation processes, and for the new soli-acid process.

Table 3.24: Estimated utilities and chemical consumption for the various alkylation techniques

<table>
<thead>
<tr>
<th>Utilities</th>
<th>Sulphuric acid</th>
<th>Hydrofluoric</th>
<th>Solid Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Values per tonne of alkylate produced</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity (kWh)</td>
<td>480 – 130</td>
<td>20 – 65</td>
<td>134</td>
</tr>
<tr>
<td>Fuel (MJ)</td>
<td>Not required</td>
<td>1000 – 3000</td>
<td>Not required</td>
</tr>
<tr>
<td>Steam (kg)</td>
<td>849 815 – 1200</td>
<td>100 – 1000</td>
<td>1028</td>
</tr>
<tr>
<td>Cooling water (m³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ΔT = 11 ºC)</td>
<td>22 40 – 83</td>
<td>62</td>
<td>0.78</td>
</tr>
<tr>
<td>Industrial water (m³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh acid (kg)</td>
<td>78 – 120</td>
<td>1.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Caustic (as 100 % NaOH) (kg)</td>
<td>0.41</td>
<td>0.57</td>
<td>Not required</td>
</tr>
<tr>
<td>Lime</td>
<td>NA</td>
<td>NA</td>
<td>Not required</td>
</tr>
</tbody>
</table>

NB: AlCl₃ and water-free CaCl₂ consumption depend on operating conditions (water content of feed- and side-reactions)

Sources: [166, Meyers, 1997], [118, VROM, 1999], [261, Canales, 2000]

Emissions

Emissions generated by the alkylation processes are summarised in Table 3.25 to Table 3.27. [108, USAEPA, 1995] and reviewed by TWG.

Table 3.25: Air emissions generated by the alkylation processes

<table>
<thead>
<tr>
<th>Air pollutant</th>
<th>Sulphuric acid</th>
<th>Hydrofluoric</th>
<th>Solid acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂, SO₂, NOₓ and other pollutants from the furnaces(*)</td>
<td>From column heating</td>
<td>From column heating furnaces</td>
<td>No furnace</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>May be released from pressure reliefs, storage, handling operations, spillages and fugitive emissions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halogens</td>
<td>NA</td>
<td>Fluoride compounds may be released from pressure reliefs, vent gas and spillages</td>
<td>No halogens</td>
</tr>
<tr>
<td>Odours</td>
<td>NA</td>
<td>Acid-soluble oil may be released from process shutdown ponds during maintenance work, particularly the de-scaling of pipes conveying hydrogen fluoride. This may be odorous</td>
<td>No odour</td>
</tr>
</tbody>
</table>

(*) Emissions from these combustion processes are addressed in an integrated way in Section 0.
### Table 3.26: Waste water generated by alkylation processes

<table>
<thead>
<tr>
<th>Water parameter</th>
<th>Sulphuric</th>
<th>Hydrofluoric</th>
<th>Solid acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water</td>
<td>Waste water produced in the alkylation process has low pH, suspended solids, dissolved solids, COD, H₂S, and spent acid.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>NA</td>
<td>HC from separator drains (surge drum, accumulator, dryer) and spillages, and of acidic effluent containing dissolved and suspended chlorides and fluorides from the settlement pit or the process shutdown ponds.</td>
<td>No liquid waste at all</td>
</tr>
<tr>
<td>Acid</td>
<td>Sulphuric acid</td>
<td>Effluents from HF scrubber are 2 – 8 m³/h with compositions min/max of 1 000 – 10 000 ppm F; after lime treatment 10 – 40 ppm F.</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.27: Solid waste generated by the alkylation techniques

<table>
<thead>
<tr>
<th>Solid waste</th>
<th>Sulphuric</th>
<th>Hydrofluoric</th>
<th>Solid acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge</td>
<td>NA</td>
<td>The flow 7 – 70 kg sludge per kg used HF (dry solids content 3 – 30 %)</td>
<td>No sludge</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerisation products are removed from the acid as a thick dark oil.</td>
<td>HC from spent molecular sieves, carbon packings and acid-soluble oil. Sludge generated in the neutralisation process contains hydrocarbons. Dissolved polymerisation products are removed from the acid as a thick dark oil.</td>
<td>No acid soluble oil - No salts</td>
</tr>
<tr>
<td>Acid/catalyst products in the sludge</td>
<td>Sludge generated in the neutralisation process contains sulphuric acid.</td>
<td>Inorganic fluorides (Na/KF) and chlorides from treatment stages. Sludge generated in the neutralisation process contains CaF₂.</td>
<td>Spent catalyst sent back to supplier for Pt recovery after years of operation</td>
</tr>
<tr>
<td>Halides</td>
<td>NA</td>
<td>Composition of sludge is 10 – 40 ppm F after lime treatment</td>
<td>No halides</td>
</tr>
</tbody>
</table>

### 3.3 Base oil production

This section gives the consumption and emission values that can be found in European refineries. These values are given for each base oil production process identified.

#### 3.3.1 Deasphalting

**Consumption**

A conventional solvent-based base oil lube complex is energy intensive. The main reason is the high amount of heat required to evaporate the solvents and to separate them from the raffinate and extract streams. Solvent losses are usually in the order of 1 % despite extensive solvent recovery. In the tower method, for example, four to eight volumes of propane are fed to the bottom of the tower for every volume of feed flowing down from the top of the tower. It is reported, taking into account the specific input of some crudes and the output of crucial specifications (e.g. CCR), that there is a need to use a higher propane rate up to 9 or 11 for 1.

As an example, the figures below give the utility requirements of a solvent deasphalting absorption (SDA) unit.
Table 3.28: Consumption data of deasphalting units

<table>
<thead>
<tr>
<th>Utility</th>
<th>Data corresponding to 1000 tonnes of feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>136 – 150 MWh</td>
</tr>
<tr>
<td>Power</td>
<td>12.2 – 21 MW</td>
</tr>
<tr>
<td>Steam</td>
<td>166 – 900 tonnes</td>
</tr>
<tr>
<td>Cooling water</td>
<td>Nil (maximum air cooling)</td>
</tr>
</tbody>
</table>

*Sources:* [166, Meyers, 1997], [261, Canales, 2000]

Table 3.29: Emission data of deasphalting units

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air emissions may arise from fugitive solvent emissions and process vents. Heater stack gas (in Section 0).</td>
</tr>
<tr>
<td></td>
<td>The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Oil components</td>
</tr>
<tr>
<td></td>
<td>Little or no solid waste generated.</td>
</tr>
</tbody>
</table>

Table 3.30: Consumption data of aromatic extraction units

<table>
<thead>
<tr>
<th>Examples of utilities consumption typical per m³ feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel absorbed</td>
</tr>
<tr>
<td>Electricity</td>
</tr>
<tr>
<td>Steam</td>
</tr>
<tr>
<td>Water cooling (ΔT = 14 °C)</td>
</tr>
</tbody>
</table>

*Source:* [212, Hydrocarbon processing, 1998] reviewed by TWG

Table 3.31: Emission data of aromatic extraction units

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fugitive solvent/VOC emissions can come from the furfural and NMP from its storage tanks. Flue-gas from fired heater (in Section 0).</td>
</tr>
<tr>
<td></td>
<td>The total amount of process water is around 2 – 4 m³ per tonne of product, containing around 15 – 25 ppm furfural, 10 – 15 ppm NMP. The water stream leaving the fractionator is likely to contain some oil and solvents.</td>
</tr>
<tr>
<td></td>
<td>Little or no solid wastes generated.</td>
</tr>
</tbody>
</table>

*Source:* [118, VROM, 1999]

3.3.2 Aromatic extraction

Consumptions

Table 3.32: Typical utility consumption of high pressure hydrogenation unit

<table>
<thead>
<tr>
<th>Utilities, typical per kt of feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
</tr>
<tr>
<td>Electricity</td>
</tr>
<tr>
<td>Net steam consumption(())</td>
</tr>
<tr>
<td>Water cooling (ΔT = 14 °C)</td>
</tr>
</tbody>
</table>

(\(\)) (50 % is recovered as condensate)
3.3.4 Solvent dewaxing

Consumptions
The utility requirements in this process together with the aromatic extractions are:

Table 3.33: Typical utility consumption of solvent dewaxing and aromatic extraction units

<table>
<thead>
<tr>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 000 – 1 300</td>
<td>60 – 160</td>
<td>300 – 800</td>
<td>10 – 20</td>
</tr>
</tbody>
</table>

Source: [118, VROM, 1999], [261, Canales, 2000]

Table 3.34: Emission data of solvent dewaxing units

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Air</th>
<th>Waste water</th>
<th>Solid wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs may arise from solvent vapour extraction from the wax filters as well as fugitive emissions. Fugitive solvent VOC emissions can come from the MEK/Toluene from storage tanks. Flue-gas from fired heater (in Section 0).</td>
<td>The solvent recovery stage results in solvent-contaminated water which is typically sent to the waste water treatment plant. Potential releases into water are hydrocarbons, sulphur compounds and organic compounds from spillages and leaks, and organic compounds from process waters from solvent recovery operations. Waste water contains 1 – 3 ppm MEK/toluene.</td>
<td>Little or no solid wastes generated.</td>
<td></td>
</tr>
</tbody>
</table>

3.3.5 Hydrofinishing

Consumptions
The utility needs for a hydrofinishing unit are:

Table 3.35: Typical utility consumption of hydrofinishing units

<table>
<thead>
<tr>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 – 550</td>
<td>25 – 40</td>
<td>100 – 150</td>
<td>5 – 15</td>
</tr>
</tbody>
</table>

Source: [118, VROM, 1999]

Table 3.36: Emission data of hydrofinishing units

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Air</th>
<th>Waste water</th>
<th>Solid wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure relief valves of the hydrofiner, solvent recovery systems and refrigerant systems; Leakages from flanges, glands and seals on pumps, compressors and valves.</td>
<td>Leakages from flanges, glands and seals on pumps, compressors and valves.</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>


### 3.4 Bitumen production

#### Consumptions

Bitumen blowing is a very low energy consuming process. Some electricity is required for the air blower, product rundown pump and overhead condensing system. The electricity utilisation in this process is 15 – 35 kWh/tonne and the steam produced in the process is 100 – 200 kg/tonne. For cooling-water utilisation it is assumed that an air cooler is used as a condenser. If a direct water quench is applied instead of scrubbing, more water is normally used.

#### Emissions

Available information has been gathered in Table 3.37.

<table>
<thead>
<tr>
<th>Table 3.37</th>
<th>Emission data for bitumen production units</th>
</tr>
</thead>
<tbody>
<tr>
<td>To air</td>
<td>Flue-gas from fired heater (see Section 0).</td>
</tr>
<tr>
<td></td>
<td>Flue-gas from the overhead vapours incinerator. The overhead vapours from bitumen production, consisting mainly of light hydrocarbons, N₂, O₂, CO₂, and SO₂, are incinerated at high temperature (~800 °C) to ensure complete destruction of components such as H₂S, CO, complex aldehydes, organic acids, PAHs and phenolics, which have a highly unpleasant odour. The flow of the oxidiser overhead is around 0.07 – 0.30 Nm³ air/kg feed.</td>
</tr>
<tr>
<td>Process waste water</td>
<td>Sour water is produced in the oxidiser overhead waste water. Its flow is up to 5 m³/tonne feed and it contains H₂S, oil, aromatics, PAHs, sulphuric acid, odorous oxidation products (ketones, aldehydes, fatty acids) and particulates.</td>
</tr>
<tr>
<td>Solid waste</td>
<td>Slop oil emulsions are formed in the oxidiser overhead slop oil. It consists of an emulsion of light oil, water and particulates.</td>
</tr>
</tbody>
</table>

### 3.5 Catalytic cracking

#### 3.5.1 Consumptions

The next table shows the energy and process materials usage in the cat crackers.

<table>
<thead>
<tr>
<th>Table 3.38:</th>
<th>Typical utility consumption of cat crackers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utility</td>
<td>FCC</td>
</tr>
<tr>
<td>Fuel (MJ/t)</td>
<td>120 – 2 000</td>
</tr>
<tr>
<td>Electricity (kWh/t)</td>
<td>8 – 50</td>
</tr>
<tr>
<td>Steam consumed (kg/t)</td>
<td>30 – 90</td>
</tr>
<tr>
<td>Steam produced (kg/t)</td>
<td>40 – 60</td>
</tr>
<tr>
<td>Cooling water (m³/t, ΔT=17 °C)</td>
<td>5 – 20</td>
</tr>
<tr>
<td>Catalyst make-up (kg/t)</td>
<td>0.4 – 2.5</td>
</tr>
</tbody>
</table>

Sources: [261, Canales, 2000], [212, Hydrocarbon processing, 1998], [118, VROM, 1999], [166, Meyers, 1997], [268, TWG, 2001]
Virtually all the heat required in a FCC or a RCC unit is generated in the regenerator.

The catalysts used consumed and released to air as emissions depend greatly on the type of product required processed and can be silica-alumina substrate carrying rare earth and/or precious metals, or can be based on zeolites—more typically consist of rare-earth exchanged zeolites on alumina matrices and clays.

### 3.5.2 Emissions

#### 3.5.2.1 Air emissions

Within a refining complex, one of the sources with major potential for atmospheric emissions is the catalytic cracking unit. Air emissions come principally from the regenerator and are mainly CO, CO\textsubscript{2}, NO\textsubscript{x}, particulates (mainly catalyst fines including their constitutive heavy metals) and SO\textsubscript{2}. The emissions from catalytic crackers are very variable. The wide variation reflects both the wide reflecting variations of feedstocks used in the cat cracker units (nitrogen, sulphur, metal contents), and the regenerator and waste heat boiler operating conditions.

Emissions from a FCC unit can increase over time as the quality of air catalyst mixing in the regenerator deteriorates as a result of wear. For example, internal mechanical damage or equipment wear/erosion could occur towards the end of run of the unit and this could significantly increase all unit emissions CO, (NO\textsubscript{x}, SO\textsubscript{2} and PM).

As already shown in Section 3.1.2, emissions from an FCC unit can be 10 – 30 % of total refinery SO\textsubscript{2} emissions (see Figure 3.13), 15 – 25 % for NO\textsubscript{x} (Figure 3.13 Table 3.4) and 30 – 40 % of particulates. However, these figures can be subject to wider variation [112, Foster Wheeler Energy, 1999]. Air emissions generated by the combustion of fuels in the FCC furnaces are treated in Section 4.5.1.

The next table shows a summary of the emission factors and emissions from FCCs

<table>
<thead>
<tr>
<th>Table 3.39: Emission data and factors found in cat crackers (with and without abatement techniques)</th>
</tr>
</thead>
</table>
| Emissions | PM | SO\textsubscript{x}  
(as SO\textsubscript{2}) | CO | HC | NO\textsubscript{x}  
(as NO\textsubscript{2}) | Aldehydes | NH\textsubscript{3} |
| Emission factors  
(kg/m\textsuperscript{3} of fresh feed) | 0.009 – 0.976 | 0.19 – 1.50 | 0.08 – 39.2 | 0.630 | 0.107 – 0.416 | 0.054 | 0.155 |
| Emission data  
(mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2}) | 40 – 150 | 320 – 2 500 | <50 – 500 | NA | 180 – 700 | NA | NA |
| NB: Values attainable in continuous operation. Emissions values as half hourly mean values Lower levels in the range are cat crackers with abatement techniques. |


In the EU region there is a growing trend towards processing more residual feedstock in FCC units in response to increasing demand for road transport fuels and a decreasing demand for residual fuels. Residual feedstock brings higher content of coke precursors, sulphur, nitrogen, Ni and V metals, and aromatics. The sulphur load increase has proportional, related effects on S content in the coke and thus on SO\textsubscript{2} emissions. The nitrogen load increase potentially leads to the increased production of NO\textsubscript{x} precursor compounds NH\textsubscript{3} and HCN, which may or may not lead to increased actual NO\textsubscript{x} emissions depending on the FCC UNIT regenerator operations.
Potential consequences of the high metals content include:

- a substantial increase in catalyst consumption and potentially higher regenerator PM losses due to increased catalyst attrition
- the formation of FeS (from the increased feed Fe content) over the equilibrium catalyst, which is then oxidised to SO₂ and SO₃ in the regenerator thus increasing flue-gas SOₓ content
- the increase of NOₓ emissions due to required antimony additions used to passivate nickel to reduce the production of hydrogen.

Residue catalytic crackers (RCC) mainly use atmospheric residue as feedstock. Hence the Conradson carbon, sulphur content and nitrogen content are higher. Therefore, RCCs are potentially a stronger source of SOₓ and NOₓ, PM and contaminated catalyst than normal FCCs. However, as consequence of the type of feedstock used in the RCC, the RCC produces more coke and hence more heat should be removed from the regenerators.

Because the cat cracker is a significant emitter of pollution in a refinery, there follows a more detailed analysis by type of pollutant.

Carbon dioxide
Carbon dioxide is generated in the catalyst regeneration train and its load depends on the size.

<table>
<thead>
<tr>
<th>Throughput (kt/yr)</th>
<th>%S in feed</th>
<th>Flue-gas flow (Nm³/h at 3 % O₂)</th>
<th>CO₂ emission load (t/yr)</th>
<th>Specific CO₂ emission (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 314</td>
<td>&lt;0.5</td>
<td>110 000</td>
<td>272 243</td>
<td>207</td>
</tr>
<tr>
<td>2 350</td>
<td>0.35</td>
<td>200 000</td>
<td>498 006</td>
<td>212</td>
</tr>
<tr>
<td>Range of emissions</td>
<td></td>
<td>130 000 – 600 000</td>
<td>160 – 220(*)</td>
<td></td>
</tr>
</tbody>
</table>

High Conradson carbon feed can lead to increasing CO₂ emissions

*Sources:* [250, Winter, 2000], [136, MRI, 1997] reviewed by TWG

Carbon monoxide
Relatively high concentrations of carbon monoxide (CO) can be produced during the regeneration of the catalyst. CO is typically converted to carbon dioxide either in the regenerator (total combustion mode) or further downstream in a carbon monoxide boiler (partial combustion mode).

In the total combustion mode, incomplete combustion may lead to releases of carbon monoxide in the total combustion. CO from full-burn units ranges typically between 50 and 1200 mg/Nm³ (depending on temperature, CO promoter level, size of unit).

In the partial combustion mode, depending on the conditions under which the regenerator is operating, the levels of CO in the regenerator exhaust gases feeding the CO boiler may be in the region of 5 to 10 %, and levels of CO in the exhaust from the CO boiler can be maintained at less than 100 mg/Nm³ depending on the type of CO boiler used [80, March Consulting Group, 1991].

<table>
<thead>
<tr>
<th>Throughput (kt/yr)</th>
<th>%S in feed</th>
<th>Flue-gas flow (Nm³/h at 3 % O₂)</th>
<th>CO concentration (mg/Nm³)</th>
<th>CO emission load (t/yr)</th>
<th>Specific CO emission (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1314</td>
<td>0.5</td>
<td>110 000</td>
<td>215 – 814</td>
<td>558</td>
<td>0.43</td>
</tr>
<tr>
<td>2350</td>
<td>0.5</td>
<td>200 000</td>
<td>125</td>
<td>194</td>
<td>0.08</td>
</tr>
</tbody>
</table>

*Source:* [250, Winter, 2000]

NB: data are related to yearly average, 3 % O₂, dry conditions
Chapter 3

CO boilers are usually used only in connection with partial-burn FCCs with CO concentrations in the flue-gas from 5 to 10 %. They are not used to further reduce CO values in a full-burn unit.

Nitrogen oxides

The wide range in NO\textsubscript{x} emissions (levels) from cat cracker regenerators (gases) reflects the main effects of different combustion conditions on FCC regenerators or FCC CO boilers, the spread in unit capacities and the coke (feed) nitrogen contents. These latter depend on crude type and upstream process configuration. NO\textsubscript{x} are generated in different ways for the two combustion modes.

In full-burn mode, key parameters potentially affecting the FCC UNIT NO\textsubscript{x} emissions are:

- uneven regenerator catalyst bed temperature and oxygen profiles and distribution;
- use of a CO combustion promoter containing platinum (contributes to NO\textsubscript{x} increase);
- antimony additions, often used for high-metal feed applications.

In partial-burn mode, key parameters potentially affecting the FCC UNIT NO\textsubscript{x} emissions are (Sources: [24, Bruhin et al. 2003]):

- the formation of NO\textsubscript{x} precursor compounds (HCN and NH\textsubscript{3}) from the coke nitrogen, depending upon the CO content. Operating conditions with higher excess CO usually favour the formation of these precursors which react to form NO\textsubscript{x} and N\textsubscript{2} in the CO boiler downstream of the regenerator;
- thermal NO\textsubscript{x} generated in the CO boiler and fuel NO\textsubscript{x} formed depending upon the nitrogen content of the supplemental fuel, the amount and type of fuel, the burners design and the operating conditions in the CO Boiler.

The final stack NO\textsubscript{x} emissions for a partial-burn regenerator may be similar to, or even higher than an equivalent full-burn regenerator. It is typically higher than a full-burn unit operating at low excess O\textsubscript{2} (<2 %). Figure 3.27 displays NO\textsubscript{x} yearly average concentrations achieved in 2007-2008 for a sample of 21 European FCC units. When available, summary information is also given on NO\textsubscript{x}-reducing techniques that were implemented on these plants (values are expressed in mg/Nm\textsuperscript{3} dry at 3 % O\textsubscript{2}). Lower emission values can be found when highest deNO\textsubscript{x} reduction additives rates are applied, or when dedicated end-of-pipe treatment techniques are implemented.

![Figure 3.27: NO\textsubscript{x} yearly average concentration from a sample of 21 European FCC units](image)

**Data displayed:**

1. Full = Full burn, Partial = Partial burn
2. Main techniques implemented on the FCC unit:
   - F1 = Feed hydrocracking
   - F2 = Low NO\textsubscript{x} CO promoter
   - F3 = NO\textsubscript{x} reducing catalyst additives
   - F4 = SCR
   - F5 = Wet scrubbing

**22 FCC sites**
Additional data received for 2009 for a feed hydrotreated (F1) FFC full combustion unit show a yearly average of 116 mg/Nm\(^3\) (Source: Emission declaration for 2009).

Note to TWG: Following table proposed to delete

Some examples of NO\(_x\) emissions from cat crackers as well as the ranges found are shown in the next table.

<table>
<thead>
<tr>
<th>Throughputs (kt/yr)</th>
<th>% S in feed</th>
<th>Flue-gas flow (Nm(^3)/h at 3 % O(_2))</th>
<th>NO(_x) concentration (mg/Nm(^3))</th>
<th>NO(_x) emission load (t/yr)</th>
<th>Specific NO(_x) emissions (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 314</td>
<td>0.5</td>
<td>110 000</td>
<td>400</td>
<td>280</td>
<td>0.34</td>
</tr>
<tr>
<td>2 350</td>
<td>0.5</td>
<td>200 000</td>
<td>500</td>
<td>775</td>
<td>0.33</td>
</tr>
<tr>
<td>1 750</td>
<td>NA</td>
<td>NA</td>
<td>45</td>
<td>45</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Ranges and averages in a sample of 20 European FCC crackers

Range: 30–2000 (average continuous monitoring) 56–1000 mg/MJ (related to throughput)

Remark: data are related to yearly average, 3 % O\(_2\), dry conditions

Table 3.42: Range and examples of nitrogen oxide emissions from cat crackers

Sources: [250, Winter, 2000], [136, MRI, 1997], [268, TWG, 2001]

Particulates

Generally a FCC UNIT is the biggest single emitter of particulates although the calciner in a coking unit is also a significant emitter. Particulate matter arises from catalyst fines from the catalyst regeneration exhaust gases and catalyst handling and disposal. The emitted catalyst is fine and is produced in a cat cracker as a result of the constant movement of the catalyst grains. In the absence of moisture or sulphuric acid condensation, the normal cause of stack plume opacity is the presence of the fine catalyst particles. In practice, operating conditions may have a large effect on particulate emissions. Table 3.43 gives three examples of particulate emissions from cat crackers. Lower values in the provided range correspond to FCC equipped with abatement techniques.

<table>
<thead>
<tr>
<th>Throughput (kt/yr)</th>
<th>Flow (Nm(^3)/h at 3 % O(_2))</th>
<th>% S in feed</th>
<th>Concentration (mg/Nm(^3))</th>
<th>PM load (t/yr)</th>
<th>Specific emissions(*) (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 314</td>
<td>110 000</td>
<td>0.5</td>
<td>17</td>
<td>11.6</td>
<td>0.009</td>
</tr>
<tr>
<td>2 350</td>
<td>200 000</td>
<td>0.5</td>
<td>50</td>
<td>44.5</td>
<td>0.033</td>
</tr>
<tr>
<td>1 750</td>
<td>NA</td>
<td>NA</td>
<td>47</td>
<td>33.8</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Ranges and averages in a sample of 20 European FCC crackers

\(40 - 500\) [25 - 189] \(40 - 500\) [13 - 340] \(100 - 000\) [0.015 - 0.100]
Avg: 69 Avg: 88 Avg: 0.040

(*) Range and average estimated from FCC capacity

Sources: [250, Winter, 2000], [136, MRI, 1997], [268, TWG, 2001]

Figure 3.28 displays the PM yearly average concentrations achieved in 2007-2008 for a sample of 20 European FCC units. When available, summary information is also given on PM-reducing techniques that were implemented on these plants. Values are expressed in mg/Nm\(^3\) dry at 3 % O\(_2\). Lower emission values are not particularly necessarily linked with the combustion mode, but are often related with the most advanced ESP or filtering techniques reported.
Additional data received for 2009 for a feed hydrotreated (F1) FFC full combustion unit show a yearly average of 25 mg/Nm³ (Source: Emission declaration for 2009).

Table 3.44: Example of composition of particulate matter generated by cat crackers when feedstock is hydrotreated

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Actual value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total particulate</td>
<td>23</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Mass flow</td>
<td>2.0</td>
<td>kg/h</td>
</tr>
<tr>
<td>Total metal content</td>
<td>&lt;0.1</td>
<td>%</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.05</td>
<td>% Ni/PM</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.02</td>
<td>% V/PM</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Platinum</td>
<td>&lt;0.004</td>
<td>% Pt/PM</td>
</tr>
<tr>
<td></td>
<td>&lt;0.001</td>
<td>mg/Nm³</td>
</tr>
</tbody>
</table>

Source: [250, Winter, 2000]

Particulates emitted by the cat cracker regenerator consist predominantly of catalyst particles with a typical size of 10 μm max. The particle size distribution shows that by weight is almost up to 90 % smaller than 10 μm. Much of this dust consists of silica/alumina, nickel and vanadium (as well as other metals) present in the feedstock. The deposited coke (including metals) on the catalyst ranges between approximately 4 and 5 % w/w. Metal compounds are enriched in the heavy residues during distillation, and are therefore present in the FCC feedstock. If hydrotreated heavy residues are used as FCC feed, heavy metal concentrations will be smaller, as shown in
Sulphur oxides
The sulphur in the feed to the cat cracker is split between liquid product streams: H₂S in the
gaseous products and SO₂ emission from the regenerator with the approximate ratio of 50/45/5.
In case of RCC, the SO₂ emissions from the regenerator can reach 20 - 30 % of sulphur in the
feed. The degree of sulphur dioxide leaving the exhaust gases from the catalytic cracker
depends on the sulphur content of the feedstock used as well as the technology used to control
these emissions. SO₃ aerosols will also contribute to the cat cracker stack plume opacity.

Table 3.45 shows some examples of yearly averages of SO₂ emissions from cat crackers:

<table>
<thead>
<tr>
<th>Throughput (kt/yr)</th>
<th>Flow (Nm³/h at 3% O₂)</th>
<th>% S in feed</th>
<th>SO₂ concentration (mg/Nm³)</th>
<th>SO₂ load (t/yr)</th>
<th>Specific SO₂ emissions (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>n.a</td>
<td>0.5</td>
<td>260</td>
<td>144</td>
<td>1.14</td>
</tr>
<tr>
<td>1300</td>
<td>110000</td>
<td>0.8</td>
<td>240</td>
<td>127</td>
<td>1.00</td>
</tr>
<tr>
<td>2200</td>
<td>200000</td>
<td>1.7</td>
<td>200</td>
<td>100</td>
<td>0.45</td>
</tr>
<tr>
<td>250</td>
<td>65000</td>
<td>1.5</td>
<td>150</td>
<td>85</td>
<td>0.36</td>
</tr>
<tr>
<td>1200</td>
<td>150000</td>
<td>2.0</td>
<td>90</td>
<td>50</td>
<td>0.18</td>
</tr>
<tr>
<td>1500</td>
<td>130000</td>
<td>2.5</td>
<td>40000</td>
<td>3100</td>
<td>0.18</td>
</tr>
<tr>
<td>800</td>
<td>70000</td>
<td>2.0</td>
<td>1100</td>
<td>70</td>
<td>0.50</td>
</tr>
<tr>
<td>2250</td>
<td>200000</td>
<td>0.5</td>
<td>1300</td>
<td>1360</td>
<td>0.70</td>
</tr>
<tr>
<td>250</td>
<td>62500</td>
<td>n.a</td>
<td>1060</td>
<td>1110</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 3.45: Sulphur oxide emissions from cat crackers (with and without abatement
techniques)

Sources: [261, Canales, 2000], [250, Winter, 2000], [107, Janson, 1999],
[112, Foster Wheeler Energy, 1999], [268, TWG, 2001]

Figure 3.29 displays SO₂ yearly average concentrations achieved in 2007-2008 for a sample of
23 European FCC units. When available, summary information is also given on SO₂-reducing
techniques that were implemented at these plants (values are expressed in mg/Nm³ dry at 3 %
O₂).

It can be noted that lower emission values are not particularly correlated with the sulphur input
in the refinery overall feedstock, nor with the FCC combustion mode. However, best
performances are linked to the highest hydrotreatment rates directly applied to the FCC
feedstock, and dedicated end-of-pipe treatment techniques that are implemented.
Chapter 3

Figure 3.29: SO₂ yearly average concentration from a sample of 23 European FCC units

Additional data received for a feed hydrotreated (F1) FCC full combustion unit show a yearly average of 82 mg/Nm³ (Source: Emission declaration for 2009).

According to CONCAWE 4/09 report, from a nine FCC unit data set, eight show SO₂ emissions under 500 mg/Nm³ and one shows up to 800 mg/Nm³. In the latter case, the unit was using supplementary fuel and firing heavy residue in the COB.

Other compounds
Hydrogen sulphide, mercaptans and ammonia may arise from sour waters from reflux condensers. Hydrocarbons (typically 80 % alkanes and typically 15 % of olefins) may be released from pressure reliefs, storage and handling operations, spillages and water discharges. Measured dioxin and PAH emission values in two European FCCs are reported above, levels of <0.016 ng TEQ/Nm³ after CO₂ combustion. [268, TWG, 2001]

Table 3.46 Examples of emission measurements in 2008 of other compounds from two catalytic crackers

<table>
<thead>
<tr>
<th>Installation</th>
<th>Abatement techniques</th>
<th>Operational Conditions /Capacity</th>
<th>Total dust mg/Nm³</th>
<th>Dioxins ng TEQ/Nm³</th>
<th>PAH (16 EPA) μg/Nm³</th>
<th>Flue-gas flow/ measurement conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>ESP, SCR and SO₂-reducing catalyst additive</td>
<td>full combustion without CO boiler/ NA</td>
<td>14 – 23</td>
<td>0.002</td>
<td>0.46 – 0.6</td>
<td>230 000 Nm³/h 2.6 – 2.7 % O₂</td>
</tr>
<tr>
<td>#2</td>
<td>ESP</td>
<td>full combustion without CO boiler/ NA</td>
<td>41 – 46</td>
<td>0.002 – 0.03</td>
<td>0.41 – 0.73</td>
<td>220 000 Nm³/h 1.4 – 1.7 % O₂</td>
</tr>
</tbody>
</table>

Source: [77, REF TWG 2010] Average value of three spot measurements under normal operating conditions
3.5.2.2 Waste water emissions

The typical flow of waste water generated by a catalytic cracking process is around 60 – 90 litres of waste water per tonne of feedstock treated. Generated waste water is typically from sour water drains and spillages from the fractionator containing some hydrocarbons (high levels of oil BOD, COD), suspended solids, sulphur compounds (H₂S), phenols, cyanides, ammonia and high pH. The next table shows the loads and composition of waste water generated in the cat crackers.

Table 3.47: Waste water emissions generated by cat crackers

<table>
<thead>
<tr>
<th>Source of waste water</th>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam used to purge and regenerate catalysts</td>
<td>Metal impurities from the feed oil</td>
<td>NA</td>
<td>ppm</td>
</tr>
<tr>
<td>Fractionator overhead reflux drum</td>
<td>Percentage of feed intake</td>
<td>7 – 10</td>
<td>% v/v</td>
</tr>
<tr>
<td></td>
<td>Flow</td>
<td>20 – 40</td>
<td>m³/h</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>10 – 200</td>
<td>ppm</td>
</tr>
<tr>
<td></td>
<td>HCN</td>
<td>51 – 1100</td>
<td>ppm</td>
</tr>
<tr>
<td></td>
<td>COD</td>
<td>500 – 2000</td>
<td>ppm</td>
</tr>
<tr>
<td></td>
<td>N-Kj</td>
<td>15 – 50</td>
<td>ppm</td>
</tr>
<tr>
<td></td>
<td>Phenols</td>
<td>5 – 30</td>
<td>ppm</td>
</tr>
<tr>
<td></td>
<td>Free oil</td>
<td>50 – 100</td>
<td>ppm</td>
</tr>
<tr>
<td>Caustic washing of hydrocarbons</td>
<td>Flow</td>
<td>128</td>
<td>m³/h</td>
</tr>
<tr>
<td></td>
<td>Phenolic caustic</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cresylic acids</td>
<td>NA</td>
<td></td>
</tr>
</tbody>
</table>

3.5.2.3 Solid wastes

There are potential releases into land from catalyst in the form of fines from particulate matter arrestment equipment and intermittent spent catalyst discharge. These solid residues are enriched in the heavy cycle oil and clarified oil (distillate of FCC UNIT) fractions. Catalyst addition rates for resid operation depend on feed metal levels. Addition rates shown are typical values covering a feed metal range of 10 – 20 ppm Ni+V+Na.

Table 3.48: Solid wastes generated in the catcracking

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow</th>
<th>Composition min/max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replacement of old catalyst</td>
<td>Regenerator, 50 tonnes/4 yr</td>
<td>Spent Catalyst: Grey, solid powder consisting of Al₂O₃, SiO₂, carbon, refractory material and metals.</td>
</tr>
<tr>
<td>Catalyst fines</td>
<td>Regenerator overhead cyclone/ESP</td>
<td>Dust containing high levels of V, Ni, Sb</td>
</tr>
<tr>
<td>Tank sludge slurry</td>
<td>Depends on slurry filtration system</td>
<td>10 - 30 % oil, depending on draining for cleaning. PAH</td>
</tr>
</tbody>
</table>
3.6 Catalytic reforming

Consumptions
Table 3.49 shows a summary of the utilities and catalyst requirements for the catalytic reforming.

Emissions

Emissions to the air
Air emissions from catalytic reforming arise from the process heater gas (addressed in Section 0), fugitive emissions (hydrocarbons from pressure relief valves and leakages) and regeneration. Hydrocarbons and dust releases may arise from venting during catalyst replacement procedures and during clean-out operations. Table 3.49 shows an example of emissions to the air generated by reformers in two European refineries. Table 3.50 also shows the emissions generated by the heaters.

Table 3.49: Typical utilities requirements for catalytic reforming

<table>
<thead>
<tr>
<th>Utilities</th>
<th>Reforming</th>
<th>Semi-regenerative process</th>
<th>Continuous regeneration process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity, kWh</td>
<td>-</td>
<td>246(*)</td>
<td>6142(*)</td>
</tr>
<tr>
<td>Specific consumption (kWh/t)</td>
<td>25 – 50</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>Fuel fired, GJ</td>
<td>-</td>
<td>185(*)</td>
<td>232(*)</td>
</tr>
<tr>
<td>Specific fuel consumption (MJ/t)</td>
<td>1400 – 2900</td>
<td>71.5 t/kt</td>
<td>232(*)</td>
</tr>
<tr>
<td>Cooling water, (m³/t, ΔT=10 °C)</td>
<td>1 – 3</td>
<td>0.12 – 3</td>
<td>5.5</td>
</tr>
<tr>
<td>High-pressure steam generated, kg/t</td>
<td>50 – 90</td>
<td>64 – 90</td>
<td>97</td>
</tr>
<tr>
<td>Boiler feed water, kg/t</td>
<td></td>
<td>170</td>
<td>22</td>
</tr>
<tr>
<td>Condensate return, t/h</td>
<td></td>
<td>88</td>
<td>113</td>
</tr>
<tr>
<td>Specific value (t/kt)</td>
<td></td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst(containing Pt) t/(Mt/yr)</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

( ) Values related to a capacity of 2351 t/d. Specific values related to capacity values
NB: First column gives ranges for all types of reformers
Sources: [118, VROM, 1999], [166, Meyers, 1997], [261, Canales, 2000]

Table 3.50: Examples of emissions to air generated by catalytic reforming

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Unit</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO</th>
<th>CO₂</th>
<th>Particulates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platformer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mider (1)</td>
<td>753.4</td>
<td>1 million Naphtha</td>
<td>mg/m³</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>t/yr</td>
<td>24.1</td>
<td>68.7</td>
<td>68.7</td>
<td>146</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>0.024</td>
<td>0.069</td>
<td>0.069</td>
<td>146</td>
<td>0.003</td>
</tr>
<tr>
<td>Platformer</td>
<td></td>
<td></td>
<td>mg/m³</td>
<td>18</td>
<td>170</td>
<td>5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>OMV</td>
<td>494.1</td>
<td>0.77 million Naphtha</td>
<td>t/yr</td>
<td>8.8</td>
<td>83</td>
<td>2.4</td>
<td>95 848</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>0.012</td>
<td>0.114</td>
<td>0.003</td>
<td>132</td>
<td>0.001</td>
</tr>
</tbody>
</table>

NB: Data are related to yearly average, 3 % O₂, dry conditions.
(1) Emissions from the Mider refinery, only limit values are given. Loads and specific emissions were calculated.
Source: [250, Winter, 2000]

In the reforming process, very little of the naphtha feed is converted to coke requiring regeneration. In the regeneration process of the catalyst in a continuous catalyst regeneration (CCR) reforming unit, a slipstream of catalyst is withdrawn, the coke (60 – 80 kg coke/tonne feed) is burned off with hot nitrogen diluted with air/steam. Trace quantities of a
promoter, normally an organic form of chlorine (such as tri- or per-chloroethylene) are added to retain catalyst activity. Moisture is removed and the regenerated catalyst is returned to the reformer.

The off-gas from catalyst regeneration varies with the reforming technology employed and the routing of the off-gas. While the off-gas stream from a CCR is continuous, the regeneration emissions from cyclic or semi-regenerative reforming processes are discontinuous. **In the cyclic or semi-regenerative units, the regeneration of catalyst and the resulting emissions are discontinuous.** The off-gas from the regenerator **The regeneration vent gas can contain air with diluted oxygen content, steam, hydrocarbons, CO₂, traces of HCl, Cl₂, H₂S, a small quantity of catalyst fines, traces of Cl₂, CO (<10 mg/Nm³ [117, VDI, 2000]), SO₂, hydrocarbons and low levels of dioxins and furans.** Depending on the technology and the system design, the regeneration vent gas may be routed over an adsorption bed, through a caustic scrubber, or combined with a basic water wash system. Air emissions of trace components vary significantly depending on the unit configuration.

<table>
<thead>
<tr>
<th>Sources</th>
<th>Abatement techniques</th>
<th>Operational conditions</th>
<th>Concentration ng TEQ/Nm³</th>
<th>Specific dioxins emission ng TEQ/tonne</th>
<th>Flue-gas flow/ measurement conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>USAEPA Study</td>
<td>?</td>
<td></td>
<td></td>
<td>0.196 ng/t (semi-regenerative)</td>
<td>1172 ng/t (CCR)</td>
</tr>
<tr>
<td>Measurements in 4 Belgian refineries</td>
<td>?</td>
<td></td>
<td>&lt;0.1-0.13 3.3-6.7 &lt;0.01 &lt;0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measurements in 2 Sweden refineries</td>
<td>a. CCR with regeneration gas recycling loop b. Discontinuous with wet scrubber</td>
<td>99 % abatement</td>
<td>a. b. To be completed</td>
<td>1. Total load: 0.045 g TEQ/yr 2. To be completed</td>
<td></td>
</tr>
</tbody>
</table>

*Source: [315, USAEPA, 2000] - [77, REF TWG, 2010]*

Studies have reported dioxins and furans in reformer effluent streams (113 ng/Nm³ TCDD-eq EADON, 131 ng/Nm³ TCDD-eq I-TEF [215, Jansson, 1999]). A study from USAEPA [315, USAEPA, 2000] shows that the PCDD/PCDF emission factors from petroleum catalytic reforming units are 0.196 ng/t for semi-regenerative units and 1172 ng/t for continuous regeneration units. Dioxin emissions measured in four Belgian refineries are <0.1-0.13; 3.3-6.7; <0.01 and <0.01 ng TEQ/Nm³ (higher values are derived from an installation with a flow of 2000 Nm³/h (eq. 1800 h/yr) [268, TWG, 2001]. These studies have not always taken into account the differences in unit configuration and regeneration vent gas routing. In some designs, the regenerator gas can normally be treated in a water or caustic scrubber to remove dust, chlorine compounds and SO₂ prior to release to the atmosphere. The storage and handling of organic chlorides used during the regeneration may also lead to releases. The organic chloride compounds used for catalyst regeneration are thermally and catalytically converted to HCl or Cl₂ in the regeneration process.

**Waste water**

In the reforming unit, with a design (water or caustic scrubbers) that generates waste water, the amount of waste water generated in the catalytic reforming is around 1 – 3 litres per tonne of feedstock. The waste water contains high-level oils, suspended solids, COD and relatively low-levels of H₂S (sulphides), chloride, ammonia and mercaptans. These compounds may also be found in the stripping stabilising tower used to remove light ends from the reactor effluent. Hydrocarbons from spillages and leaks may occur. A study shows that, in case of water released, the untreated waste water and spent caustics from the reformers can contain a wide
range of PCDD/PCDF concentrations of 0.1 pg I-TEQ\textsubscript{DF}/l to 57.2 ng I-TEQ\textsubscript{DF}/l [315, USAEPA, 2000].

**Solid wastes generated**

Spent catalyst fines (alumina silicate and metals) may be generated from the particulate abatement techniques. For process units using expensive catalysts, such as catalytic reformers (Pt), contracts with the supplier exist for taking the spent catalyst back for regeneration and/or recycling. Spent catalyst is generated is around 20 to 25 tonnes per year for a 5 million tonnes per year refinery. Most reformers do not generate a continuous solid waste stream. CCR generate a small quantity of catalyst fines that are collected and sent for platinum reclamation. CCR unit catalyst fines are typically less than 1 tonne per year for a 1.7 million tonnes per year reformer. On average, catalyst life is around 10 years. Other potential discontinuous solid wastes might include spent promoted alumina adsorbents used as chloride guards and spent molecular sieve dryer adsorbents. Some solid wastes may also be generated during the equipment maintenance. Table 3.52 gives examples of the typical composition of the sludge generated in the catalytic reformers.

Table 3.52: Composition of sludges generated in the unit separator sludge of an ultraformer

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (ppm)</th>
<th>Species</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>2.4 %</td>
<td>Ethylbenzene</td>
<td>215.8</td>
</tr>
<tr>
<td>Solids</td>
<td>97.6 %</td>
<td>Lead</td>
<td>108.6</td>
</tr>
<tr>
<td>Carbon</td>
<td>7.7 %</td>
<td>Benzene</td>
<td>92.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.5 %</td>
<td>Naphthalene</td>
<td>79.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.4 %</td>
<td>Chromium</td>
<td>75.1</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.3 %</td>
<td>Sulphate</td>
<td>72.4</td>
</tr>
<tr>
<td>Iron</td>
<td>38070</td>
<td>Phenan</td>
<td>40.2</td>
</tr>
<tr>
<td>Sulphur</td>
<td>18901</td>
<td>Vanadium</td>
<td>19</td>
</tr>
<tr>
<td>Aluminium</td>
<td>6836</td>
<td>Antimony</td>
<td>19</td>
</tr>
<tr>
<td>Calcium</td>
<td>6166</td>
<td>Fluorine</td>
<td>17.1</td>
</tr>
<tr>
<td>Sulphide</td>
<td>4658</td>
<td>Phenol</td>
<td>13.4</td>
</tr>
<tr>
<td>Magnesium</td>
<td>3405</td>
<td>Pyrene</td>
<td>9.4</td>
</tr>
<tr>
<td>Sodium</td>
<td>1059</td>
<td>Benzo(A)Pyrene</td>
<td>6.7</td>
</tr>
<tr>
<td>Xylene</td>
<td>1056.3</td>
<td>Arsenic</td>
<td>4.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>898.1</td>
<td>Selenium</td>
<td>1.9</td>
</tr>
<tr>
<td>Nitrate</td>
<td>683</td>
<td>Cyanide</td>
<td>0.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>667.6</td>
<td>Mercury</td>
<td>0.02</td>
</tr>
</tbody>
</table>

NB: Figures quoted on a moisture-free basis

Source: [80, March Consulting Group, 1991]

**3.7 Coking processes**

**Consumptions**

*Delayed coking*

Table 3.53 shows the energy and process materials usage in the delayed coking. The amount of required make-up water for the coking process depends on the evaporation losses and the bleed to the desalter. Treated effluent can be used for this. The water used for coke cutting during decoking of the drums is highly contaminated with contains (un)saturated hydrocarbons and coke particles.
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Table 3.53: Utility requirements of a delayed coking process

<table>
<thead>
<tr>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)(1)</th>
<th>Steam produced (kg/t)</th>
<th>Cooling water (m³/t, ΔT=17 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 – 1200</td>
<td>20 – 30</td>
<td>50 – 60</td>
<td>50 – 125</td>
<td>6 – 10</td>
</tr>
</tbody>
</table>

NB: Electricity including the electric motor drives for the hydraulic decoking pump. 
(1) taking into account the ensemble (including the gas concentration integrated unit) it will lead to a steam consumption around three times the production.

**Flexicoking**

Table 3.54 shows the energy and process materials usage in flexicoking.

Table 3.54: Utility requirements in the flexicoking process

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Steam produced (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 – 140</td>
<td>300 – 500 (MP)</td>
<td>500 – 600 (HP)</td>
<td>20 – 40</td>
</tr>
</tbody>
</table>

**Calcinator**

The calciner specific energy consumption figures are given per tonne of calcined coke produced.

Table 3.55: Typical utility requirements in the calcinating unit (updated TWG 2010)

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Refinery fuel gas (kg/t)</th>
<th>Steam produced (kg/t)</th>
<th>Steam consumed (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.2</td>
<td>0.03</td>
<td>2.2 t/h (115 barg)</td>
<td>2.4</td>
</tr>
</tbody>
</table>

**Emissions**

The most important health and safety aspect of these processes is the handling of the coke fines.

**Emissions to the air**

Air emissions from coking operations include the process heater flue-gas emissions (see Section 0, where emissions from heaters are included) and fugitive emissions. In addition, the removal of coke from the drum (delayed coking) can release particulate and any remaining hydrocarbons to the atmosphere. The main pollutants generated as well as the sources are described below.

- Hydrogen sulphide and sulphur compounds as mercaptans may be released from the sour water stream from reflux condensers.
- Hydrocarbons may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling operations, spillages and waste and water discharges.
- Particulate matter may be released from the kiln gas cleaning system, the rotary cooker gas cleaning system, coke handling and storage, loading operations and from the calcinator process. The back pressures of the gas discharges from the kiln are critical to maintain the flame front in the kiln. This could mean the cyclone operating conditions are dictated by the requirement of the kiln rather than the optimum conditions for dust removal. Overall particulate emissions of 10 – 460 mg/Nm³ are currently being achieved [80, March Consulting Group, 1991] [251, Krause, 2000]. Storage, crushing and handling of green coke takes place in the wet state with no releases to air. Typical size distribution profiles for particulate matter in calciner exhaust gases after passing through a cyclone system are given in Table 3.56.
Waste water
Waste water is generated from the coke removal, water bleed from coke handling, sour water from fractionator overhead, cooling operations and from the steam injection and should be treated. The amount of waste water generated in the coking processes is around ≈ 140 litres per tonne of feedstock. It contains H₂S, NH₃, suspended solids (coke fines with high metal contents), COD, high pH, particulate matter, hydrocarbons, sulphur compounds, cyanides and phenols. Detailed analysis of the contaminants of such waste waters is not available because they are transferred directly to the refinery main waste water system for treatment.

Solid wastes
Solid wastes generated in the coking processes are coke dust (carbon particles and hydrocarbons) and hot oil blowdown sludges containing hydrocarbons. Table 3.57 shows a typical analysis of these sludges.

3.8 Cooling systems
The information given in this section should be read in conjunction with the ICS BREF, [ 84, COM 2001 ] the horizontal BREF reference document on industrial cooling systems, particularly the extensive coverage it gives to the consumption of additives.

The need for cooling in a refinery depends on the processes used and on the degree to which they are integrated but, where water cooling systems are applied, it certainly accounts for the majority of water usage. In a refinery, it is important to maximise heat integration at a plant
level and at process/activity level to minimise cooling duty. Therefore, energy requirements for cooling will depend on the cooling system used together with the cooling strategy applied.

Table 3.58 shows a typical split of the cooling needs in a refinery (Hydrocracking refinery with a throughput of 7 Mt/yr).

Table 3.59 gives a distribution of the cooling capacity according to temperature range within a typical refinery. (Hydrocracking refinery with a throughput of 7 Mt/yr)

Table 3.58: Cooling needs in a refinery

<table>
<thead>
<tr>
<th>Application</th>
<th>Cooling capacity</th>
<th>MW</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process streams</td>
<td>400</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Pumps, compressors</td>
<td>10</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Vacuum systems</td>
<td>15</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>425</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Source: [119, Bloemkolk and van der Schaaf, 1996]

Table 3.59: Typical cooling duty according to temperature range

<table>
<thead>
<tr>
<th>End temperature (T)</th>
<th>Cooling duty</th>
<th>MW</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&gt;43</td>
<td>380</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>43&gt;T&gt;38</td>
<td>15</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>38&gt;T&gt;30</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>30&gt;T</td>
<td>5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>400</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Source: [119, Bloemkolk and van der Schaaf, 1996]

Consumptions
Power is consumed by pumps in a water cooling system and by fans in an air cooling system. The water cooling system uses water and requires chemicals as corrosion and bacterial growth inhibitors. For more detailed information and annual consumption figures, reference is made to the ICS BREF on cooling which can be regarded as the state of the art document on cooling systems. Both recirculating and once-through cooling water systems require additives, to prevent fouling and/or corrosion. Because once-through systems generally use surface water (either fresh or salted), the chances of fouling are higher, compared to recirculating systems. Therefore, in these systems, more anti-fouling additives (i.e. chlorinated biocides) should be used. On the other hand anti-corrosion additives are mainly applied in recirculating systems and not used in once-through systems.

Water utilisation in cooling systems is lower in a recirculating system, compared to a once-through system (up to only 3 %). In the recirculating system a certain amount of water exits the system through evaporation, as mist droplets and as bleed or blowdown to the waste water treatment system. Therefore, make-up water in the range of about five percent of the circulation rate is required, a figure equivalent to the use of 0.23 m³ of cooling water per tonne of crude oil processed. However, to make a balanced comparison between the two kinds of cooling systems, it is necessary to take into account the quality of the water used (often once-through cooling systems are fed with low quality water, marine or brackish water).

Emissions
The main 'contamination' generated by the direct environmental impact of the cooling systems is the heat, increasing the temperature of the cooling fluid used. In refinery water cooling, the increase of the temperature (ΔT) is around 10 – 15 °C.
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Water consumption (mentioned above), energy consumption (pumps, air-cooler fans) and water pollution are the main environmental issues of cooling systems. Other environment-related effects include noise production (cooling tower, pumps, air-cooler fans (97 – 105 dB(A) at source)) and plume formation (cooling tower).

The main pollutants to be considered in water cooling systems are the chlorinated and/or brominated anti-fouling additives, and anti-corrosion additives containing zinc, chromium, molybdenum etc. Special attention should be paid to the use of dispersing additives in closed cooling water systems, particularly when the bleed is routed to an oil separating water treatment unit, where it can interfere with the oil-water separation process. A once-through system coupled with a low rate of leaks and a high volume of water mean that cooling water discharges contain between 0.1 and 1 mg/l oil. Hydrocarbon emissions to air from cooling towers (as a result of leakages and stripping) may occur. Emissions to the air were reported to vary between 0.5 and 85 g hydrocarbons per m³ cooling water recirculating over the cooling tower [119, Bloemkolk and van der Schaaf, 1996]. Cooling by quenching (only used in delayed cokers within refineries) results in high vapour emissions, significant energy losses, large water use and severe water pollution.

Table 3.60: Environmental impact of different cooling systems for a typical refinery

<table>
<thead>
<tr>
<th>Emission or effect</th>
<th>Once-through</th>
<th>Once-through (closed-loop)</th>
<th>Cooling tower</th>
<th>Cooling tower (closed-loop)</th>
<th>Air coolers</th>
<th>Air-cooled (closed-loop)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal heat (MW)</td>
<td>300</td>
<td>300</td>
<td>Negligible</td>
<td>Negligible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons (kg/h)</td>
<td>2.6 - 26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical conditioning(())</td>
<td>2.6</td>
<td>2.6</td>
<td>3 – 25</td>
<td>3 – 25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water blow-down discharge (m³/h)</td>
<td>26 000</td>
<td>26 000</td>
<td>156</td>
<td>156</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Air</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Visible plume</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Water vapour (kg/h)</td>
<td></td>
<td></td>
<td>468 000</td>
<td>468 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons (kg/h)</td>
<td></td>
<td></td>
<td>13</td>
<td>(+)()</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy consumption(d) (kW)</td>
<td>3 500</td>
<td>5 500</td>
<td>5 600</td>
<td>7 000</td>
<td>2 000</td>
<td>8 700</td>
</tr>
<tr>
<td>Fresh water consumption (m³/h)</td>
<td>In closed circuit</td>
<td>624</td>
<td>624</td>
<td>624</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Other nuisances</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noise(())</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Other</td>
<td>Entrainment of fish in intake</td>
<td>Entrainment of fish in intake</td>
<td>Legionella risk in air releases</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\) Hypochlorite in once-through cooling water; anti-corrosives, hypochlorite and anti-scalants in cooling tower make-up water
\(\) See text
\(\) Suppression of plume possible at extra cost
\(\) Process energy losses not included
\(\) Possible effect: the leaking of air coolers is not a well-described phenomenon. The absence of water would suggest that corrosion is not an important factor compared to water-cooled systems. Further study would be needed for an accurate assessment.

Source: [119, Bloemkolk and van der Schaaf, 1996] Completed by TWG 2010
3.9 Desalting

The quantity of inorganic impurities in the crude oil depends very much on both the crude origin and the crude handling during transport from the crude well to the refinery.

Consumptions

The water used in crude desalting is often untreated or partially treated water from other refining process water sources. Table 3.61 shows the typical operating conditions and water consumptions in the desalters, depending on the type of crude oil used.

<table>
<thead>
<tr>
<th>Crude oil density kg/m³ at 15 °C</th>
<th>Water wash, % v/v</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;825</td>
<td>3 – 4</td>
<td>115 – 125</td>
</tr>
<tr>
<td>825 – 875</td>
<td>4 – 7</td>
<td>125 – 140</td>
</tr>
<tr>
<td>&gt;875</td>
<td>7 – 10</td>
<td>140 – 150</td>
</tr>
</tbody>
</table>

For desalting long CDU residue, 10 % w/w water on feed is common. Once the water and the oily phase have been well mixed, the water should be separated from the oil feedstock in a separating vessel by adding demulsifier chemicals (5 – 10 ppm) to assist in breaking the emulsion and/or, more commonly, by applying a high-potential electric field across the settling vessel to coalesce the polar salt water droplets. The electricity consumption used in the desalting processes varies typically from 0.075 to 0.15 kWh per tonne of crude oil.

Emissions

Air emissions

No major emissions to air are produced during the desalting processes. Air emissions from the heating process are expected (in Section 0), and fugitive emissions (hydrocarbons) may be expected.

Solid wastes generated

The quantities of desalter sludge generated depend on the solid content of the crude, the separation efficiency and the applied desludging mode and frequency. Normally a desalter clean-out is done twice a year, yielding from 60 – 1500 t/yr oily sludge, dependent on the throughput and efficiency of the process to capture solids. The sludge generated can contain iron rust, clay, sand, water (5 – 10 %), emulsified oil and wax (20 – 50 % w/w) and metals.

Waste water

The desalter is a big contributor of waste water (30 – 100 litres/tonne feedstock desalted). The desalting process creates an oily desalter sludge and a high-temperature salt waste water stream (possibly the most polluted in the refinery) which is typically added to refinery waste water treatment facilities. The waste water generated is highly contaminated. Table 3.62 shows the ranges to be expected from waste waters from desalters.
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Table 3.62: Composition of the waste water generated in the desalting process

<table>
<thead>
<tr>
<th>Water pollutants</th>
<th>Typical concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>115 – 150</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>50 – 100</td>
</tr>
<tr>
<td>Oil/oil emulsions</td>
<td>High</td>
</tr>
<tr>
<td>Dissolved hydrocarbons</td>
<td>50 – 300</td>
</tr>
<tr>
<td>Phenols</td>
<td>5 – 30</td>
</tr>
<tr>
<td>Benzene</td>
<td>30 – 100</td>
</tr>
<tr>
<td>BOD</td>
<td>High</td>
</tr>
<tr>
<td>COD</td>
<td>500 – 2000</td>
</tr>
<tr>
<td>Ammonia</td>
<td>50 – 100</td>
</tr>
<tr>
<td>Nitrogen compounds (N-Kj)</td>
<td>15 – 20</td>
</tr>
<tr>
<td>Sulphides (as H2S)</td>
<td>10</td>
</tr>
</tbody>
</table>

Source: [181, HP, 1998], [101, World Bank, 1998]

3.10 Energy system

The energy system is an important, if not the most important activity from the environmental perspective. The energy (heat and power) necessary to transform the raw materials to products is provided by the combustion of hydrocarbon fractions that mainly generates emissions to air. As it was mentioned in Section 2.10, this section contains the emissions generated by the energy system as a whole. As a consequence of this, the emissions generated by furnaces or boilers of specific processes are integrated here and they are not considered in the other sections.

3.10.1 Energy management

Energy efficiency in refineries

As the name indicates, Energy efficiency is an index for calculating a refinery’s energy efficiency. There are currently three methodologies in use in refineries briefly described below:

- The first is specific energy consumption (SEC). This is the most simple index. It is calculated as the ratio between the energy consumed by the refinery and the tonnes of feedstock processed. According to data gathered by the TWG from a sample of 50 European refineries, the specific energy consumption of European refineries (from 5th to 95th Percentiles) ranges from 1 to more than 4.6 to 3.7 GJ per tonne of throughput (crude and intermediates). Because it is a simple index, this ratio does not take account of the complexity of the refinery (more complex refineries tend to consume more energy).

- The second methodology is the products method. [318, Phylipsen, Blok et al., 1998] This method considers the products and internal energy products produced in the refinery, giving a specific energy consumption benchmark per tonne of energy product produced. Multiplying these specific energy consumptions by the amount produced within the refinery and adding all the totals together gives an energy consumption benchmark for that refinery. Some calculations based on 2008 data indicate that the best specific energy consumption figures are between 2.4 and 2.9 GJ/tonnes, whereas actual values were from 1 to 4.8. That means that some European refineries are doing better than figures that are considered a good benchmark.

- Energy intensity index (EII) is a measure used to compare energy consumption in refineries. The standard energy use is based on the energy consumption at about 300 more than 500 refineries worldwide. Since the beginning of this benchmarking (property of Solomon Associates) in the 1980s, an EII of 100 corresponds, by design, to the current average calculated for all the participating US plants. The average EII obtained in a worldwide market survey (Solomon study, 1994) was 92, with a range from 62 to 165. [107, Janson, 1999]. More energy efficient refineries correspond to the lower values of EII. Therefore, some refineries are almost three times as energy efficient as others. In 2005 the top 10% of all best EII values reported worldwide were equal to or below 75. This
index reflects the types of processes and throughput of each process in the refinery. This data is not available for all refineries and typically is considered confidential by refineries. As shown in Figure 3.30, a total of 41 European refineries have reported their EII (2006, 2007 or 2008) in TWG questionnaires, and the values have been plotted against the complexity index together with specific energy consumptions calculated for each of the concerned sites. A clear correlation is naturally observed. Within this European sample, EII ranges from 65 to 124, with an average of 93 very close to the world average, and five plants in the best 10% term of worldwide performance. Lowest EII values are typically achievable under local circumstances where low grade heat can be externally exchanged.

![Energy Intensity Index and specific energy consumption for 41 EU refineries](image)

**Figure 3.30:** Energy Intensity Index and specific energy consumption for 41 EU refineries

### 3.10.2 Energy capacity and consumptions

#### Capacity of the refinery energy system

The capacity of the individual combustion plants in a refinery varies widely from less than 10 to 200 Megawatts thermal input (MWth); and the total installed capacity ranges from several hundred to more than 1500 MWhth in the largest refineries. The energy consumed at the combustion plants of the refineries ranges from 200 to more than 17 000 TJ per year. Deep conversion refineries in general use more than three times as much energy (10% of crude intake) as simple hydroskimming refineries (3%) [101, World Bank, 1998].

#### Gasification plant

An example of IGCC unit produces 130 t/h of syngas mainly composed of CO and H₂ in the ratio 1:1 (calorific values of 9600 – 10 000 kcal/kg) starting from 58 t/h of feedstock (calorific value of the heavy residue varies between 8800 and 9200 kcal/kg, sulphur content: 3.5 – 7% and metal content: 300-800 ppm). A solid effluent in the form of a filter cake (about 160 – 400 kg/h dry) is discharged and sent to external plants for recovery of the metals. Two Claus units...
recover 4 t/h of elemental sulphur from the H2S recovered in the acid gas removal section. A tail
gas treatment section that permits an overall sulphur recovery of 99.9 %, follows the Claus units
[297, Italy, 2000].

Refinery fuels
The baseline ratio of gas to liquid refinery fuel used in a refinery is a function of a number of
factors, important amongst which are the size, degree of complexity, LPG recovery efficiency
and extent to which refinery fuel gas is processed into other products (e.g. olefins) or exported
to adjacent chemicals plants (either directly or as energy from common facilities). It varies from
80/20 or 70/30 (gas/liquid) at a standalone, moderately complex refinery to 40/60 at a highly
complex site which also services a chemicals complex. However these ratios can be increased
when energy conservation measures are applied and the gas availability becomes sufficient for
the energy supply of the refinery. Table 3.63 illustrates the calorific value and the sulphur
content of the different fuels as well as its calorific value.

Table 3.63: Properties of the fuels used within a refinery (updated TWG 2010)

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Calorific value (MJ/kg)</th>
<th>Sulphur content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery gas</td>
<td>29 – 49</td>
<td>20 – 4000 mg H2S/Nm³</td>
</tr>
<tr>
<td>Hydrogen gas</td>
<td>55 – 70 (LHV)</td>
<td>20 – 1200 mg H2S/Nm³</td>
</tr>
<tr>
<td>Catalyst coke from FCC</td>
<td>38 – 40</td>
<td>0.11 – 0.3 % S</td>
</tr>
<tr>
<td>Liquid refinery fuel</td>
<td>40</td>
<td>≤0.1 – ≤4 % S</td>
</tr>
</tbody>
</table>

There are great differences in the characteristics of the liquid refinery fuel used in European
refineries. The data from a CONCAWE report show that in 1995 some 20 % of the total liquid
refinery fuel used in the refineries had a sulphur level between 3 and 4 %, another 20 % a
sulphur level of 2 to 3 %, some 40 % a sulphur level between 1 and 2 %, and 20 % a sulphur
level below 1 %. However, it is worth to mention that some European refineries use heavier
liquid refinery fuels (up to 7 %). 2006 about 50 % of oil fired has a sulphur content of ~1 % or
less, only 10 % of refineries using oil with more than 2 % sulphur in 2006, compared with 20 %
in 2002 and 35 % in 1998. The average sulphur content was 1.7 % in 1998, 1.34 % in 2002 and
1.33 % in 2006 [63, CONCAWE 2010].

Table 3.64 shows the chemical characteristics of three different liquid fuels.

Table 3.64: Chemical properties of several typical heavy liquid oils

<table>
<thead>
<tr>
<th>Property</th>
<th>High sulphur</th>
<th>Intermediate sulphur</th>
<th>Low sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur % by weight</td>
<td>2.2</td>
<td>0.96</td>
<td>0.50</td>
</tr>
<tr>
<td>Carbon % by weight</td>
<td>86.25</td>
<td>87.11</td>
<td>87.94</td>
</tr>
<tr>
<td>Hydrogen % by weight</td>
<td>11.03</td>
<td>10.23</td>
<td>11.85</td>
</tr>
<tr>
<td>Nitrogen % by weight</td>
<td>0.41</td>
<td>0.26</td>
<td>0.16</td>
</tr>
<tr>
<td>Ash %</td>
<td>0.08</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Vanadium (ppm)</td>
<td>350</td>
<td>155</td>
<td>70</td>
</tr>
<tr>
<td>Nickel (ppm)</td>
<td>41</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Sodium (ppm)</td>
<td>25</td>
<td>10</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Iron (ppm)</td>
<td>13</td>
<td>9</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Source: [345, Molero de Blas, 2000]

The nitrogen and sulphur contents are two of the most important chemical parameters and are
responsible among other factors for the emissions of NOx and SOx. Ash content combined with
high sulphur can directly effects particulate matter emissions. The following Figure 3.31 shows
the distribution of nitrogen and sulphur contents in various types of vacuum residues according
to their geographical origin.
Steam generation
Steam generation requires a energy input of 2 700 – 3 200 MJ per tonne of steam produced. Conditioning chemicals are dosed to the BFW in low concentrations and comprise the following groups of chemicals: anti scaling agents, corrosion inhibitors and anti foaming agents. A 100 t/h steam generation system requires approximately 1.5 – 3 t/yr corrosion inhibitors and 2 – 4 t/yr anti-scaling agents. These conditioning chemicals are included below:

- One type of conditioning chemicals is corrosion inhibitors (mainly oxygen scavengers and alkaline compounds). Sulphite (<60 bar), oximes, hydroxyl amines, and hydrazine (declining use due to safety issues) etc. are commonly applied as oxygen scavengers for deaerated boiler feed water prior to pumping into the boiler. Commonly applied alkaline compounds are sodium phosphates (which are also hardness binders), caustic, ammonia and neutralising amines.
- Anti-scaling agents such as polyacrylates and phosphonates that are rest hardness binders and dispersing agents are the second type.
- Anti-foaming agent, in general intermittently dosed, to combat foaming in case the condensate contains oil or organics are the third type.

3.10.3 Emissions

3.10.3.1 Air emissions

General aspects
Since emissions to water are minimal and very little is generated in the way of solid waste, emissions to air are the primary ones. emissions, both from the energy system and from the refinery as a whole. The sum of flue-gas flows generated from all combustion processes associated with the energy system (i.e. central power plant, process furnaces, standalone boilers and eventual gas turbines) in a refinery range from around 1 – 20 GNm³/yr (40 000 00 to more than 700 000 2 million Nm³/h at 3 % O₂), which corresponds to 0.2 – 2 million Nm³/t of feedstock processed.

The main releases to air from combustion processes are stack gases containing oxides of sulphur, oxides of nitrogen, oxides of carbon (carbon monoxide and carbon dioxide) and – particularly important when liquid refinery fuel or coke is combusted – particulate matter including PM₁₀ and metals (e.g. V, Ni). When operating properly and when burning cleaner...
fuels such as refinery fuel gas, low-sulphur fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significantly higher. Incomplete combustion may lead to releases of carbon monoxide, smoke and, if heavy fuel oils are used, particulate matter. As a result of that, combustion plants are major contributors to the release of air emissions from refineries. The level of pollutants emitted will depend on the quality of the fuels burnt, which can vary considerably. There are conflicting factors in a combustion process which contribute to emission levels. For example, combustion conditions which favour low particulate emissions for liquid refinery fuel, i.e. excess air, high temperature, good air/fuel mixing and good fuel-atomisation, are not favourable for low-NO\textsubscript{x} emissions.

Refinery fuel gas, if properly treated, is a low polluting fuel. Liquid refinery fuels generate more emissions to the air than refinery fuel gas. Gas-fired heaters and boilers generate little dust and lower SO\textsubscript{2} emissions, as the refinery fuel gases are usually cleaned in amine scrubbers. NO\textsubscript{x} emissions are also much lower than these of liquid-fired boilers and heaters.

By way of example, Table 3.65 and Table 3.67 show, respectively, the air emissions generated by gas and liquid refinery fuels in two power plants used in European refineries.

Table 3.65: Air emissions from a power plant fired with refinery fuel gas

<table>
<thead>
<tr>
<th>Fuel Consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>CO\textsubscript{2}</th>
<th>CO</th>
<th>NO\textsubscript{x}</th>
<th>Particulates</th>
<th>SO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>561.4</td>
<td>41 000</td>
<td>mg/m\textsuperscript{3}</td>
<td>42 &lt;80</td>
<td>135 &lt;100</td>
<td>1</td>
<td>1 – 20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>t/yr</td>
<td>108 917</td>
<td>23.6</td>
<td>75.7</td>
<td>0.6</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>2 657</td>
<td>.58</td>
<td>1.85</td>
<td>0.014</td>
<td>1.81</td>
</tr>
</tbody>
</table>

NB: Data in table yearly average, 3 % O\textsubscript{2}, dry

Source: [247, UBA Austria, 1998] updated TWG AT 2010

Table 3.66: Air emissions from a power plant fired with heavy fuel oil

<table>
<thead>
<tr>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>CO\textsubscript{2}</th>
<th>CO</th>
<th>NO\textsubscript{x}</th>
<th>Particulates</th>
<th>SO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 234.4</td>
<td>491.8</td>
<td>mg/m\textsuperscript{3}</td>
<td>20 18 – 79</td>
<td>554 60 – 98</td>
<td>20 2 – 3</td>
<td>200 55 – 159(\textsuperscript{1})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>t/yr</td>
<td>102 6130</td>
<td>262</td>
<td>2089</td>
<td>268</td>
<td>2666</td>
</tr>
<tr>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>3200</td>
<td>.24</td>
<td>6.5</td>
<td>0.24</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Notes: Data in table monthly average, 3 % O\textsubscript{2}, dry.

(\textsuperscript{1}) The fuel primarily used consists of the visbreaker residue, with a sulphur content up to 7 %

The flue-gas is treated in a SNO\textsubscript{x} plant FGD unit (Wellman Land). RFG and natural gas are co-fired with heavy fuel oil.

Source: [247, UBA Austria, 1998] updated TWG AT 2010

Table 3.67: Air emissions from Mider refinery power plant burning refinery liquid residue

<table>
<thead>
<tr>
<th>Emissions parameters</th>
<th>Raw gas</th>
<th>Clean gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume, wet (m\textsuperscript{3}/h, 7 % O\textsubscript{2})</td>
<td>171 690</td>
<td>188 249</td>
</tr>
<tr>
<td>Gas temperature (°C)</td>
<td>180 – 200</td>
<td>up to 72</td>
</tr>
<tr>
<td>Particulates (mg/m\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>220</td>
<td>&lt;10</td>
</tr>
<tr>
<td>NO\textsubscript{x} (mg/m\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>800</td>
<td>&lt;150</td>
</tr>
<tr>
<td>SO\textsubscript{2} (mg/m\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>6 500</td>
<td>&lt;400</td>
</tr>
<tr>
<td>SO\textsubscript{4} (mg/m\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>650</td>
<td>&lt;400</td>
</tr>
</tbody>
</table>

NB: It includes a FGD process. Liquid refinery fuel contains 7 % of sulphur.

Source: [247, UBA Austria, 1998]
These follows an analysis of the air emissions produced by the energy system, pollutant per pollutant.

Carbon dioxide
Combustion processes of fossil fuels produce CO₂ as a result of the combustion of hydrocarbons. The amount of CO₂ emitted to the atmosphere by European refineries varies from 0.15 to 5.5 million t per year (range depending on the type of refinery and the energy integration). The specific CO₂ emissions (calculated from 5th to 95th percentiles within a sample of 58 European refineries) range from 0.02 to 0.82 basically 0.1 to 0.4 tonnes of CO₂ per tonne of crude oil feedstock processed. CO₂ emissions from power plants in the refineries correspond to around 42 % of the CO₂ emitted by the refinery. The use of liquid fuels results in lower thermal efficiencies and higher CO₂ emissions than the use of gaseous fuels.

Table 3.68 shows the sources (type of fuels) of the CO₂-emissions of the refining industry. The table also includes the calculated emission factors for CO₂ for various refinery fuels.

Table 3.68: CO₂ emission factors for different types of fuels

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Typical composition (% w/w)</th>
<th>kg CO₂/kg fuel</th>
<th>kg CO₂/GJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>30 H/35 C1/35 C2 % v/v</td>
<td>2.83</td>
<td>43</td>
</tr>
<tr>
<td>Natural gas</td>
<td>100 % methane</td>
<td>2.75</td>
<td>56</td>
</tr>
<tr>
<td>LPG</td>
<td>50 C3/50 C4</td>
<td>3.02</td>
<td>64</td>
</tr>
<tr>
<td>Distillate Fuel oil</td>
<td>60 P/10 O/30 A</td>
<td>3.22</td>
<td>74</td>
</tr>
<tr>
<td>Residual Fuel</td>
<td>50 P/50 A</td>
<td>3.26</td>
<td>79</td>
</tr>
<tr>
<td>Coke</td>
<td>90 C/10 ash</td>
<td>3.30</td>
<td>117</td>
</tr>
</tbody>
</table>

(abbreviations: Carbon, Hydrogen, Paraffins, Olefins, Aromatics)

Sources: [115, CONCAWE, 1999] [259, Dekkers, 2000]

Carbon monoxide
One of the products of partial combustion processes is carbon monoxide. The CO emissions, which range from 20 – 42 mg/Nm³ at 3 % O₂, are very dependent on the type of fuel used and the completeness of the combustion process. Specific emission values for CO are 0.58 kg CO per tonne of refinery fuel gas and 0.24 kg CO per tonne of liquid fuel. [247, UBA Austria, 1998].

Nitrogen oxides
NOx emissions from a refinery energy system depend on the fuel type, fuel nitrogen or hydrogen content, combuster equipment design and operating conditions. The formation and release of NOx from combustion processes arises from the oxidation of nitrogen present in the fuel source and/or the air used. Accordingly, large differences in the NOx emission level can be expected between refineries and even between different combustion installations at the same refinery at different times. Differences in temperature, residence time and oxygen concentration result in varying levels of thermally formed NOx. The influence of temperature is most important, with NOx emissions increasing exponentially with temperature.

Gaseous fuels typically release less NOx per unit of energy compared with liquid fuels, especially liquid refinery fuels. Oil burning normally leads to higher levels of NOx releases for several reasons: especially the problem of fuel NOx arising from the nitrogen content (0.03 – 1 %), the way in which the plant is often operated so as to balance NOx and particulate releases, and the frequent design requirement for firing in combination with gas. However, the latter statement is only true for non-abated emissions, since the inclusion of secondary measures can reduce both NOx and particulate emissions. One refinery in 1996 found that fuel oil can generate about three times more NOx than gas fuels. NOx factors (NOx produced per tonne of fuel combusted), used by some refineries to report NOx emissions, indicate NOx from oil firing to be two to three times that from gas firing. However data from other refineries, particularly these
based on stack monitoring, indicate that NO\textsubscript{x} from oil can be as much as five or six times that from gas (e.g. see Table 3.65 and Table 3.66).

Figure 3.32 gathers the NO\textsubscript{x} equivalent concentration (expressed as yearly average in mg/Nm\textsuperscript{3} dry at 3 % O\textsubscript{2}) of all flue-gases emitted by the overall energy system of 30 European refineries. For each site, a summary information is given on the existence of typical NO\textsubscript{x}-related techniques implemented at various parts of the energy system, and on the portion of total gaseous fuels (refinery fuel gas + eventual external natural gas supply) in the site energy mix. Most sites emit in the range 100 – 500 mg/Nm\textsuperscript{3}. As expected, a clear correlation is observed between the highest gaseous fuel ratios in the site energy breakdown and the lowest NO\textsubscript{x} equivalent concentrations.

Additional data received for 2009 show, for energy system, a yearly average of 71 mg/Nm\textsuperscript{3} of NO\textsubscript{x} emissions (Source: Questionnaire 1 updated with emission declaration for 2009).

<table>
<thead>
<tr>
<th>Source</th>
<th>Gas</th>
<th>Liquid refinery fuel (HFO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process furnaces</td>
<td>70 – 1300</td>
<td>280 – 1000</td>
</tr>
<tr>
<td>Boilers</td>
<td>100 – 1100</td>
<td>300 – 1000</td>
</tr>
<tr>
<td>Turbines (6 – 15 % O\textsubscript{2})</td>
<td>15 – 1050</td>
<td>200 – 150\textsuperscript{2}</td>
</tr>
</tbody>
</table>

All figures are NO\textsubscript{x} as NO\textsubscript{2} (@ 3 % O\textsubscript{2}, mg/Nm\textsuperscript{3}).

*The lower range relates to natural gas firing
# for gasoil/jet oil

Table 3.69: NO\textsubscript{x} emissions ranges for existing installations

Source: [45a, Sema and Sofres, 1991], [115, CONCAWE, 1999]

The fired heaters, boilers and gas turbines running on refinery blend gas produce lower NO\textsubscript{x} emissions than FCCs. Specific NO\textsubscript{x} emissions related to energy consumption range from 15 to 200 mg/MJ for furnaces with 100 % gas fuel. Specific NO\textsubscript{x} emissions related to the throughput range from 84 to 700 tonnes of NO\textsubscript{x} per million tonnes of crude oil processed. The NO\textsubscript{x} load ranges from 20 to more than 2000 tonnes per year.
Particulates
Under normal conditions, the solids in the flue-gases of a furnace or boiler consist mainly of coke particles with some cenospheres, depending on firing conditions. The particulate emission of oil-fired equipment may vary considerably since they depend on a number of more or less independent parameters such as: fuel type, burner design, oxygen concentration at the outlet of the radiant section, the flue-gas outlet temperature of the radiant box, and the residence time of the fuel droplets. The particle size of the particulate matter (PM) from furnaces and boilers on HFO is in the order of 1 μm. The PM in flue-gases can take any of the following four forms:

- soot where the particle size is below 1 μm (the visible smoke from a stack is caused by all particles but mainly these with a particle size between 0.5 and 5 μm);
- cenospheres: they originate from the liquid phase wastes of combustion of heavy oil droplets at relatively low temperature (<700 °C), the size is equal to or larger than that of the original oil droplets;
- coke particles, formed through liquid phase cracking in combustion at high temperatures (>700 °C), the particle size is generally from 1 to 10 μm;
- fine particles (<0.01 μm): their contribution to the total mass emission is negligible.

The PM in the flue-gas of furnaces and boilers fired with heavy fuel oil is a mix of metal compounds and soot/coke. Metals (mainly V and Ni) are a natural constituent (indigenous) of the crude. Soot and coke result from imperfections of the combustion process. Contaminants such as sand, rust and other metals, and coke particles of the fuel itself, may also contribute to the formation of particulates. The indigenous metal content of the heavy fuel oils (see Section 2.10), and which can be calculated from the metal content of the crude oil from which the HFO is made) is the basis for calculating the minimum ash content of the HFO and therefore also the basis for the PM in the flue-gas. Ash contents are higher than the metal content itself (as the metal compounds are in the ash), and generally lie in the range 500 – 1500 ppm (0.05 - 0.15 % w/w). In practice the PM content is normally higher by a factor of 2 – 4, because unburnt fuel (soot) adheres to the metallic PM, and because aerosols of SO₃ are also monitored as PM.

The range of the unabated PM (150 – 500 mg/Nm³) is typical for the current burners application applied nowadays (steam atomisation and low-NOₓ), assuming all measures are taken to achieve good combustion (optimum oxygen content and lowest practicable NOₓ in the flue-gas) and is directly related to the ash content of the fuel. For older furnaces, liquid refinery fuel-fired flue-gas levels may range from 500 to 1000 mg/Nm³. For boilers, all these figures are on average lower. For a new optimal burner design with steam atomisation this can be well below 200 mg/Nm³. The range of 150 – 500 mg/Nm³ represents the current typical range with liquid refinery fuels employed (ash contents) and burners installed (low-NOₓ with steam atomisation). Table 3.70 shows the particulate emission range found in current European refineries.

Table 3.70: Particulate emissions ranges for existing installations

<table>
<thead>
<tr>
<th>Refinery fuel gas</th>
<th>Liquid refinery fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process furnaces</td>
<td>0.4 – 2.4</td>
</tr>
<tr>
<td>Boilers</td>
<td>&lt;5</td>
</tr>
<tr>
<td>CHP</td>
<td>2 – 3(1)</td>
</tr>
<tr>
<td>Turbines (@15 % O₂)</td>
<td>NA</td>
</tr>
</tbody>
</table>

NB: All figures in mg/Nm³ @ 3 % O₂ (monthly average)
(1) The flue-gas is treated in a SNOₓ plant
RFG and natural gas are co-fired with heavy fuel oil

Sources: [45a, Sema and Sofres, 1991], [247, UBA Austria, 1998] updated TWG NL 2010
Sootblowing is an operation that is carried out at regular intervals to remove soot from the furnace that is accumulating on the furnace equipment and hampers proper functioning. During this operation the PM content of the exhaust gas can reach values of 2000 mg/Nm$^3$. Abatement techniques installed for normal operations will be effective to reduce the PM emissions from this operation.

**Sulphur oxides**

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Heavy fuel oil residues normally contain significant proportions of sulphur and nitrogen, depending mainly on their source and the crude origin. Data from the last CONCAWE sulphur survey [ 63, CONCAWE 2010 ] show that the average SO$_2$ content in the flue-gas of refinery energy systems (from oil/gas firing) is 1350 mg/Nm$^3$ has been roughly reduced by a factor of almost two between 1998 and 2006. The weight average (site contributions being ponderated according to site productions) has been calculated to 594 mg/Nm$^3$.

Figure 3.33 gathers the SO$_2$ equivalent concentration (expressed as yearly average in mg/Nm$^3$ dry at 3% O$_2$) of all flue-gases emitted by the overall energy system of 34 European refineries. For each site, a summary of information is given on factors likely to influence SO$_2$ emissions from the concerned refinery combustion plants: the sulphur input from the overall feedstock, and the portion of total gaseous fuels (refinery fuel gas + eventual external natural gas supply) in the site energy mix. Most sites emit in the range 50 – 1500 mg/Nm$^3$. As expected, a clear correlation is observed between the highest gaseous fuel ratios in the site energy breakdown and the lowest SO$_2$ equivalent concentrations reported here.

![Figure 3.33: Distribution of SO$_2$ yearly average equivalent concentrations from the energy system of a sample of 34 European refineries](image-url)
55% of the flue gas from oil/gas that is burnt, is at less than 1000 mg/Nm$^3$.

### Table 3.71: Sulphur dioxide emissions ranges for existing European refineries

<table>
<thead>
<tr>
<th>Source</th>
<th>Range (mg/Nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process furnaces</td>
<td>3–1700</td>
</tr>
<tr>
<td>Boilers</td>
<td>3–1700</td>
</tr>
<tr>
<td>Turbines (@15% O$_2$)</td>
<td>3–1700</td>
</tr>
</tbody>
</table>

*The lower range relates to natural gas firing. Higher value corresponds to untreated refinery fuel gas without sulphur abatement.

#The lower range relates to combustion process of very low sulphur liquid refinery fuel with abatement technique. Higher value corresponds to liquid sulphur fuel (4.1%) without abatement.

Table 3.71: Sulphur dioxide emissions ranges for existing European refineries

In air-blown gasification of coke, the sulphur content will be about 4000 mg/Nm$^3$ per percent sulphur in the feed.

**Volatile organic compounds**

Fugitive VOC emissions may occur from storage of fuels as well as uncombusted fuels. No data have been made available on that. Note for the TWG: VOC data are gathered in Section 3.1.2.5

### 3.10.3.2 Waste water

Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. The waste water generated in the energy processes comes mainly from the boiler feed water (BFW) system. The main streams are the boiler blowdown (1 to 2% of the BFW intake) and the BFW preparation regeneration wash (2–6% of the BFW produced). The main pollutants and composition of the first stream are COD: 100 mg/l N-Kj; 0–30 mg/l PO$_4$; 0–10 mg/l. The BFW preparation regeneration stream is combined with NaOH/HCl for pH neutralisation. Normally no biotreatment is required.

### 3.10.3.3 Solid wastes generated

Releases to land may result from the routine collection of grit and dust and arisings during cleaning procedures. The composition is 0.5–1% w/w Ni and 2–3% w/w V in furnaces and 1–3% Ni/V for boilers. The amount depends on the furnace design and the liquid fuel quality, but in boilers varies from zero to 10 tonnes per year. Liquid refinery fuel tank bottom sludge and bundle cleaning sludge are generated in the storage tanks. The flow depends on the liquid refinery fuel quality and the presence of fuel tank mixers. Depending on the mode of draining, 20–80% is oil.

### 3.11 Etherification

KOM conclusion 3.6: TWG to update etherification processes and techniques, notably TAME and other C5/C6 ethers (for BREF sections 2.11 and 3.11)

⇒ Info expected from industry and SK: No extra info made available

**Consumptions**

The etherification reaction is exothermic and cooling to the proper reaction temperature is critical in obtaining optimal conversion efficiency. Methanol is needed for the production of these ethers. The utility consumptions in Table 3.72 are specified per tonne of MTBE processed in an oxygenate unit.
Table 3.7: Utility requirements in the etherification processes

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 – 20</td>
<td>1000 – 2000</td>
<td>2 – 8</td>
</tr>
</tbody>
</table>

**Emissions**

*Air emissions*
Potential releases into air are of hydrocarbons into air come from pressure reliefs on vessels, depentaniser column overheads drum and distillation column reflux drum, methanol plant, steaming vents on scavengers and reactor catalyst.

*Waste water*
Potential releases into water are of hydrocarbons, methanol and ethers to water come from spillages and water bleed from methanol recovery. The water bleed is generated at a flow of 1 – 2 m³/t and with a composition of COD: 50 – 200 mg/l and a N-Kj: 5 – 20 mg/l. Some components that can be found in this waste water are methanol (ethanol), ethers and formic acid (acetic acid).

*Solid wastes generated*
Waste generated is the spent catalyst/resin with no possibility of regeneration. Every two years, it should be changed and steamed to flare before recycling. The catalyst is recycled for recovery of its palladium content. Some efforts in the recycling of the resin have not successful.

### 3.12 Gas separation processes

**Consumptions**
The electricity demand of a gas separation process varies between 15 and 20 kWh per tonne of feedstock processed. These processes also consume between 300 and 400 kg of steam per tonne of feedstock and between 1 and 2 m³/t of cooling water (ΔT=10°C).

**Emissions**

*Air emissions*
Potential releases into air include hydrocarbons from pressure reliefs on vessels, regeneration vent gas from molecular sieves, C₁/C₂ refinery fuel gas, refrigeration system leaks, storage and handling operations. Mercury if present in the feedstock of the refinery, will concentrate in overhead sections, particularly coolers. LPG, tops and naphtha coolers are most likely involved. Steaming that contaminated equipment may give mercury emissions to atmosphere. Mercury is sometimes found upon opening equipment for inspection and maintenance.

The final process in LPG production is the addition of some odorants. The odorants used are typically volatile organic sulphur compounds, i.e. mercaptans and sulphides. Potential releases into air include leaks or spillages of odorant and vapours displaced during tank filling or from thermal expansion of blanket gas. They also include the displaced vapours residue products if these techniques are used, including a small release of sulphur dioxide from combustion of the odorant.

*Waste water*
Potential releases into water include spillages of hydrocarbons, H₂S, NH₃ and amines.

*Solid wastes generated*
Potential releases into land include hydrocarbons from contaminated spent molecular sieves and from odorant addition including solid waste such as materials used to absorb odorant spillage.
3.13 Hydrogen-consuming processes

Consumptions
In this section, two groups of processes have been included: hydrocracking and hydrotreatments. Both types of processes are catalytic and consume hydrogen. Table 3.73 shows approximate hydrogen consumption for hydrotreatment and hydrocracking of various feedstocks.

Table 3.73: Hydrogen consumption data

<table>
<thead>
<tr>
<th>Process</th>
<th>% S w/w in crude</th>
<th>% S w/w in feed</th>
<th>Nm³ of H₂ per tonne of feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep atmospheric residue conversion</td>
<td>1 – 2</td>
<td>2 – 3.5</td>
<td>260 – 500</td>
</tr>
<tr>
<td>Hydrocracking vacuum gas oil</td>
<td>0.5 – 0.8</td>
<td>2 – 3</td>
<td>260 – 400</td>
</tr>
<tr>
<td>Cycle oil hydrogenation</td>
<td>0.3</td>
<td>3</td>
<td>370</td>
</tr>
<tr>
<td>Hydrotreating</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCC naphtha/coker naphtha</td>
<td>0.05 – 0.01</td>
<td>1</td>
<td>110</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.1 – 0.02</td>
<td>0.1</td>
<td>11</td>
</tr>
<tr>
<td>Straight-run naphtha</td>
<td>0.01</td>
<td>0.05</td>
<td>4</td>
</tr>
<tr>
<td>Hydrodesulphurisation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCC gas oil/coker gas oil</td>
<td>0.1</td>
<td>1</td>
<td>130</td>
</tr>
<tr>
<td>High-sulphur gas oil to 0.05 % S</td>
<td>0.05</td>
<td>0.35</td>
<td>200</td>
</tr>
<tr>
<td>High-sulphur gas oil to 0.2 % S</td>
<td>0.04</td>
<td>0.3</td>
<td>44</td>
</tr>
<tr>
<td>Low-sulphur gas oil to 0.05 % S</td>
<td>0.04</td>
<td>0.15</td>
<td>17</td>
</tr>
<tr>
<td>Low-sulphur gas oil to 0.2 % S</td>
<td>0.03</td>
<td>0.1</td>
<td>13</td>
</tr>
<tr>
<td>Hydroconversion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal content &lt;500 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: [166, Meyers, 1997], [118, VROM, 1999]

3.13.1 Hydrotreatments

Hydrotreatment units consumptions
The H₂ consumption, and consequently the energy requirement, significantly increase in the order naphtha (0.05 % H₂), distillate (0.3 % H₂) and residue hydrotreating (1.8 % H₂). Table 3.74 shows the utility requirements for different hydrotreatments.

Table 3.74: Utility requirements for different hydrotreatments

<table>
<thead>
<tr>
<th>Process</th>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10°C)</th>
<th>Wash water (kg/t)</th>
<th>H₂ (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha processed</td>
<td>200 – 350</td>
<td>5 – 10</td>
<td>10 – 60</td>
<td>2 – 3</td>
<td>40 – 50</td>
<td>1 – 15</td>
</tr>
<tr>
<td>Distillate processed</td>
<td>300 – 500</td>
<td>10 – 20</td>
<td>60 – 150</td>
<td>2 – 3</td>
<td>30 – 40</td>
<td>1 – 15</td>
</tr>
<tr>
<td>Residue processed</td>
<td>300 – 800</td>
<td>10 – 30</td>
<td>60 – 150</td>
<td>2 – 3</td>
<td>30 – 40</td>
<td>10 – 100</td>
</tr>
<tr>
<td>Hydroconversion</td>
<td>600 – 1000</td>
<td>50 – 110</td>
<td>200 – 300 (steam produced)</td>
<td>2 – 10</td>
<td>=</td>
<td>=</td>
</tr>
</tbody>
</table>

Note: Hydroconversion is an exothermic reaction and the heat generated in the reactor system is partially recovered in the feed product exchanger. Already in table 3.75
Source: [45a, Sema and Sofres, 1991], [118, VROM, 1999]

Table 3.75: Catalysts used in hydrotreatments

<table>
<thead>
<tr>
<th>Process</th>
<th>Composition</th>
<th>Cycle lengths/average consumption (t/ Mt feedstock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodesulphurisation</td>
<td>CoO/MoO₃/Al₂O₃</td>
<td>1 year/46</td>
</tr>
<tr>
<td>Denitritification</td>
<td>Ni/Mo catalyst</td>
<td>↓ 2 – 6 years/46</td>
</tr>
<tr>
<td>Demethalisation</td>
<td>NA</td>
<td>&lt;1 year/NA</td>
</tr>
<tr>
<td>Saturation of olefins and aromatics</td>
<td>Ni/ Mo catalyst</td>
<td>1 year/NA</td>
</tr>
<tr>
<td>Hydrogenation of light dienes</td>
<td>NA</td>
<td>2 years/NA</td>
</tr>
</tbody>
</table>
Chapter 3

Emissions from hydrotreatment units

Emissions to air

Air emissions from hydrotreating may arise from process heater flue-gas (dealt with in Section 3.10), vents, fugitive emissions and catalyst regeneration (CO₂, CO, NOₓ, SOₓ). The off-gas stream may be very rich in hydrogen sulphide and light fuel gas. The fuel gas and hydrogen sulphide are typically sent to the sour gas treatment unit and sulphur recovery unit. Hydrocarbons and sulphur compounds may be emitted to air from pressure relief valves; leakages from flanges, glands and seals on pumps, compressors and valves, particularly on sour gas and sour water lines; venting during catalyst regeneration and replacement procedures or during cleaning operations. The following Table 3.76 show two examples of emissions from hydrotreating processes. These air emissions include the emissions generated by the combustion of fuel required in these processes.

Table 3.76: Examples of air emission generated by hydrotreatment units

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO</th>
<th>CO₂</th>
<th>Particulates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha hydrotreater</td>
<td>1 160 000 mg/m³</td>
<td>Naphtha 205.9 t/yr</td>
<td>142</td>
<td>15</td>
<td>2</td>
<td>40152</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 780 000 mg/m³</td>
<td>Kerosene. GO 135.8 t/yr</td>
<td>8.1</td>
<td>33</td>
<td>0.7</td>
<td>26341</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 820 000 mg/m³</td>
<td>VGO 72.4 t/yr</td>
<td>51.6</td>
<td>32.6</td>
<td>0.7</td>
<td>19466</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Middle distillate</td>
<td>34 000 000 mg/m³</td>
<td>Naphtha 205.9 t/yr</td>
<td>7.1</td>
<td>20.3</td>
<td>20.3</td>
<td>39 937</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>72 000 000 mg/m³</td>
<td>GO 205.9 t/yr</td>
<td>7.1</td>
<td>20.3</td>
<td>20.3</td>
<td>39 937</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum distillate</td>
<td>VGO 578.2 t/yr</td>
<td>18.6</td>
<td>53.2</td>
<td>53.2</td>
<td>164 776</td>
<td>2.7</td>
<td></td>
</tr>
</tbody>
</table>

(‘) Raw gas was treated in a flue-gas desulphurisation (Wellman Lord)
Data are related to yearly average, 3% O₂, dry conditions.
(‘) Since 2010, Schwechat refinery use only gas (except for SNO₂ power plant unit) with the following emissions
SO₂: 1 – 20 mg/Nm³
NOₓ: <100 mg/Nm³
CO: <80 mg/Nm³
PM: <1 mg/Nm³
Source: [250, Winter, 2000] updated TWG 2010

Table 3.76: Examples of air emission generated by hydrotreatment units

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO</th>
<th>CO₂</th>
<th>Particulates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha hydrotreater</td>
<td>1 500 000 mg/m³</td>
<td>Naphtha 205.9 t/yr</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>39 937</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 000 000 mg/m³</td>
<td>GO 205.9 t/yr</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>39 937</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum distillate</td>
<td>VGO 578.2 t/yr</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>39 937</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

NB: Emissions are only limit values. Loads and specific emissions were calculated.
Data are related to yearly average, 3% O₂, dry conditions.
Waste water
Hydrotreating and hydroprocessing generate a flow of waste water of 30 – 55 l/tonne. The waste water contains H₂S, NH₃, high pH, phenols, hydrocarbons, suspended solids, BOD and COD. This process sour water and should be sent to the sour water stripper/treatment. Potential releases into water include HC and sulphur compounds from spillages and leaks, particularly from sour water lines. In distillate hydrotreatments, solid deposits such as (NH₄)₂SO₄ and NH₄Cl are formed in the cooler parts of the unit and must be removed by water wash.

Solid wastes generated by hydrotreatments
These processes generate spent catalyst fines (aluminium silicate and metals Co/Mo and Ni/Mo 50 – 200 t/yr for 5 Mt/yr refinery). For process units using expensive catalysts, contracts with the supplier exist for taking the spent catalyst back for regeneration and/or recycling. This practice is also being adopted for other types of catalysts. During the last 20 years the use of catalytic processes has increased considerably and hence also the regeneration and rework services, particularly for Ni/Mo and Co/Mo hydrotreating catalysts. Molecular sieve beds are sometimes used to capture the water content of some streams (e.g. distillate hydrodesulphurisation).

3.13.2 Hydrocracking
Consumptions of hydrocracking units
Hydrocracking is an exothermic process. The heat generated in the reactors is partially recovered in a feed/product heat exchanger. A significant amount of heat is required in the fractionation section. Catalysts used in this process are typically cobalt, molybdenum, nickel or tungsten oxides impregnated on alumina. Fluorided alumina, activated clay, silica-alumina or zeolites are also present. Average consumption of catalysts is 57.4 t/Mt of feedstock. A small amount of coke-like material is formed which accumulates over time on the catalyst. This deactivates the catalyst, requiring regeneration off-site every one to four years by burning off the coke. Water is removed by passing the feed stream through a silica gel or molecular sieve dryer. The utility requirements for hydrocracking are the following:

Table 3.77: Utility consumption of hydrocracking units

<table>
<thead>
<tr>
<th></th>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam produced (kg/t)</th>
<th>Cooling water (m³/t, ΔT=17°C (*ΔT=10°C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocracking</td>
<td>400 – 1 200</td>
<td>20 – 150</td>
<td>30 – 300</td>
<td>10 – 300</td>
</tr>
<tr>
<td>Hydroconversion</td>
<td>600 – 1 000</td>
<td>50 – 110</td>
<td>200 – 300</td>
<td>2 – 10</td>
</tr>
</tbody>
</table>

Source: [45a, Sema and Sofres, 1991], [118, VROM, 1999]

Emissions from hydrocracking units

Emissions to air
Heater stack gas contains CO, SOₓ, NOₓ, hydrocarbons and particulates that generate smoke, grit and dust in flue-gas (covered in Section 2.10), fugitive emissions (hydrocarbons) and catalyst regeneration (CO₂, CO, NOₓ, SOₓ, and catalyst dust). Fuel gas and bleed stream will contain H₂S and should be further treated. VOCs are generated by the non-condensable from vacuum ejectors set-condensors.

Waste water
Hydrocracking generates a flow of waste water of 50 – 110 l per tonne processed. It contains high COD, suspended solids, H₂S, NH₃ and relatively low-levels of BOD. The sour water from the first stage HP separator, LP separator, and overhead accumulator should be sent to the sour water stripper/treatment. Effluents from hydroconversion processes may occasionally contain metals (Ni/V).
Chapter 3

Solid wastes

Hydrocracking also generates spent catalysts fines (metals from crude oil, and hydrocarbons). Catalyst should be replaced once every one to three years generating an average of 50 – 200 t/yr for a refinery of 5 Mt/yr. Hydroconversion normally generates between 100 and 300 t/yr of spent catalysts which contain more heavy metals than hydrocracking catalysts.

3.14 Hydrogen production

Consumptions

Steam reforming

The steam reformer has to supply a large amount of heat at high temperature for the steam reforming reaction by burning fuel, with the result that a large amount of heat is lost in the flue gas. Hydrogen plants are one of the most extensive users of catalysts in the refinery. Typical utility requirements for steam reforming plant feeding natural gas are given in Table 3.78 (no electrical power for compression is required). Global fuel consumption of a unit includes the one for hydrogen production plus that associated with steam export to nearby installations.

Fuel requirement values indicated in Table 3.78, are these associated with hydrogen production strictly. They refer to large sized equipment (50 000 Nm³/h of H₂ or more). Achieving such values requires both to use the technique described further in Section 4.14.1 (preheating feed process, steam superheating, combustion air preheating) and to use PSA separation process in order to recover energy contained in by-products, mainly CO, fed back to burners (up to 90% recovery of the required energy for steam reforming).

As more and more steam is produced and exported, total energy requirements can be higher. Values of the electricity requirement do not include product compression. Neither is cooling for such compressors included in the values presented for water cooling utility.

Table 3.78: Utility requirements for steam reforming (large sized recent equipment)

<table>
<thead>
<tr>
<th>Fuel (MJ/t H₂)</th>
<th>Electricity (kWh/t)</th>
<th>Steam produced (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 000 – 80 000</td>
<td>800 – 1 200</td>
<td>2 000 – 8 000</td>
<td>50 – 300</td>
</tr>
<tr>
<td>20 000 – 30 000</td>
<td>200 – 400</td>
<td>200 – 400</td>
<td>25 – 100</td>
</tr>
</tbody>
</table>

Source: [45a, Sema and Sofres, 1991] TWG 2010 (EIGA)

and On average these processes produce 2 600 3 000 – 3 600 Nm³ of hydrogen (240 – 310 kg) per tonne of feedstock. Catalyst for reforming is 25 – 40% nickel oxide deposited on a low-silica refractory base. The catalyst used in the reformer furnace is not regenerable and is replaced every four or five years. Longer lifetime can be achieved when feed is light, such as CH₄, of constant quality and the catalyst is well sulphur-protected. Lifetime doubling may be achieved, especially when desulphurised feed is first fed to a pre-reformer unit installed upstream of the reformer.

A refinery with a capacity of five million tonnes of crude per year will consume 50 tonnes per year.

The composition of the product depends on the purification technique, as shown in Table 3.79.

Table 3.79: Composition of product hydrogen in steam reforming

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wet scrubbing technique</th>
<th>Pressure-swing adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen purity, % v/v</td>
<td>95 – 97</td>
<td>99 – 99.99</td>
</tr>
<tr>
<td>Methane, % v/v</td>
<td>2 – 4</td>
<td>100 ppm v/v</td>
</tr>
<tr>
<td>CO+CO₂, ppm v/v</td>
<td>10 – 50</td>
<td>10 – 50</td>
</tr>
<tr>
<td>Nitrogen, % v/v</td>
<td>0 – 2</td>
<td>0.1 – 1.0</td>
</tr>
</tbody>
</table>

Source: [166, Meyers, 1997]
Coke gasification

Coke gasification produces between 2 600 and 3 500 Nm$^3$ of hydrogen (210 – 300 kg) per tonne of coke gasified. Figure 3.34 shows a scheme of the hydrogen production from a coke gasifier and the amount of hydrogen produced per tonne of petroleum coke.

![Coke gasification diagram](image)

Figure 3.34: Petroleum coke commercial process

Heavy fuel gasification

Bitumen and heavy fuel can be gasified. Bitumen characteristics that have been used in the gasification are shown in next table.

Table 3.80: Bitumen characteristics that can be used as partial oxidation feedstock

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15 ºC</td>
<td>1.169</td>
<td>kg/l</td>
</tr>
<tr>
<td>Carbon</td>
<td>85.05</td>
<td>% w/w</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>8.10</td>
<td>% w/w</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.80</td>
<td>% w/w</td>
</tr>
<tr>
<td>Sulphur</td>
<td>6.00</td>
<td>% w/w</td>
</tr>
<tr>
<td>Ash</td>
<td>0.05</td>
<td>% w/w</td>
</tr>
<tr>
<td>Vanadium</td>
<td>600</td>
<td>ppm</td>
</tr>
<tr>
<td>Nickel</td>
<td>200</td>
<td>ppm</td>
</tr>
</tbody>
</table>

Source: [166, Meyers, 1997]

Air emissions

Steam reforming

NO$_x$ emissions are the most important to consider. Other emissions such as SO$_x$ or water emissions are minimal, because low-sulphur fuel is typically used and there are few emissions other than flue-gas. The choice of heat recovery system can have a major effect on NO$_x$ production, since both the amount of fuel fired and the flame temperature will be affected. NO$_x$ emissions from a steam reforming unit using gas or light gasoline as fuels and with low-NO$_x$ burners are 25 – 40 mg/MJ (100 – 140 mg/Nm$^3$, 3 % O$_2$) [107, Janson, 1999]. Other emissions, such as CO$_2$, originate from carbon in the feed.
Chapter 3

**Coke gasification**

Sulphur sorbents, such as limestone (CaCO$_3$) or dolomite (Mg, Ca carbonate), are normally used in the gasifier, drastically reducing the sulphur content. Sulphur composition in the exhaust gas ranges from 600 to 1 200 mg/Nm$^3$ of H$_2$S and COS. If no sorbent is used, the sulphur content of the gas will be in proportion to the sulphur in the feed. In oxygen-blown gasification, the sulphur content will be about 10 000 mg/Nm$^3$ per percent sulphur in the feed. Ammonia is formed in the gasifier from the fuel-bound nitrogen. Ammonia in the product gas typically contains less than 5 % of the fuel-bound nitrogen when limestone is present in the gasifier.

**Heavy fuel gasification**

For the Mider Refinery, data are available concerning air emissions of the partial oxidation unit and are given in Table 3.81.

**Table 3.81: Example of air emissions generated by heavy fuel gasification**

<table>
<thead>
<tr>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>SO$_2$</th>
<th>NO$_x$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>Particulates</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 452.8</td>
<td>670 000</td>
<td>mg/m$^3$</td>
<td>35</td>
<td>158</td>
<td>100</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>t/yr</td>
<td></td>
<td>t/yr</td>
<td>243.4</td>
<td>1099</td>
<td>695.5</td>
<td>475 843</td>
<td>34.8</td>
</tr>
<tr>
<td>kg/t feed</td>
<td></td>
<td>kg/t feed</td>
<td>0.363</td>
<td>1.64</td>
<td>1.038</td>
<td>710</td>
<td>0.052</td>
</tr>
</tbody>
</table>

NB: For the emissions only limit values are given. Loads and specific emissions were calculated.

Data are related to yearly average, 3 % O$_2$, dry conditions

Source: [247, UBA Austria, 1998]

**Solid waste**

**Coke gasification**

The solid waste from the process consists mainly of spent limestone and metals from the petcoke. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm. Volatile metals and alkalis tend to accumulate on the particulate as the gas is cooled. The particulates contain a high percentage of carbon and are usually sent with the ash to a combustor, where the remaining carbon is burned and the calcium sulphide is oxidised to sulphate. In this hot-gas clean-up system, there is no aqueous condensate produced, although some may be produced in subsequent processing of the gas. The solid waste from the process consists mainly of spent limestone and metals from the petcoke. After processing in the combustor/sulphator, this material is sent to disposal. Vanadium and nickel are found in most petroleum cokes in concentrations far greater than in coals or lignites. They remain in the ash product.

**Hydrogen purification**

Several adsorber beds are used, and the gas flow is periodically switched from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is normally accumulated in a vessel and used as fuel at a convenient location.

**3.15 Integrated refinery management**

**Emissions from European Refineries as a whole**

Next calculations are based on SO$_2$ emissions from 76 European refineries (annual figures) in 1998 (CONCAWE). The refinery emissions of 387 ktonnes comprise 7.4 % of the global sulphur intake from feedstock (ranging from 2 % to 10 %).

The breakdown of these annual emissions globally for the Western European sites is about:
• 65% from the combustion, representing a consumption of 28.5% liquid fuel of 1.7% S content and 65% of fuel gas
• 13% from the FCC units
• 11% from the sulphur recovery units
• and the 11% complementary % from flare and miscellaneous sources.
Bubble values are based on calculated (*) yearly averages for all refineries participating: total emissions divided by total (calculated stoichiometric required) flue gas emitted. Thus \( \sum (S_{\text{unit1}} + S_{\text{unit2}} + S_{\text{FCC}} + S_{\text{SRU}} + S_{\text{FLARE}}) \) divided by \( \sum \) (Volume flue gas resulting from burning different types of fuels). The results are shown in next table:

<table>
<thead>
<tr>
<th>Bubble values (mg/Nm(^3))</th>
<th>European</th>
<th>ATL-area</th>
<th>MED-area</th>
<th>NWE-area</th>
<th>OTH-area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global average</td>
<td>1600</td>
<td>&gt;2000</td>
<td>&gt;2200</td>
<td>&lt;700</td>
<td>&lt;400</td>
</tr>
<tr>
<td>Combustion weighted average</td>
<td>1000</td>
<td>1290</td>
<td>1540</td>
<td>570</td>
<td>310</td>
</tr>
<tr>
<td>Geographical contribution of the areas (% FOE)</td>
<td>100%</td>
<td>26%</td>
<td>25%</td>
<td>30%</td>
<td>10%</td>
</tr>
</tbody>
</table>

Expressed in term of 'Global Average Bubble', the mass of sulphur emitted per volume of flue gas calculated for the reporting sites represents an annual Western European average concentration of 1600 mg/Nm\(^3\), all units of the refineries included for all types of refineries.

Expressed in term of 'Combustion Bubble' only due to fuels burned within the refinery site, thus excluding FCC and SRU. the distribution of calculated annual value of each individual site is reported in a graph according to their respective and cumulative contribution to the total fuel use in Europe.

The geographical splitting in the three major zones confirms variation between areas, representative of these different operational conditions through Europe.

The results of last three surveys from years 1992, 1995 and 1998 are given in Figure 3.35, a weighted average for the annual bubble of 1000 mg/Nm\(^3\) is calculated representing a significant decrease from previous surveys for which the average combustion bubble was 1350 mg/Nm\(^3\).

![Calculated annual combustion bubble for European refineries](image)

**Figure 3.35:** Historical and distribution trend of calculated annual SO\(_2\) combustion bubble for EU refineries

The four areas are:
- **NWE** – Northwest Europe (mainland France, United Kingdom, Belgium, the Netherlands, Germany and Denmark)
- **ATL** – Atlantic (Ireland, Portugal and the Atlantic coasts of France and Spain)
- **MED** – Mediterranean (Spain, the med coast of France, Italy and Greece)
- **OTH** – Others (Norway, Sweden, Finland, Austria, Hungary and Switzerland)
Chapter 3

Source: CONCAWE surveys
The lower part of the curves represents sites which are combining:

- burning more gas than liquid fuels
- lower sulphur content in liquid fuel used
- high sulphur content marketed products
- and/or control techniques of SO₂ emissions.

Then it is a combination of what kind of operating window they have been running in (crude/feedstock, supply and demand situation, plant design limitations, etc.) and the local availability of refinery fuels and natural gas for burning in the refinery. It is only in this complex context that any reference to ‘good’ performance should be seen.

Refinery management activities
Emission integrated management
Some of the air emissions issues are by its nature refer to many processes or activities than consequently can be considered as a refinery as a whole issue. Under these issues, we can include sulphur emissions and VOC emissions.

Emissions in abnormal circumstances
Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard. Emergency situations are normally regulated in the refinery permit. Quantification of these emissions is difficult.

Start-up and shutdown
Conditions such as start-up and shutdown operations occur fairly infrequently, and are normally of short duration. Modern designs include fully automated fail-safe start-up and shutdown systems with interlocks to maximise safety and to minimise risk and emissions. Start-up and shutdown of a full refinery or part of the installation may result in substantial emissions to atmosphere, mainly VOC, SO₂, CO₂ and particulates. Effluent drainage and treatment facilities could also be temporarily overloaded. Refinery design and operational constraints call for safe and environmentally acceptable management and disposal of emissions, discharges and waste in upset conditions. Start-up and shutdown procedures, and hence emissions and discharges, vary according to the type of unit and the purpose of the shutdown. If a particular unit is only to be depressurised and heavy components flushed out for a temporary stop, the emissions will be far less than if all equipment must be purged, steamed out and filled with air to allow workers to enter. Stringent safety and health care procedures are normal practice in present-day refineries. Not only personnel but also contractors have to adhere to these procedures. Nevertheless, occasional accidents take place and safety precautions should be practised regularly. Shutdown or blowdown can also have an impact on neighbouring dwellings (noise and light flaring).

Heat exchangers cleaning
The bundles of heat exchangers are cleaned periodically to remove accumulations of scale, sludge and any oily wastes. Because chromium has almost been eliminated as a cooling water additive, wastes generated from the cleaning of heat exchanger bundles no longer account for a significant portion of the hazardous wastes generated at refining facilities. The sludge generated (oil, metals and suspended solids) may contain lead or chromium, although some refineries which do not produce leaded gasoline and which use non-chrome corrosion inhibitors typically do not generate sludge that contains these constituents. Oily waste water is also generated during heat exchanger cleaning. VOC emissions may occur during these processes.

Utilities management
Water management
Surface water run-off is intermittent and will contain constituents from spills to the surface, leaks in equipment and any materials that may have collected in drains. Run-off surface water also includes water coming from crude and product storage tank roof drains.
The daily sanitary waste water production of an individual is about 120 litres, so the total sanitary effluent of the refinery can be easily calculated. Normally this domestic effluent is collected in a septic tank and then treated in the waste water treatment plant.

Ballast water is relevant to these refineries that have crude receipt facilities or handle large product tankers or inland barges. This ballast water can be high in volume and salt content (seawater), and heavily polluted with oil. It can easily lead to an upset of existing effluent treatment systems. The use of ballast water tanks is therefore an important equalisation tool for feeding the water in a controlled way to either the process water system or the continuously oil-contaminated system, if the COD is lower than 100 ppm. As more and more tankers are equipped with segregated ballast tanks, the ballast water problem is slowly phasing out.

Water used in processing operations also accounts for a significant portion of the total waste water. Process waste water arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Because process water often comes into direct contact with oil, it is usually heavily contaminated and requires adequate treatment before reuse or discharging.

The water usage depends both on purpose and complexity of the refinery. While there are usually opportunities to economise on water use, the scope for major reductions in existing refineries is sometimes limited. Sixty three European refineries gave the following data on water usage (data in annual averages).

<table>
<thead>
<tr>
<th>Metric</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual average fresh water usage</td>
<td>4.2 million tonnes/year</td>
</tr>
<tr>
<td>Range</td>
<td>0.7 to 28 million tonnes/year</td>
</tr>
<tr>
<td>Average refinery throughput</td>
<td>6.9 million tonnes/year</td>
</tr>
<tr>
<td>Average water usage per tonne throughput</td>
<td>0.62 tonne/tonne throughput</td>
</tr>
<tr>
<td>Range</td>
<td>0.01 to 2.2 tonne/tonne throughput</td>
</tr>
</tbody>
</table>

The recorded fresh water consumption is that taken from:

- Potable (mains) water
- River water
- Privately extracted groundwater (including in some cases contaminated groundwater extracted for purposes of treatment)

It does not include:

- Recycled final effluent
- Storm water
- Ballast water from ships
- Waste water from adjoining facilities
- Seawater

**Blowdown systems**

The gaseous component of the blowdown system typically contains hydrocarbons, hydrogen sulphide, ammonia, mercaptans, solvents and other constituents, and is either discharged directly to the atmosphere or is combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulphur oxides when flared. The liquid is typically composed of mixtures of water and hydrocarbons containing sulphides, ammonia and other contaminants, which are sent to the waste water treatment plant.

Seal drum blowdown generates an effluent of 1 – 2 m³/h and 10 times as much in the case of emergency, with a composition of: COD, 500 – 2 000 mg/l, H₂S, 10 – 100mg/l, phenol, 5 – 30 mg/l, NH₃, oil and suspended solids, 50 – 100 mg/l.
3.16 Isomerisation

The main environmental problems for isomerisation, apart from the energy consumption, are the catalyst promotion and the reduction of possible side-effects.

Consumptions
The total energy requirement depends mainly on the isomerisation catalyst technology used, the configuration including hydrogen recycle, on the hydrocarbon recycle operation (2 – 2.5 times higher than once-through), and the technology used to separate the n-paraffins; absorption/desorption process or a deisohexaniser column. The isomerisation processes require an atmosphere of hydrogen to minimise coke deposits but the consumption of hydrogen is negligible. The utility requirements for the isomerisation process vary widely depending on the design options. An example of the utility requirements for an isomerisation process is shown in Table 3.82:

Table 3.82: Utility requirements in the isomerisation processes

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, T=10°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 – 30</td>
<td>300 – 600</td>
<td>10 – 15</td>
</tr>
</tbody>
</table>

Catalyst life can range from two to more than ten years depending on unit operation. The chloride promoted catalyst (chlorinated alumina containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activities, to avoid catalyst deactivation and potential corrosion problems. See Section 2.16 for further information about the type of catalysts used.

Table 3.83 shows the utility and chemical requirements for the adsorption process for a feed rate of 600 tonnes per day.

Table 3.83: Utilities and chemical requirements of an adsorption process

<table>
<thead>
<tr>
<th>Utilities and chemical requirements of the adsorption process</th>
<th>Value (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel consumed (90 % furnace efficiency) MW</td>
<td>9</td>
</tr>
<tr>
<td>Water (ΔT = 17 °C), m³/day</td>
<td>2159</td>
</tr>
<tr>
<td>Power, kWh</td>
<td>1455</td>
</tr>
<tr>
<td>Steam at 10,5 kg/cm², saturated, kg/h</td>
<td>2.8</td>
</tr>
<tr>
<td>Hydrogen consumption, Nm³/day</td>
<td>17.7</td>
</tr>
<tr>
<td>Soda consumption (kg)</td>
<td>8.4</td>
</tr>
<tr>
<td>Hydrogen chloride (kg)</td>
<td>6</td>
</tr>
<tr>
<td>Catalyst consumption (kg)</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Source: [166, Meyers, 1997], [337, Journal, 2000]

Emissions

Air emissions
Air emissions may arise from the process heater (used in some designs), vents and fugitive emissions. Emissions from process heaters are analysed in Section 0. Other emissions are HCl (potentially in light ends from organic chloride added to maintain catalyst activity), vents and fugitive emissions, pressure reliefs on surge drum, separators and column reflux drum, regeneration vent gas from dryers, storage and handling operations, spillage (hydrocarbons). Releases of hydrogen may occur from pressure relief on the hydrogen system. Product stabilisation, however, does result in small amounts of LPG (C₃+C₄, rich in i-C₄) and in stabiliser vent (H₂+C₁+C₂) products. The stabiliser vent products are usually used as refinery fuel. In the chlorided-alumina catalyst isomerisation design, fuel gas is normally caustic-treated to remove HCl.
Chapter 3

Process waste water
Potential releases into water include hydrocarbons from the reflux drum boot drain and spillages. With the chlorided alumina isomerisation catalyst design, additional waste water is generated by spent sodium hydroxide from the scrubber system. In this design, the process waste water contains chloride salts, caustic wash, relatively low traces of H$_2$S and NH$_3$ and has high pH. Brine from the feed dryer (desiccant, water free CaCl$_2$) contains dissolved CaCl$_2$ and hydrocarbons. Its flow depends on moisture content and is usually drained to the effluent treatment plant.

Residual wastes generated
Potential releases to land include hydrocarbons from spillages/contaminated molecular sieves and catalyst. Calcium chloride sludge (or other desiccants) is the waste generated in this process. Catalyst used in these processes normally is regenerated by the catalyst manufacturers. Platinum is then recovered from the used catalyst off-site. Molecular sieves can be used as feed drying agent. The flow and composition are plant-specific and the spent molecular sieves are disposed of as non-regenerable solid waste.

3.17 Natural gas plants

Consumptions
Water and energy consumption within a natural gas plant is shown in Table 3.84:

Table 3.84: Example of utility consumption in natural gas plants

<table>
<thead>
<tr>
<th>Water and Energy consumption</th>
<th>Existing plant (Kårstø Plant)</th>
<th>New Plant (Ormen Lange Plant at Nyhamna)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>88 million Nm$^3$/day of rich gas 840 t/h unstabilised condensate</td>
<td>70 million Nm$^3$/day export gas 8 400 Nm$^3$/day condensate</td>
</tr>
<tr>
<td>Fuel gas</td>
<td>60 tonnes/h at full capacity</td>
<td>8 tonnes/h</td>
</tr>
<tr>
<td>Power (gas power)</td>
<td>775 MW</td>
<td>2 x 42.1 MWth installed</td>
</tr>
<tr>
<td>Water (steam production)</td>
<td>60 m$^3$/h</td>
<td>NA</td>
</tr>
<tr>
<td>Seawater cooling</td>
<td>44 000 m$^3$/h</td>
<td>14 400 Nm$^3$/h (Energy flux ~160 MW for normal operations)</td>
</tr>
</tbody>
</table>

(*) Norske Shell operates the gas plant at Nyhamna for the processing of gas and condensate from the Ormen Lange gas field offshore Norway

Source: [290, Statoil, 2000] Updated TWG NO 2010

Emissions

Emissions to air
The major emission sources in the natural gas processing industry are compressors, boilers and furnaces, acid gas wastes, fugitive emissions from leaking process equipment and, if present, glycol dehydrator vent streams. Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethylbenzene and xylene, as well as a wide range of less toxic organics.

Potential release routes for prescribed substances and other substances which may cause harm are shown in Table 3.85.

Emissions of SO$_2$ will result from gas sweetening plants only if the acid waste gas from the amine process is flared or incinerated. Most often, the acid waste gas is used as a feedstock in nearby sulphur recovery (see Section 4.25.5.2) or sulphuric acid plants. When flaring or incineration is practised, the major pollutant of concern is SO$_2$. Most plants employ elevated smokeless flares or tail gas incinerators for complete combustion of all waste gas constituents, including virtually 100 percent conversion of H$_2$S to SO$_2$. Little results from these devices in the
way of particulates smoke or hydrocarbons and, because gas temperatures do not usually exceed 650 ºC, no significant quantity of nitrogen oxides is formed. Emission factors for gas sweetening plants with smokeless flares or incinerators are presented in Table 3.86. Factors are expressed in units of kilograms per 1 000 cubic metres. Emission data for sweetening processes other than amine types are very meagre, but a sulphur mass balance will give accurate estimates for sulphur dioxide (SO₂).

Table 3.85: Releases to the environment commonly associated with the natural gas processes

<table>
<thead>
<tr>
<th>Type of process</th>
<th>H₂S</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO₂</th>
<th>CO</th>
<th>Organic compounds</th>
<th>Oily waters</th>
<th>N₂</th>
<th>Spent catalysts/adsorbents</th>
<th>Sand/corrosion products</th>
<th>Acids/alkalis/salts, etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-shore reception</td>
<td>A(*)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas treatment processes</td>
<td>A(*)</td>
<td>A</td>
<td>A</td>
<td>AW</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid gas processes</td>
<td>A(*)</td>
<td>A</td>
<td>A</td>
<td>AW</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen removal</td>
<td>A(*)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon removal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas compression</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Condensate treatment</td>
<td>A</td>
<td>A</td>
<td>AW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L</td>
<td></td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>Field water treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>W</td>
<td></td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>Flares/vents</td>
<td>A(*)</td>
<td>A(*)</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas storage sites</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>AW</td>
<td>W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) If sour gas is being processed
NB: A: air, W: water, L: land
Source: [144, HMIP UK, 1997]

Table 3.86: Emission factors for gas sweetening plants

<table>
<thead>
<tr>
<th>Amine process</th>
<th>kg/10³ Nm³ gas processed</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>SOₓ (as SO₂)</td>
<td>26.98</td>
<td>Assumes that 100 % of the H₂S in the acid gas stream is converted to SO₂ during flaring or incineration and that the sweetening process removes 100 % of the H₂S in the feedstock.</td>
</tr>
<tr>
<td></td>
<td>0.408(*)</td>
<td>For an emission ratio of 0.75 %</td>
</tr>
<tr>
<td></td>
<td>0.272(*)</td>
<td>For an emission ratio of 0.50 %</td>
</tr>
<tr>
<td>CO</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25(*)</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>-</td>
<td>Flares or incinerator stack gases are expected to have negligible hydrocarbon emissions.</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Negligible</td>
<td></td>
</tr>
</tbody>
</table>

Sources: [136, MRI, 1997]
(*) [ 54, Gallauner et al. 2009 ]

Emissions to water
Routine process-derived liquid effluent produced by natural gas plants is normally derived mainly from formation water arising from the drying of the gas and associated condensate. The effluent principally occurs as condensed steam from the glycol or methanol regeneration plants and usually contains a number of organic contaminants which may include glycol, methanol,
aliphatic and aromatic hydrocarbons, amines and mercaptans. The presence of these contaminants typically causes the effluent to have a very high biochemical and chemical oxygen demand. The process of refining natural gas which contains mercury can generate waste water which contains that metal.

**Solid waste**

Natural gas refining gives rise to relatively small quantities of process wastes. These typically include occasional disposal of spent catalysts, activators, corrosion inhibitors, absorbents, adsorbents, filter cartridges, separator dusts, etc and they may be contaminated with trace amounts of hydrocarbons. Some natural gas sources contain traces of Hg which should be collected (generating spent adsorbent) and safely disposed of. For every 1000 kg of sludge treated, 12 kg of metallic mercury is produced. Total sludge production within some Dutch natural gas plants is on average 250 tonnes/year with a maximum of 400 tonnes/year. This corresponds to 3-5 tonnes of mercury annually.

### 3.18 Polymerisation

**Consumptions**

The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst. Typically 0.2 grammes of phosphoric acid are consumed to produce 1 tonne of polymer or 1.18 kg of catalyst (phosphoric acid + support) per tonne of product. Catalyst life is normally limited to three to six months, depending on unit size and operating conditions. A typical unit, capable of producing 25 tonnes of polymerised gasoline per day, is customarily filled with 12 tonnes of catalyst.

Caustic solution is used to remove mercaptans from the propene/butene feed, then amine solution to remove hydrogen sulphide, then water to remove caustics and amines. It is finally dried by passing through a silica gel or molecular sieve dryer.

Table 3.87 shows the typical utility consumption of a polymerisation process.

**Table 3.87: Utility consumption in polymerisation process**

<table>
<thead>
<tr>
<th>Utility</th>
<th>Consumption</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric power</td>
<td>20 – 28 kW</td>
<td>kW/t of product</td>
</tr>
<tr>
<td>Steam</td>
<td>0.7 – 1.1 t</td>
<td>t/t of product</td>
</tr>
<tr>
<td>Cooling water</td>
<td>4.4 – 6.0 t</td>
<td>t/t of product</td>
</tr>
</tbody>
</table>

*Source: [166, Meyers, 1997]*

**Emissions**

**Emissions to air**

Potential releases into air include hydrocarbons from pressure reliefs, storage and handling operations, spillages and water and waste discharges, and of particulate matter from catalyst fine from handling and disposal of spent catalysts. Sulphur dioxide and H2S may arise during the caustic washing operation.

**Process waste water**

Potential releases into water include hydrocarbons from sour water purge from the washtower, condenser drains and spillages, and of particulate matter from spillages of catalyst fines. Waste water streams will contain caustic wash and sour water with amines and mercaptans. Its more important parameters are H2S, NH3, caustic wash, mercaptans and ammonia, and low pH (2 – 3) due to the phosphoric acid.
Solid waste generated
Spent catalyst containing phosphoric acid, which typically is not regenerated, is occasionally disposed of as a solid waste. Potential releases into land include acids in solid form and hydrocarbons from spent catalyst. Typically, 0.4 grams of used silica is disposed of per tonne of polymer gasoline produced.

3.19 Primary distillation units

Consumptions
Despite the high level of heat integration and heat recovery that is normally applied, crude distillation units are among the most intensive energy-consuming units in a refinery, because the total volume of crude oil being processed has to be heated to the elevated processing temperature of 350 °C. The overall energy consumption of a refinery is normally dominated by a few processes. Atmospheric and vacuum distillation accounts for 35 – 40 % of the total process energy consumption followed by hydrotreating with approx. 18 – 20 % [195, The world refining association, 1999]. The various processes downstream of the CDU make use of the elevated temperatures of the product streams leaving the CDU. The number of side-streams in a high vacuum unit is chosen to maximise heat integration of producing streams at different temperatures, rather than to match the number of products required. The utility requirements for the atmospheric and vacuum distillation units are:

Table 3.88: Utility requirements for atmospheric and vacuum distillation units

<table>
<thead>
<tr>
<th>Type of unit</th>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, AT=17 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
<td>400 – 680</td>
<td>4 – 6</td>
<td>25 – 30</td>
<td>4.0</td>
</tr>
<tr>
<td>Vacuum</td>
<td>400 – 800</td>
<td>1.5 – 4.5</td>
<td>20 – 60</td>
<td>3 – 5</td>
</tr>
</tbody>
</table>

NB:: Replacement of the steam ejectors by vacuum pumps will reduce steam consumption and waste water generation but increase the electricity consumption.

Sources: [118, VROM, 1999], [261, Canales, 2000], [268, TWG, 2001]

Emissions

Air emissions
Potential releases into air are from:

- Flue-gases arising from the combustion of fuels in the furnaces to heat the crude oil. These emissions are treated in Section 0.
- Pressure relief valves on column overheads; relief from overhead accumulators are piped to flare as well as the vent points.
- Poor containment in overhead systems, including barometric sumps and vents.
- Glands and seals on pumps, compressors and valves.
- De-coking vents from process heaters. During furnace decoking (once or twice a year) some emission of soot can occur if operation is not properly controlled in terms of temperature or steam/air injection.
- Venting during clean-out procedures.
- Some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of non-condensable light hydrocarbons and hydrogen sulphide passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide. The quantity of these emissions depends on the size of the unit, the type of feedstock and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated. Oily sour
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water is also generated in the fractionators. The emissions of non-condensables from vacuum ejector set condensors are between 50 and 200 kg/h, depending on furnace design and type of crude and throughput. They include hydrocarbons and H2S.

- Fugitive emissions from atmospheric and vacuum distillation units account for 5 – 190 t/yr for a refinery with a crude capacity of 8.7 Mt/yr [79, API, 1993].

Table 3.89 gives some examples of the air emissions generated by the atmospheric and vacuum distillation units by two European refineries. This table includes the emissions from combustion of fuels in the furnaces.

Table 3.89: Examples of air emissions generated by crude oil and vacuum distillation units

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>SO2</th>
<th>NOx</th>
<th>CO</th>
<th>CO2</th>
<th>Particulates</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDU</td>
<td>8 200 000</td>
<td>Crude oil t/yr</td>
<td></td>
<td>46</td>
<td>107</td>
<td>6</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>OMV Schwechat</td>
<td>1536.9</td>
<td>kg/t feed</td>
<td>0.009</td>
<td>0.02</td>
<td>0.001</td>
<td>36</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>CDU TOTAL</td>
<td>8 500 000</td>
<td>Crude oil t/yr</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>8</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Mittel-deutschalnd</td>
<td>1138.8</td>
<td>kg/t feed</td>
<td>0.004</td>
<td>0.012</td>
<td>0.012</td>
<td>26</td>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>Vacuum distillation OMV Schwechat</td>
<td>2 485 000</td>
<td>mg/m³</td>
<td>264</td>
<td>10</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>289.9</td>
<td>Atm. Res. t/yr</td>
<td>205</td>
<td>78</td>
<td>2.9</td>
<td>76 170</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>0.083</td>
<td>0.031</td>
<td>0.001</td>
<td>31</td>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>Vacuum distillation TOTAL Mittel-deutschalnd</td>
<td>4 500 000</td>
<td>mg/m³</td>
<td>700(1)</td>
<td>264</td>
<td>10</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>639.5</td>
<td>Atm. Res. t/yr</td>
<td>19.8</td>
<td>56.6</td>
<td>56.6</td>
<td>182 252</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>0.004</td>
<td>0.013</td>
<td>0.013</td>
<td>41</td>
<td></td>
<td>0.001</td>
</tr>
</tbody>
</table>

(1) Raw gas was treated in a flue gas desulphurisation (Wellman Lord)

Note: Data are related to yearly average, 3 % O2, dry conditions

For the emissions from the Mider refinery, only limit values are given. Loads and specific emissions are calculated.

Source: [250, Winter, 2000]

Process waste water

Process waste water generated in the atmospheric distillation units is 0.08 – 0.75 m³ per tonne of crude oil processed. It contains oil, H2S, suspended solids, chlorides, mercaptans, phenol, an elevated pH, and ammonia and caustic soda used in column overhead corrosion protection. It is generated in the overhead condensers, in the fractionators and can also become contaminated from spillages and leaks. The overhead reflux drum (gasoil dryer condensator) generates 0.5 % water on crude + 1.5 % steam on feed with a composition of H2S 10 – 200 mg/l and NH3 10 – 300 mg/l. Sour water is normally sent to water stripper/treatment.

Waste water (sour water) is generated in the vacuum distillation units from process steam injection in the furnace and the vacuum tower. It contains H2S, NH3 and dissolved hydrocarbons. If steam ejectors and barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated (± 10 m³/h) containing also H2S, NH3.

Residual wastes generated

Sludges can be generated from the cleaning-out of the columns. The amount depends on the mode of desludging and the base solid and water content of the crude processed. The range of solid waste generation from a crude unit of 8.7 Mt/yr ranges from 6.3 – 20 t/day.
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3.20  Product treatments

Consumptions

*Gasoline sweetening*
Utility requirements in the gasoline sweetening process are:

Table 3.90: Typical utility consumption of a gasoline sweetening process

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Caustic (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 10</td>
<td>10 – 25</td>
<td>0.02 – 0.15</td>
</tr>
</tbody>
</table>

Sources: [261, Canales, 2000], [118, VROM, 1999] [166, Meyers, 1997]

*Catalytic dewaxing*
Catalytic dewaxing catalysts typically last 6 to 8 years. During that time, they are regenerated as needed. Typical cycles last 2 to 4 years between regenerations. Utilities needed in the catalytic dewaxing process are summarised in the following table.

Table 3.91: Typical utility consumption of catalytic dewaxing units

<table>
<thead>
<tr>
<th>Utilities for a feed capacity of 3500 tonnes per stream day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power, kW</td>
</tr>
<tr>
<td>Steam (tracing only)</td>
</tr>
<tr>
<td>Cooling water, m³/h</td>
</tr>
<tr>
<td>Condensate, m³/h</td>
</tr>
<tr>
<td>Fuel absorbed, MW</td>
</tr>
</tbody>
</table>

Source: [166, Meyers, 1997]

Emissions

*Air emissions*
Potential releases into air from oxidation-extraction processes include hydrocarbons, sulphur compounds (e.g. disulphides) and nitrogen compounds from sour water drains, pressure relief valves, vents from feed vessels, spillages and leakages from flanges, glands and seals on pumps and valves – particularly from overhead systems and fugitive emissions. Emissions may occur from the spent air from the disulphide separator that contains less than 400 ppm of disulphides and is normally incinerated.

*Process waste water*
Product treating processes does not generate much waste water. The potential releases into water are from spillages and leakages (hydrocarbons), and the sulphur and nitrogen compounds arising from inadequate stripping performance.

*Residual wastes generated*
In the extraction process, an oily disulphide waste stream leaves the separator. Most refineries are able to regenerate their spent caustic, but sometimes they have to dispose of some excess quantities of spent caustic, mainly from caustic pre-wash activities. Usually these quantities are small and can be managed within their effluent treatment system or they are disposed of externally via contractors or may be reused elsewhere. From the extraction process, the disulphide recovered can be sold as product, or be recycled to a hydrotreater or incinerator. The amount of spent caustic generated varies between 0.05 - 1.0 kg/tonne feed and contains sulphides and phenols. Concentration of organic compounds in spent caustic solutions is typically higher than 50 g/l.
Table 3.92: Typical emissions from the catalytic dewaxing process

<table>
<thead>
<tr>
<th>Catalytic dewaxing process</th>
<th>Air</th>
<th>Waste water</th>
<th>Solid wastes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue-gas from fired heater (in Section 0).</td>
<td>none</td>
<td>Potential releases into land are from disposal of spent catalytic dewaxing catalyst. (50 t/yr for a 50000 t/yr hyrofining process). Spent Ni-W catalysts containing sulphur and carbon sent to specialised off-site regeneration companies. After two - three regenerations catalyst is disposed of and subjected to metal reclaiming.</td>
<td></td>
</tr>
<tr>
<td>VOCs may arise from venting during catalyst regeneration/replacement procedures and cleaning.</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

3.21 Storage and handling of refinery materials

Consumptions

No energy or process material is required for balancing lines, double seals or floating roofs on tanks. However, some tanks need mixers (a heavy user of power) and some need heating too. Handling refinery materials also requires electricity for the pumps that move the materials through the pipes.

Emissions

Air Emissions

Air emissions, and more specifically VOC emissions, are the main emissions that occur during the storage and handling activities of refinery materials. Emissions from hydrocarbon liquids in storage occur because of evaporative loss of the liquid during storage and as a result of changes in the liquid level. Even if equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries. Moreover, fugitive emissions in storage systems are mainly from imperfect seals or tank fittings. However, it is generally the case that the amount of emissions depends much more on the vapour pressure of the product (higher vapour pressure tend to produce higher VOC emissions) than on the type of tank. The amount of emissions from a particular tank will directly depend on the vapour pressure of the product stored. A study of petroleum refinery emissions found that the majority of tank losses occurred through tank seals on gasoline storage tanks [108, USAEPA, 1995]. Since that time, emissions from gasoline tanks in Europe have been significantly reduced by the installation of control measures mandated by Directive 94/63 on the control of VOC emissions resulting from the storage of petrol.

VOC emissions from storage can represent more than 40% of the total VOC emissions and are normally the biggest emitter in a refinery. The emissions from tanks have been estimated by using API estimations [100, API 2002]. As an example, these estimations suggest that annual emissions of 320 tonnes per year can lead to an annual emission of 320 tonnes per year from the storage systems. It is a much lower figure than the one calculated from the DIAL measurements: 1900 tonnes per year for a refinery processing 11 million tonnes per year [107, Janson, 1999]. However, API methods have been updated and storage losses can be predicted with acceptable accuracy [259, Dekkers, 2000]. A CONCAWE study [229, Smithers, 1995] which was the only trial of DIAL where measurements were conducted over a reasonably long period showed that there was good reasonable agreement between DIAL and the latest API estimation methods as to when the test times were long enough. In that case, the estimation methods is acceptable to provide annual inventory values. It is important to take into account that the API emissions factor method assumes that no technical problems occurs with the considered tank.

When transferring liquids to vessels at atmospheric pressure, the vapour phase (often air, but also inert) in the receiving vessel is often emitted to atmosphere. Such loading operations are recognised as having an impact on the environment due to the presence of VOCs. VOC emissions from blending come from blending tanks, valves, pumps and mixing operations. The amount depends on design and maintenance of the systems. Although barge loading is not a factor for all refineries, it is an important emissions source for many facilities. One of the largest
Chapter 3

Sources of VOC emissions identified during the Amoco/USAEPa study was fugitive emissions from the loading of tanker barges. It has been estimated that during the loading of products with high partial pressure, 0.05% of the throughput can be emitted to the air. As previously stated, through the impact of directive 94/63, air emissions have been significantly reduced in Europe, including, these from barge loading of gasoline.

VOC emissions to the air from cavern storage of hydrocarbon materials can be prevented by connecting the gas spaces of several caverns, so the breathing gases when filling one cavern are led to the other caverns. In the case of only one cavern the breathing gases must be sent to the air. However, For a given product, the VOC emissions in this case from cavern storage are generally slightly lower than from a conventional aerial vessel (or group of vessels) of the same capacity because the yearly average temperature of storage is lower (5 – 10 ºC).

Waste water
Leaking flanges and valves may contaminate rainwater. The amount depends on the maintenance service. Liquid tank bottoms (primarily water and oil emulsions) are periodically drawn off to prevent their continued build up. That waste water is contaminated with tank product. Oil levels up to 5 g/l in tank water bottoms can be found [101, World Bank, 1998]. However, if the draw off rate of the water is too high, oil can be entrained with the water, thereby giving a false high reading of oil in the water.

The groundwater leaking into underground storage systems (caverns) should be pumped out and led to the waste water treatment system of the refinery. The amount of water depends on the solidity of the rock and how carefully the fractures in the rock are sealed by injection of concrete [256, Lameranta, 2000]. The quality of waste water depends on the product (or crude) which is stored in the cavern. Typically the waste water contains hydrocarbons as emulsion and water soluble components of stored liquid. Some examples of waste water generated by cavern storage is given in Table 3.93.

<table>
<thead>
<tr>
<th>Cavern</th>
<th>Volume of the cavern (m³)</th>
<th>Product</th>
<th>Seeping water removed (m³/yr)</th>
<th>Amount of hydrocarbons discharged after oil separation (kg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40 000</td>
<td>Light fuel oil</td>
<td>22 300</td>
<td>49</td>
</tr>
<tr>
<td>B</td>
<td>2x75 000</td>
<td>Heavy fuel oil</td>
<td>25 800</td>
<td>104</td>
</tr>
<tr>
<td>C</td>
<td>50 000</td>
<td>Light fuel oil</td>
<td>36 900</td>
<td>40</td>
</tr>
<tr>
<td>D</td>
<td>105 000</td>
<td>Light condensate</td>
<td>140</td>
<td>NA</td>
</tr>
<tr>
<td>E</td>
<td>52 000</td>
<td>Propane/butane</td>
<td>80</td>
<td>NA</td>
</tr>
<tr>
<td>F</td>
<td>150 000</td>
<td>Propane/butane</td>
<td>150</td>
<td>NA</td>
</tr>
<tr>
<td>G</td>
<td>430 000</td>
<td>Heavy fuel oil</td>
<td>50 000</td>
<td>76</td>
</tr>
<tr>
<td>H</td>
<td>100 000</td>
<td>Car fuel (diesel)</td>
<td>5 000</td>
<td>NA</td>
</tr>
<tr>
<td>I</td>
<td>100 000</td>
<td>Car fuel (petrol)</td>
<td>3 000</td>
<td>NA</td>
</tr>
</tbody>
</table>

Source: [256, Lameranta, 2000]

Waste and soil contamination
The primary subsurface (soil and groundwater) contamination threats posed by above-ground storage tanks include the disposal of sludges from the bottoms of the tanks during periodic cleaning of tanks for inspections, loss of product from the tanks during operations such as tank water drainage, and product leakage to the ground caused by tank or piping failures or overfilling accidents. Spills may result in contamination of soil from handling processes, especially in loading, mainly due to human error. Storage tank bottom sludge contains iron rust, clay, sand, water, emulsified oil and wax, phenols and metals (lead for leaded gasoline storage tanks). Table 3.94 shows some analyses of sludges taken from the sewerage system around tank storage facilities. The analyses are unique to that site and are reproduced to show what may occur.
Table 3.94: Composition of the sludge taken from four different sewer systems close to the storage tanks

<table>
<thead>
<tr>
<th>Species</th>
<th>Tank field sewers (two different sources)</th>
<th>Gasoline tank field sewers</th>
<th>Distillate tank field sewers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source 1</td>
<td>Source 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids</td>
<td>92.7 %</td>
<td>91.2 %</td>
<td>81 %</td>
</tr>
<tr>
<td>Oil</td>
<td>7.3 %</td>
<td>8.8 %</td>
<td>19 %</td>
</tr>
<tr>
<td>Carbon</td>
<td>26.9 %</td>
<td>27.1 %</td>
<td>44.9 %</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.2 %</td>
<td>15.1 %</td>
<td>7.8 %</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.2 %</td>
<td>&lt;0.6 % (†)</td>
<td>0.4 %</td>
</tr>
<tr>
<td>Sulphur</td>
<td>64441</td>
<td>70034</td>
<td>58222</td>
</tr>
<tr>
<td>Iron</td>
<td>25000.0</td>
<td>174024.0</td>
<td>62222.0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>9317.0</td>
<td>2695.0</td>
<td>4430.0</td>
</tr>
<tr>
<td>Sulphide</td>
<td>8327.0</td>
<td>3624.8</td>
<td>4325.9</td>
</tr>
<tr>
<td>Aluminium</td>
<td>4193.0</td>
<td>3969.0</td>
<td>8148.0</td>
</tr>
<tr>
<td>Nitrate</td>
<td>2290.4</td>
<td>10.8</td>
<td>91.9</td>
</tr>
<tr>
<td>Sodium</td>
<td>1180.0</td>
<td>772.0</td>
<td>770.0</td>
</tr>
<tr>
<td>Sulphate</td>
<td>1037.3</td>
<td>165.5</td>
<td>19.3</td>
</tr>
<tr>
<td>Xylene</td>
<td>746.9</td>
<td>&lt;4.2 (†)</td>
<td>1121.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>478.3</td>
<td>&lt;4.2 (†)</td>
<td>794.1</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>158.4</td>
<td>&lt;4.2 (†)</td>
<td>106.8</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>130.4</td>
<td>27.6</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>80.7</td>
<td>&lt;4.2 (†)</td>
<td>35.6</td>
</tr>
<tr>
<td>Phenol</td>
<td>71.4</td>
<td>129.5</td>
<td>-</td>
</tr>
<tr>
<td>Nickel</td>
<td>68.3</td>
<td>106.1</td>
<td>500.7</td>
</tr>
<tr>
<td>Lead</td>
<td>55.9</td>
<td>492.4</td>
<td>308.1</td>
</tr>
<tr>
<td>Chromium</td>
<td>35.4</td>
<td>70.5</td>
<td>154.1</td>
</tr>
<tr>
<td>Pyrene</td>
<td>30.0</td>
<td>&lt;105.0 (†)</td>
<td>-</td>
</tr>
<tr>
<td>Carbonate</td>
<td>29</td>
<td>2.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Vanadium</td>
<td>27.0</td>
<td>72.0</td>
<td>49.0</td>
</tr>
<tr>
<td>Antimony</td>
<td>19.0</td>
<td>42.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Phenols</td>
<td>18.6</td>
<td>&lt;105.1 (†)</td>
<td>-</td>
</tr>
<tr>
<td>Fluorine</td>
<td>15.5</td>
<td>&lt;105.1 (†)</td>
<td>-</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>&lt;7.8 (‡)</td>
<td>&lt;105.1 (‡)</td>
<td>-</td>
</tr>
<tr>
<td>Selenium</td>
<td>7.0</td>
<td>&lt;4.0 (†)</td>
<td>4.3</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5.0</td>
<td>16.1</td>
<td>14.5</td>
</tr>
<tr>
<td>Mercury</td>
<td>4.0</td>
<td>1.6</td>
<td>9.5</td>
</tr>
<tr>
<td>Cyanide</td>
<td>0.6</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt;0.3 (†)</td>
<td>39261.0</td>
<td>13185.0</td>
</tr>
</tbody>
</table>

(†) Below Detection Limit Shown
(‡) Estimated Value Below Detection Limit

Note: Figures quoted on a moisture free basis, all units mg/kg unless otherwise stated.
Figures do not sum to 100% because of double counting.

Source: [80, March Consulting Group, 1991]
Chapter 3

3.22 Visbreaking and other thermal conversions

3.22.1 Visbreaking

Consumptions
Table 3.95 represents typical utility consumptions for a visbreaker:

<table>
<thead>
<tr>
<th>Utility (unit)</th>
<th>Consumption range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel (MJ/t)</td>
<td>400 – 800</td>
</tr>
<tr>
<td>Electricity (kWh/t)</td>
<td>10 – 15</td>
</tr>
<tr>
<td>Steam consumed (kg/t)</td>
<td>5 – 30</td>
</tr>
<tr>
<td>Cooling water (m³/t, ΔT=10°C)</td>
<td>2 – 10</td>
</tr>
</tbody>
</table>

Note: the power consumption given is for furnace cracking.

Sources: [118, VROM, 1999], [261, Canales, 2000]

For visbreaking, fuel consumption accounts for about 80 % of the operating costs with a net fuel consumption of 1 - 1.5 % w/w on feed. Fuel requirements for soaker visbreaking are about 30 - 35 % lower.

Emissions

Air Emissions

Air emissions from visbreaking include emissions from the combustion of fuels in the process heaters (discussed in Section 0), vents and fugitive emissions. A sour water stream is generated in the fractionator. The gas produced contains H₂S and should be further treated. Hydrogen sulphide and mercaptans are released from the sour water stream from reflux condensers. Hydrocarbons are released from pressure reliefs on reflux drums and vessels, storage and handling operations, spillages and discharges of waste water. Particulate emissions occur during furnace decoking and cleaning operations about twice a year.

Table 3.96 shows the air emissions from visbreaking processes in two European refineries.

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel Consumption (GWh/yr)</th>
<th>Throughput (Mt/yr)</th>
<th>Units</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO</th>
<th>CO₂</th>
<th>Particulates(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMV Schwechat</td>
<td>87.9</td>
<td>1.02 Atm. residue</td>
<td>mg/m³</td>
<td>47</td>
<td>183</td>
<td>5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>t/yr</td>
<td>4.2</td>
<td>16.5</td>
<td>0.5</td>
<td>17 057</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>0.004</td>
<td>0.016</td>
<td>00</td>
<td>16.7</td>
<td>00</td>
</tr>
<tr>
<td>TOTAL Raffinerie</td>
<td>306.6</td>
<td>1.20</td>
<td>mg/m³</td>
<td>35</td>
<td>100</td>
<td>100</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Mitteldeutschland</td>
<td></td>
<td></td>
<td>t/yr</td>
<td>13</td>
<td>50.6</td>
<td>1.4</td>
<td>59 480</td>
<td>0.3</td>
</tr>
<tr>
<td>Mider Refineries</td>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>0.011</td>
<td>0.042</td>
<td>0.001</td>
<td>50</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: For the emissions from the Mider refinery, only limit values are given. Loads and specific emissions were calculated.

NB: Data are related to yearly average, 3 % O₂, dry conditions.

(*) No information available on PM size

Source: [247, UBA Austria, 1998]
**Process waste water**
The fractionator overhead gas is partly condensed and accumulated in the overhead drum to separate into three phases a hydrocarbon gas stream, a hydrocarbon liquid stream and a sour water stream. The sour water stream should be sent to the sour water stripper for purification.

The flow of waste water generated in the visbreaking process from the sour water drain is around 56 litres per tonne of feedstock. It represents between one and three % volume on feed intake.

Table 3.97 shows the range of composition of the visbreaker waste water.

**Table 3.97: Typical composition of the waste water produced in visbreaking**

<table>
<thead>
<tr>
<th>Substance or parameter</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>High</td>
</tr>
<tr>
<td>Free oil</td>
<td>50 – 100</td>
</tr>
<tr>
<td>COD</td>
<td>500 – 20 00</td>
</tr>
<tr>
<td>H₂S</td>
<td>10 – 200</td>
</tr>
<tr>
<td>NH₃ (N-Kj)</td>
<td>15 – 50</td>
</tr>
<tr>
<td>Phenols</td>
<td>5 – 30</td>
</tr>
<tr>
<td>HCN</td>
<td>10 – 300</td>
</tr>
</tbody>
</table>

**Solid wastes generated**
The waste generated in visbreaking comes from the cleaning and turnaround of the process. It is generated discontinuously at a rate of 20 to 25 tonnes per year for a 5 million tonnes per year refinery. It contains between 0 and 30 % of oil/sludge.

Next sections cover the emissions arising from refinery processes that are used for the treatment of waste gas, waste water and solid waste. These techniques are described in Chapter 4 (Sections 4.25 to 4.27). The main objective of these processes is to reduce the concentration of pollutants in the effluents. Obviously the loads and concentrations of pollutants in these streams will be reduced by these processes, but some pollutants will remain in the streams and other may be generated. That is the purpose of the following next three sections. Emissions from the refinery as a whole are included in Section 3.1.

### 3.22.2 Thermal gasoil units (TGU)

**Emissions**

**Table 3.98** Example of emissions of a thermal gasoil unit in an European site – All data are monthly average from 2009 – 15 % O₂.

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel consumption (GWh/yr)</th>
<th>Annual capacity (tonnes/yr)</th>
<th>Units</th>
<th>SO₂</th>
<th>NOₓ</th>
<th>CO</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGU OMV Schwechat</td>
<td>450.1</td>
<td>730 000</td>
<td>mg/m³</td>
<td>0</td>
<td>27 – 38</td>
<td>2 – 16</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>t/yr</td>
<td>&lt;0.1</td>
<td>41.7</td>
<td>9.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>
3.23 New high conversion techniques

KOM conclusion 3.6: TWG to review existing/new ‘bottom end’ high conversion processes.
→ Info expected from industry and UK

Note for the TWG: if some of these techniques are reported in Chapter 2.23, and if information on their emissions are available, they will be reported here. No information available

3.24 Emissions from techniques for the elimination or valorisation of external waste used as secondary raw material

KOM conclusion 2.4: TWG to provide info on such applied techniques.
→ info still expected, in particular from CZ, SK

Note for the TWG: if some of these techniques are reported in Chapter 2, and if information on their emissions are available, they will be reported here. No information available

3.25 Emissions from waste gas treatment techniques

This section includes end-of-pipe or abatement techniques of CO, CO₂, NOₓ, particulates, sulphur compounds, VOC, combined techniques for the abatement of air pollutants, odour and noise.

3.25.1 Sour gas treatments

The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. The area of the amine treating unit poses health risks because of the presence of H₂S, possibly by inadvertent leakages.

3.25.2 Sulphur recovery units (SRU)

In 1995, the average percentage of sulphur recovered in the SRU represented 42.6 % of the sulphur entering the refinery with the crude oil. From the data gathered for a sample of 50 European sites by the Technical Working Group (TWG) set up for the review of this BREF document, this percentage can be estimated for the period 2007 - 2008 at 44.7 % (50th percentile). However, this median value hides a rather wide range of site performances from 10.7 to 79.9 % (5th to 95th percentile).

Sulphur is recovered in these units called sulphur recovery units, extensively described in Section 4.25.5. As already shown on Figure 3.12 and Figure 3.13 in Section 3.1.2.4, they represent around the 10 – 25 % of the SO₂ emissions from refineries, even if the fuel gas volume from SRU represent only around 1.5 % of the total flue-gas volume emitted by a refinery.

The sulphur recovery yield of SRUs operated in a sample of 47 European sites is displayed in Figure 3.35. Values reflect the overall SRU performance including the utilisation factor achieved by the whole set of available treatment lines. As far as Claus process-based units are concerned, the yield is in the ranges from 95 to 99.99 %, with a median value (50th percentile) around 98.5 %.
From questionnaire data collection, SRU SO$_2$ emissions range from \( 4000 \text{ to } 52\,000 \text{ mg/Nm}^3 \). Emissions from these units typically contain some H$_2$S, SO$_x$ and NO$_x$. They also generate process waste water that contains H$_2$S, NH$_3$, amines and Stretford solution. Residual wastes are spent catalysts. The next table shows two examples of emissions from European refineries.

### Table 3.99: Examples of air emissions generated by sulphur recovery units

<table>
<thead>
<tr>
<th>Installation</th>
<th>Fuel consumption (GWh/yr)</th>
<th>Throughput (t/yr)</th>
<th>Units</th>
<th>SO$_2$ (mg/m$^3$)</th>
<th>NO$_x$</th>
<th>CO (t/yr)</th>
<th>CO$_2$ (t/yr)</th>
<th>Particulates (mg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRU OMV Schwechat (1)</td>
<td>27.2</td>
<td>63 900 of sulphur</td>
<td></td>
<td>700(1)</td>
<td>70</td>
<td>100</td>
<td>20</td>
<td>2.7</td>
</tr>
<tr>
<td>SRU TOTAL Mitteldeutschland</td>
<td>131.4</td>
<td>90 000 of sulphur</td>
<td></td>
<td>4322</td>
<td>200</td>
<td>100</td>
<td>25492</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>kg/t feed</td>
<td>1.5</td>
<td>0.15</td>
<td>82.4</td>
<td>0.042</td>
</tr>
</tbody>
</table>

(1) At the time of data collection, raw gas was treated in a flue-gas desulphurisation (Wellman Lord) NB: Data are related to yearly average, 3 % O$_2$, dry conditions.

For the emissions from the Mitteldeutschland refinery, only limit values are given. Loads and specific emissions were calculated.

(1) No information available on PM size

Source: [247, UBA Austria, 1998]
3.25.3 Flares

Flaring is both a source of air emissions and has the potential to burn valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. It is generally restricted to unplanned shutdowns or emergency cases. More information is available in the CWW BREF [6, EC 2003]

Consumptions
The main utilities that flare systems will use are refinery fuel gas or nitrogen for purging the flare headers, fuel gas for the pilot burners and steam for heating purposes. However, the consumption of these utilities is very low under normal operating conditions.

Emissions
Flaring activity varies according to the real-time opportunity for refinery management optimisation. It may lead to extreme values during incidents, shutdowns or major maintenance periods. As an example, the following gives the evolution of the annual flare output for a German refinery which faced a major maintenance period for the installation of a new technique in 2007, as compared with the seven previous years.

<table>
<thead>
<tr>
<th>Year</th>
<th>Crude input (Mt/yr)</th>
<th>Flare output (t/yr)</th>
<th>Flaring ratio ((\ell_{\text{fl}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>3.08</td>
<td>704</td>
<td>0.23</td>
</tr>
<tr>
<td>2001</td>
<td>3.42</td>
<td>201</td>
<td>0.06</td>
</tr>
<tr>
<td>2002</td>
<td>3.40</td>
<td>560</td>
<td>0.16</td>
</tr>
<tr>
<td>2003</td>
<td>3.43</td>
<td>1003</td>
<td>0.29</td>
</tr>
<tr>
<td>2004</td>
<td>3.53</td>
<td>390</td>
<td>0.11</td>
</tr>
<tr>
<td>2005</td>
<td>3.41</td>
<td>753</td>
<td>0.22</td>
</tr>
<tr>
<td>2006</td>
<td>3.35</td>
<td>165</td>
<td>0.05</td>
</tr>
<tr>
<td>2007</td>
<td>2.53</td>
<td>6155</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Another example, from two refineries in Sweden, gives the following flaring ratios.

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Flaring ratio ((\ell_{\text{fl}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preem Gothenburg refinery</td>
<td>0.6</td>
</tr>
<tr>
<td>Preem Lysekil refinery</td>
<td>0.8</td>
</tr>
</tbody>
</table>

They Flares emit at least CO, CO\(_2\), SO\(_2\) and NO\(_x\). Under specific conditions, flaring leads to soot formation and VOC emissions. Small amounts of complex hydrocarbons (e.g PAH), may also be released. Based on [86, SFT 2009] there is a clear link between soot formation and small emissions of PAH compared to other sources. Emissions of dioxins from flaring were considered as not existing mainly due to the absence of necessary formation conditions. Conditions for emissions of PCB were regard as highly unlikely.

The composition depends on a number of factors including the composition of flare gas, flaring rate, flare system, wind and the system being relieved and combustion efficiency at the flare tip.

Flares are a very important point source of refinery emissions. Some plants still use older, less-efficient waste gas flares. Because these flares usually burn at temperatures lower than necessary for complete combustion (minimum 850°C), larger emissions of hydrocarbons and particulate, as well as H\(_2\)S, can occur. No data are available to estimate the magnitude of these emissions. Emissions of VOC and soot are also present and they depend on the system being relieved and combustion efficiency at the flare tip.

Noise from a flare has two components: flow noise and combustion noise. Flow noise occurs when the flare gas is flowing out of the flare tip with high speed. The greater the amount of flare gas, the more noise. Combustion noise is generated in the combustion zone. A short intense flame, where the energy turnover is fast and in low volume, generates more noise than if this occurs in a larger volume.
3.26 Emissions from waste water treatment techniques

Large volumes of waste water are produced by the petroleum refining industry. Waste water treatment plants are advanced environmental protection systems for the control of surface water pollution. Waste water treatment plants are a significant source of refinery air emissions, water emissions and solid wastes. Sources of contamination of water with hydrocarbons are desalters (40%), storage tanks (20%), slop systems (15%) and other processes (25%).

Process effluent volume can be compared to the volumes of process effluent discharged (excluding once-through cooling water). Although related, the values are not identical given that there are other sources of water to the effluent system including rainwater on plant surfaces, water separated from crude, ballast water, etc. Moreover, some water will be consumed by evaporation, be used in chemical reactions, etc. As a general trend, refineries are progressively treating less crude or throughput compared to their capacity because of more complex refining schemes, products specifications, and choices (e.g. more gasoil and less gasoline). Thus, the effluent volume per tonne of throughput also depends on the operations performed at the refinery.

Table 3.102 displays the data on water discharge volumes that has been made available to the TWG for 63 European refineries with dedicated waste water treatment plant. Data displayed here is drawn from released waste water while those in Table 3.3 are from consumption water. are (all in annual averages):

- Annual average effluent volume: 3.6 million m$^3$/year
- Range: 0.07 to 21 million m$^3$/year
- Average effluent per tonne throughput: 0.53 m$^3$/tonne throughput
- Range: 0.09 to 1.6 m$^3$/tonne throughput

Table 3.102: Summary data on the volume of waste water from 41 European refineries

<table>
<thead>
<tr>
<th>Type of waste water</th>
<th>Volume discharged</th>
<th>Unit</th>
<th>Range (5th – 95th percentiles)</th>
<th>Median (50th percentile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water from process(*)</td>
<td>Annual</td>
<td>million m$^3$/yr</td>
<td>0.55 – 10</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>Specific</td>
<td>m$^3$/t</td>
<td>0.11 – 1.57</td>
<td>0.38</td>
</tr>
<tr>
<td>Waste water from cooling</td>
<td>Annual</td>
<td>million m$^3$/yr</td>
<td>0 – 212</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Specific</td>
<td>m$^3$/t</td>
<td>0 – 58</td>
<td>0.08</td>
</tr>
<tr>
<td>Potentially contaminated rain water</td>
<td>Annual</td>
<td>million m$^3$/yr</td>
<td>0.09 – 2.3</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>Specific</td>
<td>m$^3$/t</td>
<td>0.02 – 0.2</td>
<td>0.08</td>
</tr>
<tr>
<td>Total waste water</td>
<td>Annual</td>
<td>million m$^3$/yr</td>
<td>0.54 – 212</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Specific</td>
<td>m$^3$/t</td>
<td>0.15 – 11.68</td>
<td>0.44</td>
</tr>
</tbody>
</table>

(*) Waste water from process: Waste water annual release reported as from process

Sources: [TWG site questionnaires]; annual averages reported for 2006, 2007 or 2008 - Dedicated WWTP

Emissions

Air emissions

The air emissions from waste water treatment plants stem from evaporation (hydrocarbons, benzene, H$_2$S, NH$_3$, mercaptans) from the numerous tanks, ponds and sewerage system drains that expose its surfaces into air. The sewerage system and the waste water treatment in a refinery may be sources of odour nuisance, particularly from open drains and from oil separators. VOCs are also emitted during air stripping in flotation units and in the biotreater. The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [117, VDI, 2000]:
Chapter 3

- 20 g/m² per hour for open oil separator
- 2 g/m² per hour for covered oil separator
- 2 g/m² per hour for flotation
- 0.2 g/m² per hour for biological treatments

Other methods to calculate emissions are available such as Litchfield correlation. [Add ref to 21 NL- Diffuse emissies en emissies bij op- en overslag.pdf]

Emissions to water
Potential releases into water consist of the residual substances contained in the effluent after treatment. Depending on the nature of the refinery and the treatment efficiency, these may include carbon compounds (insoluble and soluble), nitrogen compounds (organic and inorganic; oxidised and reduced), sulphur compounds (oxidised and reduced), and metals and their compounds. Include hydrocarbons (dissolved and suspended), organic compounds (notably phenols), sulphur compounds (notably sulphides), ammonia/ammoniacal compounds and their derivatives after treatment. Traces of heavy metals are also likely to be present, arising from the desalting of crude oil feedstock and from caustic soda if this contains trace contaminants, notably mercury. More information on effluent composition downstream waste water treatment based on questionnaire data collection (2008) in this subject is included in Section 3.1.3.

Solid wastes generated
Solid wastes are generated in the form of sludges from a number of the treatment units. Primary treatments generate API separator sludge (phenols, metals and up to 10% oil), chemical precipitation sludge (chemical coagulants, oil), DAF floats (up to 30% oil), biological sludges (metals, <0.5% oil, suspended solids) and spent lime. Secondary treatment generates biomass waste which is typically treated anaerobically and then dewatered. Flotation units and biotreaters generate the largest quantities of sludges in the waste water treatment plants. DAF units produce significant quantities of sludges. The limited information reported in the survey (for three units [115, CONCAWE, 1999]) indicated an annual sludge production of about 2400 tonnes per year for a throughput of 600 m³/h. The induced air flotation generates 600 tonnes per year with a unit operating at 600 m³/h.

Refinery waste water collection and pretreatment systems generate important amounts of solid wastes that have been in direct contact with hydrocarbons:

- Settleable solids (specific gravity greater than water) can separate from waste water in the collection and primary treatment systems. The collection system can include individual drain systems serving production areas as well as other areas affected by refinery activities and may include basins and/or tank systems to contain and manage peak flows of storm water.
- Suspended solids (specific gravity less than or equal to water) may be separated and extracted in gas flotation or sand filtration processes. Secondary biological treatment processes can generate important amounts of excess biosolid waste that must be continually removed from the process as soluble substances are assimilated into new biomass in the bioreactors.

Table 3.103 shows the composition of the different sludges generated in the waste water treatment plants.
Table 3.103: Examples of analysis of refinery sludges

<table>
<thead>
<tr>
<th>Species</th>
<th>API separator</th>
<th>Activated sludge</th>
<th>Settling basin plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids</td>
<td>90.4 %</td>
<td>94.3 %</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Oil</td>
<td>9.6 %</td>
<td>5.7 %</td>
<td>0.3 %</td>
</tr>
<tr>
<td>Carbon</td>
<td>25.8 %</td>
<td>13.1 %</td>
<td>1.7 %</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>13.1 %</td>
<td>51.8 %</td>
<td>6.3 %</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.6 %(*)</td>
<td>1.7 %</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Sulphur</td>
<td>40733</td>
<td>9479.0</td>
<td>4214.0</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.3 %</td>
<td>0.2 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Iron</td>
<td>48269.0</td>
<td>10900.0</td>
<td>7131.0</td>
</tr>
<tr>
<td>Aluminium</td>
<td>43177.0</td>
<td>2322.0</td>
<td>4878.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>11609.0</td>
<td>4692.0</td>
<td>8104.0</td>
</tr>
<tr>
<td>Sulphide</td>
<td>6180.2</td>
<td>2165.9</td>
<td>1037</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4878.0</td>
<td>1351.0</td>
<td>1767</td>
</tr>
<tr>
<td>Sodium</td>
<td>1711.0</td>
<td>3981.0</td>
<td>3971</td>
</tr>
<tr>
<td>Xylene</td>
<td>469.5</td>
<td>9.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>288.2</td>
<td>46.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Lead</td>
<td>279.0</td>
<td>49.3</td>
<td>15.2</td>
</tr>
<tr>
<td>Phenol</td>
<td>265.0</td>
<td>46.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>252.5</td>
<td>37.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Nitrate</td>
<td>228.1</td>
<td>2066.4</td>
<td>194.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>138.5</td>
<td>9.5</td>
<td>32</td>
</tr>
<tr>
<td>Styrene</td>
<td>134.4</td>
<td>47</td>
<td>16.0</td>
</tr>
<tr>
<td>Vanadium</td>
<td>99.0</td>
<td>18.0</td>
<td>24.0</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>82.5</td>
<td>9.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>80.0</td>
<td>8.1</td>
<td>11.2</td>
</tr>
<tr>
<td>Fluorine</td>
<td>59.1</td>
<td>46.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Antimony</td>
<td>49.0</td>
<td>14.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>42.6</td>
<td>46.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Phenol</td>
<td>40.3</td>
<td>46.9</td>
<td>16.0</td>
</tr>
<tr>
<td>Selenium</td>
<td>35.4</td>
<td>26.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>13.2</td>
<td>9.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Sulphate</td>
<td>12.2</td>
<td>2767.8</td>
<td>285.3</td>
</tr>
<tr>
<td>Arsenic</td>
<td>6.5</td>
<td>15.2</td>
<td>5.2</td>
</tr>
<tr>
<td>Mercury</td>
<td>3.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cyanide</td>
<td>1.0</td>
<td>7.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

(*) Below detection limit shown
NB: Figures do not sum to 100 % because of double counting.
Figures quoted on a moisture-free basis, all units mg/kg unless otherwise stated.
Source: [80, March Consulting Group, 1991]
3.27 Waste generation

An important issue when considering refinery waste is that there are still many differing definitions between countries, which makes comparisons of waste difficult.

Sludges

The amount of sludge generated depends on the types of processes and the availability of incineration. As a common figure, the generation rate of solid waste and sludges is normally less than 0.5 % of crude processed, but in some refineries it is less than 0.3 %. Annual sludge generation was 1250 kt per year (in 1993), some 0.2 % of refinery intake.

In 1993, CONCAWE carried out a survey of waste in Western European refineries [82, CONCAWE, 1995]. In this survey 89 refineries reported their sludge production from all sources as one million tonnes. That means an average of 11 000 t per year per refinery. This figure represents a 0.20 % of the crude oil processed by these refineries. However, a variation range from 2.5 % to less than 0.02 % was found in European refineries, with the value being independent of the type of refinery. From that million tonnes of waste, 45 % was sludge, 20 % other refining wastes and the rest non-refining wastes. Sludges come from stabilisation processes (4.7 % of the total sludge generated after treatments), waste water sludges (39.8 %) and sludges with no treatment (55.5 %).

The main disposal routes for sludge are shown in the table below for 2008.

Table 3.104 Sludge disposal main routes

<table>
<thead>
<tr>
<th>Technique disposal</th>
<th>Total %</th>
<th>On-site %</th>
<th>Off site %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incineration</td>
<td>51.40</td>
<td>39.60</td>
<td>11.80</td>
</tr>
<tr>
<td>Landfarming</td>
<td>7.20</td>
<td>3.60</td>
<td>3.60</td>
</tr>
<tr>
<td>Reprocessing</td>
<td>32.40</td>
<td>25.20</td>
<td>7.20</td>
</tr>
<tr>
<td>Anaerobic digestion</td>
<td>0.90</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Landfill</td>
<td>7.20</td>
<td>–</td>
<td>7.20</td>
</tr>
<tr>
<td>Fertiliser</td>
<td>0.90</td>
<td>–</td>
<td>0.90</td>
</tr>
</tbody>
</table>

The total amount of identified other refining wastes which are specific to the refining process (e.g. spent catalysts, tank scales, contaminated soils, etc.) produced in 1993 by the 89 European refineries reporting was 201 983 tonnes (i.e. 0.04 % w/w of the total refinery throughput). Data provided by 16 EU+ refineries show that the specific production of waste ranges from 133 to 4200 t/million t of crude. Table 3.105 shows an example of the waste production routes statistics for 2007 and 2009 in refineries.

Table 3.105 Waste generation of an European refinery

<table>
<thead>
<tr>
<th>Waste category</th>
<th>Non-hazardous waste 1997 (t)</th>
<th>Hazardous waste 1997 (t)</th>
<th>Sum 1997 (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Landfill</td>
<td>2962</td>
<td>1109</td>
<td>4071</td>
</tr>
<tr>
<td>Material recycling and thermal treatment</td>
<td>202</td>
<td>2401</td>
<td>2603</td>
</tr>
<tr>
<td>Biological treatment</td>
<td>100</td>
<td>37</td>
<td>137</td>
</tr>
<tr>
<td>Chemico-physical treatment</td>
<td>24</td>
<td>48</td>
<td>72</td>
</tr>
<tr>
<td>Total</td>
<td>3585</td>
<td>1350</td>
<td>4935</td>
</tr>
</tbody>
</table>

Note: Waste includes waste generated by storage tanks.

Table 3.106 Waste generation of an European refinery

Source: [250, Winter, 2000]
Table 3.105 Waste routes and transfers in refinery sector in 2007 and 2009

<table>
<thead>
<tr>
<th>Type of waste and transfer</th>
<th>Routes</th>
<th>2007</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tonnes</td>
<td>Number of sites</td>
</tr>
<tr>
<td>Hazardous waste in the country</td>
<td>Disposal</td>
<td>294 000</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td>306 000</td>
<td>98</td>
</tr>
<tr>
<td>Hazardous waste outside the country</td>
<td>Disposal</td>
<td>3 000</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td>34 000</td>
<td>30</td>
</tr>
<tr>
<td>Total hazardous waste</td>
<td>Disposal</td>
<td>637 000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non hazardous waste</td>
<td>Disposal</td>
<td>372 000</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Recovery</td>
<td>538 00</td>
<td>61</td>
</tr>
<tr>
<td>Total non-hazardous waste</td>
<td></td>
<td>900 000</td>
<td></td>
</tr>
</tbody>
</table>

Sources: E-PRTR and CONCAWE

Spent catalyst

Hydroprocessing requires the use of catalysts to remove impurities and to convert the oil into more useful products. The catalysts used consist mainly of oxides of nickel, cobalt and molybdenum on an alumina carrier. During hydroprocessing operations the catalysts are loaded with sulphur, vanadium and coke. The porosity of the catalysts decreases and their activity is reduced, which eventually requires replacement of the catalyst in the reactors. Consequently, the catalysts become spent and must be replaced.

Co/Mo catalysts from hydrodesulphurisation, hydrocracking, hydrotreating: for a 5 Mt/yr refinery, spent catalyst amounts can vary from 50 - 200 t/yr.

Ni/Mo catalysts are typically used in hydrotreaters and hydrocracking units. A 5 Mt/yr refinery generates typically 20 - 100 t/yr spent Ni/Mo catalyst.

Ni/W catalysts are used in lube oil hydrofinishing. This category experiences limitations for disposal in view of the high tungsten content (24 % w/w). A 50000 t/yr lube oil plant can generate 50 t/yr of this catalyst waste.

FCC spent catalysts, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries (world production is about 0.5 Mt/yr). A 1 Mt/yr FCC unit generates 400 - 500 t/yr predominantly as FCC fines if an ESP is installed. For a RCC this amount can be a factor of 5 - 10 higher, depending on the type of feed as spent catalyst is withdrawn from the regenerator.

Reformer and isomerisation catalysts are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved. Typical average amounts involve 20 - 25 t/yr for a 5 Mt/yr refinery. If necessary guard beds of HDS catalysts are used for protection and extension of the lifetime of the expensive catalysts.

Hydrodemetallisation catalysts typically have high vanadium contents (10 - 20 %) and are currently alumina based (used to be silica). The annual amount for regeneration is in the order of 500 - 1000 t/yr for Hycon (Shell Pernis NL) dependent on the feed quality.

Zn containing beds from H2 plants are typically recycled to the Zinc industry where ZnS ores are processed. Amounts are some 50 t/yr.

In hydrodesulphurisation, hydrotreating and hydrocracking, the world catalyst production (and thus also the generation of spent catalysts) grew in the last 10 years considerably during the 1990s and was estimated at 100 kt/yr (1998). Current At the same time, regeneration capacity was estimated at 125 kt/yr. It was also estimated that 5 - 10 % of this category of spent catalysts was still being landfilled.
# Chapter 3

Table 3.106: Composition of spent catalysts from various sources in % w/w

<table>
<thead>
<tr>
<th>Process</th>
<th>S</th>
<th>C</th>
<th>Mo</th>
<th>V</th>
<th>Ni</th>
<th>Co</th>
<th>Al</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC, RCC</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>4 – 8 000(*)</td>
<td>2 – 3 000(*)</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Reforming and isomerisation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>0.5 Pt, Pa, Rh</td>
</tr>
<tr>
<td>Hydro processing</td>
<td>6 – 16</td>
<td>10 – 30</td>
<td>4 – 8</td>
<td>2 – 12</td>
<td>1 – 2</td>
<td>1 – 2</td>
<td>20 – 30</td>
<td></td>
</tr>
<tr>
<td>Claus plant</td>
<td>5</td>
<td>5</td>
<td>4 – 8</td>
<td></td>
<td></td>
<td></td>
<td>20 – 30</td>
<td></td>
</tr>
<tr>
<td>Hydrofinish</td>
<td>5</td>
<td>1 – 2</td>
<td>2 – 4</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>24 W</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>5 – 15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>30 Zn</td>
</tr>
<tr>
<td>Hydro-de metallisation</td>
<td>5 – 15</td>
<td>10 – 30</td>
<td>10 – 20</td>
<td>2 – 5</td>
<td></td>
<td></td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

(*) In ppm
3.28 Monitoring

KOM conclusion 2.5: Please TWG still to provide sector-specific info on monitoring equipment, practises and calculation methods for:
- measuring/calculation of PM (PM$_{2.5}$ and PM$_{10}$ if relevant), NO$_x$, SO$_2$ and fuel gas composition, flare gas composition and or flare emissions (1), fugitive VOC (2)
- European methodologies to calculate CO$_2$ emissions, reports from individual refineries on CO$_2$ emissions with respect to ETS and national legislation
So far, info has been made available from:
(1) DE
(2) FR, NL, SE, CONCAWE
Info still expected from NO, UK

There is an IPPC specific document [46, EC 2003] on monitoring (MON), and completed by an expanding series of literature published by competent authorities at federal and national levels (e.g. HMIP Technical Guidance Notes in UK) on monitoring. These reference documents containing information on theory, methodology and related techniques. and providing technical information on monitoring techniques. It should be considered that the requirements and frequency of sampling, analysis and type of monitoring requirements are site and/or process specific. They are influenced by consideration of the anticipated volume and composition of the waste streams and normally are included in the permits. The MON document includes also provides guidance to permit writers on compliance assessment and environmental reporting, and That document also encourages the comparability and reliability of monitoring data across Europe.

This section aims to give recommendations on the scope and frequency (continuously or discontinuously) of monitoring streams in a refinery. Monitoring should be undertaken during commissioning, start-up, normal operation, and shutdown unless it is agreed that it would be inappropriate to do so.

The monitoring system should allow adequate processing and emission control. Some elements of A monitoring system could in a refinery generally includes:

- continuous monitoring of pollutants for high volume flows with high variability in pollutant concentrations;
- periodic monitoring or the use of emission relevant parameters for flows with a low variability and calculation based on high-quality emission factors;
- regular calibrating of measurement equipment;
- periodic verification of measurement by simultaneous comparative measurements.

In order to have a good idea of the emissions generated by an installation (e.g. a refinery), the emissions need to be quantified. This will give to the refinery and permit writer the ability to know where the actions to reduce a certain pollutant may be more economical. Typically abating higher emissions at high concentrations is more economical than lower emissions at low concentrations. As consequence, a quantification of the emissions for each single refinery is the first starting point in any environmental assessment. This quantification may contain a full mass balance also considering other outputs (e.g. products).

3.28.1 Monitoring of air emissions

In many refineries the bubble concept is applied for some air pollutants. The concept is to consider the refinery as a whole and to sum up concentrations and volumes of all the emission sources. From this is calculated the average concentration of the pollutants regardless of the source or stack. This type of concept is applied to sulphur dioxide and other air pollutants in
**Chapter 3**

Some European countries and in the EU Large Combustion Plant Directive. More information can be found in 4.15.2. SO₂, NOₓ, particulate matter, and CO are typically continuously monitored (on-line or predictive) in the refineries. Records of the volumes are also required for the calculation of the load (tonnes of pollutant per year) or for the application of the bubble concept. Table 3.107 shows the locations where the main air pollutants are typically continuously monitored in a refinery.

Table 3.107: Overview Examples of the most common air emission continuous monitoring in oil refineries

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Example of monitoring</th>
<th>Location where normally is measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur dioxide</td>
<td>Continuous if P &gt;30 MW (except for natural gas)</td>
<td>FCC UNIT regenerators</td>
</tr>
<tr>
<td></td>
<td>Continuous if P &gt;20 MW and desulphurisation unit (elsewhere, daily estimation)</td>
<td>Sulphur recovery units (i.e. from tail gas incinerators) Incinerators or furnaces used to burn sour gas or liquid fuels Bitumen production units</td>
</tr>
<tr>
<td></td>
<td>or P &gt;100 MW</td>
<td>Gasification units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coking processes</td>
</tr>
<tr>
<td>Oxides of nitrogen</td>
<td>Continuous if &gt;30 MWh (except for natural gas)</td>
<td>Combustion processes</td>
</tr>
<tr>
<td></td>
<td>Continuous if P &gt;20 MW and abatement unit or P &gt;100 MW</td>
<td>FCC UNIT regenerators</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gasification units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coking processes</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Continuous if &gt;10 MW</td>
<td>FCC UNIT regenerators (for partial combustion type units if CO release is significant)</td>
</tr>
<tr>
<td></td>
<td>Continuous if &gt;50 MW</td>
<td>Combustion processes</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>Continuous for solid and liquid fuels if &gt;10 MW</td>
<td>Combustion processes burning fuel oil</td>
</tr>
<tr>
<td></td>
<td>Non relevant for natural gas or RFG (Examples from Austria)</td>
<td>FCC UNIT regenerators</td>
</tr>
<tr>
<td></td>
<td>Continuous if &gt;50 MW (Examples from France - P expressed as MW th)</td>
<td>Coking processes and petroleum coke calciners and coolers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gasification units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Catalyst regeneration (e.g. reforming)</td>
</tr>
<tr>
<td>Other common emission components to air commonly monitored:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>carbon dioxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>nitrous oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td>volatile organic compounds (VOCs)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>heavy metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hydrogen fluoride</td>
<td></td>
</tr>
<tr>
<td></td>
<td>halide compounds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ammonia NH₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hydrocarbons (as unburned hydrocarbons, UHC)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dioxins and/or POPs</td>
<td></td>
</tr>
</tbody>
</table>

Next information The following sections include monitoring practices that have been found in European refineries.
3.28.1.1 Sulphur monitoring

It can be expected that the operators compute site sulphur balances over appropriate time periods as a part of monitoring their operations. The time period may vary according to the circumstances (e.g. how often feedstocks change) but could typically be quarterly. In the case of SO₂, the amount emitted by combustion processes may be calculated from the analysis of the fuel being burnt. In some countries (e.g. France), sulphur balance is established daily by the operator and sent monthly to the competent authorities.

3.28.1.2 Gases coming Emissions from combustion processes

Wherever a combustion process (other than flaring) is used for the destruction of hydrogen sulphide or hydrocarbons, its effectiveness can be demonstrated indirectly by continuously monitoring the temperature and oxygen content of the exhaust gas. Visual and olfactory assessments of releases from incinerators, flares, furnaces and other sources liable to cause a nuisance emission can be made when appropriate, particularly during upset/start-up/shutdown conditions.

The monitoring of emissions is carried out to determine the substances in the clean gas so that they can be reported, or to control the combustion process or abatement plant. Gaseous releases from gas turbines used for electrical generation or gas compression are typically also monitored.

In order to relate emission concentrations to mass releases, it will be necessary to measure or otherwise determine the gas flow. Additionally, in order to relate measurements to reference conditions, the temperature will need to be determined. The determination of oxygen and water vapour content may also be required. Monitoring and averaging periods required by the type of substances and the techniques used need to be reported.

3.28.1.3 Flares and flare gas monitoring

Note to TWG: text moved to section 4.25.7

3.28.1.4 Diffuse VOC monitoring

Diffuse VOC emissions are emissions arising from direct contact of gaseous or liquid volatile organic compounds with the environment (atmosphere, under normal operating circumstances). These can result from:

- inherent design of the equipment (e.g. uncovered oil/water separators)
- operating conditions (e.g. non collected vent of a fixed roof tank during loading)
- or fugitive emissions caused by an undesired gradual loss of tightness from a piece of equipment and a resulting leak. Fugitive emissions are a subset of diffuse emission.

VOC emissions by refineries come mainly from fugitive diffuse emissions. Four major diffuse emissions sources can be identified.

1. Fugitive emissions by leaking equipment, such as valves, flanges, pumps, safety valves, etc. They usually account for 20 – 50 % of the total refinery VOC emission.
2. Crude oil and products storage. Emissions from fixed roof tanks are due to the venting of storage tanks during operations or to breathing due to variation of ambient temperature. Emissions from floating roof tanks occur from losses from seals and roof fittings They typically represent 20 – 40 % of the refinery emissions.
3. Loading and unloading facilities, including lorries, boats, trains, road tankers, rail tank cars, barges and sea-going vessels. They account for 5 – 10 % of site emissions.
4. Waste water treatment plants, where a gradual release of VOC may occur at all water/air interfaces. Depending on VOC reducing techniques applied, WWTPs usually generate 5 – 30% of the total site emissions.

**Overview of available methods for detection/quantification**

Main available methods with their respective field and scale of application are displayed in Table 3.108. It can be remarked that all these methods are complementary and all potentially useful in order to build up an efficient monitoring programme. Some are appropriate for the detection and/or the quantification of spot sources, whereas others are devoted to area sources, and unit-scale or even site-scale accumulated global emissions. Moreover, each of these methods enables the monitoring of a different scope of VOC species, as seen in Table 3.109.

However, on one hand, it has to be emphasised that calculation methods based on emission factors and algorithms are reported to be unreliable and give significantly underestimated results, in particular for tank farms, cokers and flares [50, White, 2008] [51, Chambers et al, 2006]. On the other hand, a CONCAWE report [62, CONCAWE 2008] highlighted the potential errors introduced by using short term values for extrapolation to annual ones due to the temporal variations in the emissions from diffuse sources. Some estimation algorithms (e.g. for storage) have been derived from extensive tests and are designed specifically to provide long term estimates.

<table>
<thead>
<tr>
<th>Table 3.108: Overview of main available methods for VOC detection and quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of diffuse VOC source</td>
</tr>
<tr>
<td>------------------------------</td>
</tr>
<tr>
<td>Small individual equipment (pumps, valves, flanges, etc)</td>
</tr>
<tr>
<td>Storage tanks</td>
</tr>
<tr>
<td>Loading/unloading facilities</td>
</tr>
<tr>
<td>Water treatment plants</td>
</tr>
<tr>
<td>Full scale unit/Whole site</td>
</tr>
</tbody>
</table>

NB: D = detection; Q = quantification

(1) The detection exhaustivity regarding mass flow rate has to be confirmed
(2) Active area sources can be detected if they generate individual plumes that can be distinguished from the rest of the site, and if emissions occur during the measurement
(3) Algorithms designed for annual emission quantification
Table 3.109: Overview of VOC species according to the measuring method applied

<table>
<thead>
<tr>
<th>VOC species</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>Y</td>
</tr>
<tr>
<td>Alkenes</td>
<td>Y</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Y</td>
</tr>
<tr>
<td>Cyclic hydrocarbons</td>
<td>Y</td>
</tr>
<tr>
<td>Methane</td>
<td>Y</td>
</tr>
<tr>
<td>Total VOC</td>
<td>Y</td>
</tr>
</tbody>
</table>

(1) When based on IR light  
(2) When based on UV light  
(3) Poor for light aromatics when based on passive systems.  
(4) With GC/MS used for speciating samples

**Description, main features and limitations of most used measuring techniques**

This section gives a short description of the four monitoring techniques based on actual measuring which are most commonly used for the monitoring of diffuse VOC emissions. Respective costs, detection limits together with a comparison of their specific advantages and drawbacks are summarised in Table 3.111. Calculation methods cannot be considered measurements and will not be described in this section.

**Method EN 15446:2008: conventional VOC ‘sniffing’**

This method was originally developed as a support for the implementation of a LDAR programme (see Section 4.25.6.1) for the detection and ranking of leaking equipment pieces to be repaired. The first step is the detection (‘sniffing’) which is achieved using hand-held VOC analysers measuring the *ambient* atmospheric VOC concentration adjacent to the equipment as shown in Picture 3-1. The most frequently used measuring techniques are the flame ionisation (FID) and the photo-ionisation (PID), calibrated to operate in the range of 10 – 100000 ppmv. The probe is characterised by a ‘response factor’ which takes into account the sensitivity to the actual VOC mixture measured compared to a reference gas, and a ‘response time’ defined as the time needed to register 90 % of a concentration step change. Both factors greatly influence the results and have to be optimised according to the EN 15446 standards.

![Picture 3 - 1: Leak concentration measurement](image1.png)  
![Picture 3 - 2: Bagging of a leaking valve](image2.png)
For mass flow quantification, the second step proposed by the standard method consists of bagging the source component as shown in Picture 3.2. This bagging is the only step of this method allowing for a direct measurement at the source of emission. However, as bagging is an extremely burdensome operation and is not always possible, mathematical correlation curves can be derived from statistical results obtained from a sufficiently large number of previous measurements of both leak concentration (Step 1) and mass flow (Step 2) made on similar components. Very few refineries have developed such correlation curves corresponding to their own set of components, related VOC leakage mixtures, and concentration measurement skills and real practices. Alternatively they use generic curves from the literature based on extensive measurement campaigns carried out on US facilities in the 1950-1980s and 1990s.

**Optical gas imaging techniques (OGI)**

Optical imaging uses small lightweight hand-held cameras which enable the visualisation of gas leaks in real time, so that they appear as ‘smoke’ on a video recorder together with the normal image of the component concerned. This technique is primarily used to easily and rapidly locate significant VOC leaks e.g. on process components, storage tanks fittings, pipeline flanges or vents. Most current commercial OGI cameras fall under one of these two categories.

- **Active systems** where the image is produced by a back-scattered IR laser light reflected on the component and its surroundings. The laser wavelength is optimised to be absorbed by the VOC concerned.
- **Passive systems** based on the natural IR radiation off the equipment and its surroundings. The contrast of the VOC image is based on the plume IR absorption and the heat radiance difference between the plume and its background. An optical filter selects the optimal IR wavelength according to the VOC nature.

Detection limits are related to the minimal thermal gradient for visualisation, and will depend on the gas temperature, the distance from the source, and the wind speed. Although these are higher than achieved by ‘sniffing’, OGI technology can more efficiently identify the main fugitive emission sources. The mass emission rate is still not directly quantified. Specific work is being done in order to propose and validate appropriate OGI emission factors based on comparison with EN 15446 quantification on the same set of components in an actual unit. In addition, the US API also developed OGI leak/no-leak factors.

**Differential absorption lidar (DIAL)**

DIAL is a laser-based technique using differential adsorption LIDAR (light detection and ranging) which is the optical analogue of some radio wave based RADAR. As shown in Figure 3.36, the technique relies on the back-scattering of laser beam pulses by atmospheric aerosols, and the analysis of spectral properties of the returned light collected with a telescope. As each molecule present will absorb and re-emit a typical light, the returned beam acts as an optical signature of the concentration of most molecules present between the DIAL source and the reflecting particulate. By sampling the returned light pulse rapidly according to time, it is possible to distinguish how far each sample of the light pulse has travelled and, thus, locate it with the precision of a few meters in optimum conditions.
The laser beam and the optical reception system are rotated in order to cover a plane crossing the atmospheric VOC plume. The result of it is a 2-dimension map where the concentration can be integrated, as shown on Figure 3.37.

To obtain mass emission flux, the concentration data across the plume section should be multiplied by the wind velocity reported perpendicularly to the measurement plane.

Wind data availability, accuracy and representatibility are essential for reducing quantification uncertainties.

Typical sensitivities and maximum distance ranges are given in Table 3.110 for various emitted VOCs and other compounds of interest. Sensitivities apply at a range of 200 m for a 50 m width plume.

Table 3.110: DIAL Sensitivity and maximal distance range for various emitted compounds

<table>
<thead>
<tr>
<th>Infrared DIAL system</th>
<th>UV/Visible DIAL system</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Species</strong></td>
<td><strong>Sensitivity (ppb)</strong></td>
</tr>
<tr>
<td>Methane</td>
<td>50</td>
</tr>
<tr>
<td>Acetylene</td>
<td>40</td>
</tr>
<tr>
<td>Ethylene</td>
<td>10</td>
</tr>
<tr>
<td>Ethane</td>
<td>20</td>
</tr>
<tr>
<td>Higher alkanes</td>
<td>40</td>
</tr>
<tr>
<td>HCl</td>
<td>20</td>
</tr>
<tr>
<td>N2O</td>
<td>100</td>
</tr>
<tr>
<td>Methanol</td>
<td>200</td>
</tr>
</tbody>
</table>
Various field validation measurements were performed and gave the following results:

- Repeated DIAL measurements downwind of a calibrated (10 kg/h) source of methane agreed to within +/- 10% of emitted value;
- Comparison with a line of pumped absorption tube samplers inside a chemical plant agreed with DIAL measurements of aliphatic hydrocarbons to within +/- 12%, and toluene to within +/- 15%;
- VOC emission measurements from a petrochemical storage facility made by DIAL and standard point sampling methods agreed to within +/- 8%;
- SO₂ plume from a tail gas incinerator (340 kg/h) agreed within -11%;
- NO plume from a gas turbine power plant (66 kg/h) agreed within +1%.

However, the overall uncertainty in industrial field conditions is evaluated at around 30 – 50%, most of it from wind speed evaluation. As with all short term measurement techniques, the extrapolation to provide values of annual emissions for inventory purposes introduces further potential for error, particularly as the majority of refinery VOC sources have significant emission variations with time.

![Typical DIAL concentration map obtained with DIAL measuring system](image)

**Solar Occultation Flux (SOF)**

The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband IR or UV/Visible sunlight spectra along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes.
The system is permanently guided to the sun by a solar tracker mirror, which reflects the sunlight into the spectrometer independent of its position. On short distance segments identified by GPS coordinates, path-integrated concentrations in mg/m² are calculated for various species present between the sun and the system. Results can be gathered on the same map for the whole measuring itinerary, giving an overall shape of main emitting areas and associated concentrations as shown in Picture 3-5.

The spectral retrieval is based on a multivariable analysis in which lab-recorded calibration spectra from literature are fitted to the actual spectra measured, for all target species but also for other interfering species like H₂O and CO₂. Alkanes, which correspond (in mass) to the main part of refinery VOCs, are summed but cannot easily be distinguished due to spectral overlap based on common C-H bond vibration. On the contrary, individual olefins can be measured with good specificity. Aromatics cannot be measured directly. In case of need, canister samples are taken at various positions downwind of the target source, and resulting mass distributions are used for the calculation of missing concentrations in the plume on a prorata basis.

The overall uncertainty for quantification in industrial field conditions is evaluated around 35 – 40 %, most of it from wind speed evaluation and retrieval process stability along itinerary segment sampling.

Picture 3-5: Overall shape of alkane emissions from an oil refinery as measured with SOF (the white arrow indicates the wind direction)
Picture 3-6: Detection of high leaking storages within a refinery tank farm using SOF
### Table 3.111: Overview of performances, costs, advantages and drawbacks of diffuse VOC measuring techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Detection limit</th>
<th>Indicative costs (EUR)</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN 15446</td>
<td>10 ppm at leak source; &lt; 10 mg/h for correlated mass flow Increasing with wind</td>
<td>5 000 – 25 000 for one detector, depending on complexity 60 000 per campaign (2 000) for a 30 000 component site 600 000 for a mini 6-month campaign in a complex refinery</td>
<td>Low detection limit Low instrumentation cost Applicable in hazardous/congested areas</td>
<td>Not applicable to diffuse area sources Direct mass flow measurement not possible Low reproducibility (standard deviation 50 %) and repeatability (standard deviation 35 %) on measured concentration Low reproducibility (standard deviation 40 %) and repeatability (standard deviation 25 %) on indirect mass flow calculations High manpower requirement and operational costs (500 components per day per surveyor). Fully applicable to components only accessible by staircases or ladders (typically around 80 %).</td>
</tr>
<tr>
<td>OGI</td>
<td>4 – 60 g/h (&lt;35mK @ 30 °C) depending on operational conditions 3 000 – 10 000 ppm</td>
<td>70 000 – 110 000 for one camera</td>
<td>High mobility Low manpower requirement (5000 components per day per surveyor) Large monitoring scope, including remote or non accessible large leaks detection Limited training required for operators</td>
<td>Presence of a background surface imperative for the active system Sensitivity related to actual thermal gradients: OGI is less efficient with uniform temperature conditions Not applicable to explosive atmospheres, but can be used under permit to work scheme; Not applicable with rain or fog.</td>
</tr>
<tr>
<td>DIAL</td>
<td>10 – 50 ppbv at 200 m for a 50m-width plume Increasing through dust and water vapour plumes</td>
<td>A single 1 – 2 week campaign costs around 30 000 – 100 000 including data processing and report Device investment &gt;0.2 million</td>
<td>Well established Open path ‘single-ended’ system independent from sun direction Day and night Significant area sources can be localised with horizontal plane scanning (e.g. tank farm) Possible ‘free space’ on-site calibration using calibrated gas mixtures Well adapted to flare emission monitoring</td>
<td>Limited commercial availability Logistics (12 m long – 7 to 12 t lorry) Heavy rain and fog not suitable No precise location of individual point sources Uncertainty of mass flow calculations (wind) ‘Snap shot’ measuring: must be repeated to take into account temporal variations (e.g. tank farms) Upwind sources cannot be simultaneously subtracted: need an additional determined without upstream shot scan (time and logistics constraints)</td>
</tr>
<tr>
<td>SOF</td>
<td>0.5 – 1 mg/m² 1 kg/h can be detected at 50 m distance</td>
<td>A single 2 week campaign costs around 60,000 including data processing and report Device investment &gt;0.2 million</td>
<td>Recent but well established Well adapted to whole site estimates Significant area sources can be localised Well adapted to flare emission monitoring Comparatively simpler, quicker and cheaper than DIAL in favourable meteo conditions</td>
<td>Limited commercial availability Only daytime and sunny conditions No precise location of individual point sources No range resolved data for alkane species No direct measurement for aromatics Uncertainty of mass flow calculations (wind + unknown VOC plume height) Idem DIAL for ‘snap shot’ measuring and upwind sources.</td>
</tr>
</tbody>
</table>
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The site may be equipped to monitor all process vents and possible sources of fugitive losses. A Leak Detection and Repair (LDAR) programme can be implemented (see Section 4.23.6.1) in order to prevent these. An assessment of the total hydrocarbon emissions from the site on a regular basis can be made. Records can be kept of the individual contributions to each total.

VOC emissions can be estimated by USAEPA Method 21 (emission factors for different type of equipment) or by mass balance (feedstock—products). Perhaps one should add that another way of monitoring HC emissions from all sources is through the mass balance between feed stock and products. Other methods have been developed and proven in recent years for the monitoring of VOC emissions, as well as locating sources of VOC emissions, typically using laser absorption techniques (DIAL) of considerable sophistication. Mobile versions are available which can be used to plot pollutant concentration plumes and calculate pollutant flux, including three-dimensional resolution. Whilst having recognised limitations, they have been used successfully in the oil and gas industries. In most of this monitoring campaigns the measurements have been divided into four areas: Process area, product tank farm, crude oil tank farm and water treatment plant. DIAL method has been used in a number of refineries and in many cases, the results appear to be higher than those derived from the API estimations. However, in these trials, the sampling period was very short. In the only trial where a long-term survey was conducted, the results gave reasonable agreement with the API estimations [229, Smithers, 1995]. Next paragraph gives an example of monitoring of VOC within a refinery as well as the discrepancies that they have found using estimation method and DIAL measurement.

Before the measurements, it was estimated a VOC emissions of about 200 tonnes per year at a certain European refinery. The DIAL measurements and annualisation of the results suggested a yearly emission exceeding 1000 tonnes. Especially emissions from tanks were higher than expected. In all cases, emissions estimates using API methods gave lower emissions than estimates based on the DIAL monitoring. In some cases, the discrepancies are very large. By using the method for estimating fugitive emissions proposed by USAEPA [244, USAEPA, 1992] the emissions from the process area 1Mtonnes per year refinery have been estimated to 125 tonnes per year. Extrapolations of the DIAL measurements to a yearly emission give emissions of 500–600 tonnes per year [107, Janson, 1999]. For the total emission from the refinery, the use of estimation methods suggests that the emissions are 600–1100 tonnes per year. Extrapolations of DIAL measurements indicate a yearly emission of 1600–2600 tonnes for medium refineries. During the same exercise of measurements it was also found that the dominating fraction of fugitive emissions was alkanes within interval C_8–C_10. Aromatics contributed to about 9–15% of the total emission [107, Janson, 1999]. However, it is important to notice that the composition of the vapour will depend heavily on refinery configuration and what happens to be leaking at the time of the measurement of the VOC.

Site-scale VOC monitoring and quantification using available measuring techniques

A number of investigations have been carried out in the US and Europe since the 1990s in order to compare the results given by conventional methods (e.g. TANKS emission factors for tank farms, EN 15446 point measuring with correlation curves for production units) with DIAL and more recently, with SOF long-range screenings. Generally, results obtained with the latter have been shown to be higher (usual factors 2–5, exceptionally sometimes more). Reasons were often linked to:

- results obtained with DIAL and SOF were made from extrapolated short term measurements and have been compared to annual inventory emission estimates made by conventional methods;
- large missing sources, which were not taken into account in conventional methods (e.g. gasoline blenders in a tank farm, cooling towers, unknown leakage located in remote parts of pressurised process units, tank cleaning operations);
- underestimating assumptions about some key emission factors (e.g. flares, crude oil tanks, gashoil tanks, hot heavy fuel oil tanks) and the average massic composition of VOC mixtures (part of heavy alkanes evaporated from tanks).
However, one comprehensive study in which DIAL was used for a long, continuous period (four days), compared to a typical measurement period of a few hours, showed that there was agreement between the DIAL estimate and calculations using TANKS.

Modern fugitive VOC monitoring should be more and more based on exhaustive screening methods and real measurements. It must benefit from recent improvements of component-scale conventional methods together with specific opportunities introduced by short and long range optical and airborne remote techniques.

Site level monitoring of the overall VOC diffuse emissions from refineries should be derived from a well balanced approach using all complementary techniques described below, and can be conducted mostly using the following steps.

- Fugitive emissions from leaking components can be evaluated within the implementation of a rigorous LDAR programme, using sniffing methods associated with correlation curves better established at the site level from the bagging of key equipment or, when not available, proposed in updated literature. The part of evaluation relying upon a statistical calculation for ‘not-sniffed’ individual components should be minimised as far as possible, as it most likely increases the overall estimate uncertainty significantly correlation curves developed for specific component types (e.g. by US EPA). Non-accessible sources are taken into account, as described in EN 15446, using these factors.
- OGI cameras should be introduced within ‘smart’ LDAR programmes for easier and faster identification of significant leaking components, in particular in remote areas, allowing for a better LDAR prioritisation and focus. This includes the identification of leaks from storage tank roof seals and fittings which can not be detected by LDAR or by DIAL/SOF technique.
- Permanent or chronic emissions from area sources (e.g. tank farms, WWTPs) still estimated from emission factors should be regularly validated by actual physical measurements, using point samplers (e.g. pumped sorbent tubes) or time correlation tracers (TCT).
- A regular full screening and quantification of site emissions should be undertaken with an appropriate combination of complementary methods, e.g. SOF and/or DIAL campaigns, using the results for trend evaluation in time, cross checking and updating/validation of the ongoing LDAR programme.

Sources: [32, Mellqvist et al. 2008 ], [50, White. 2008 ][51, Chambers et al. 2006 ] [59, TOTAL - Béraud-Dufour, P 2009 ], [60, ENI - A. Selvaggi 2009 ], [61, INERIS 2009 ] [62, CONCAWE 2008 ]

3.28.1.5 Odour monitoring

Note for TWG: After considering the comments received, the section on odour monitoring have been moved from 4.25.9 to the present section.

Pollution by Odour is potentially related to the emission of a large number of chemical substances and compounds. In oil and gas refining, these are most likely to be mainly:

- sulphur compounds (e.g. hydrogen sulphide, mercaptans, sulphides, disulphides)
- nitrogen compounds (e.g. ammonia, amines)
- hydrocarbons (e.g. aromatics).

The perception of an odour in the surroundings of a refining plant and, eventually, the nuisance related to it, and the possibility to prevent or reduce this nuisance will depend on various parameters, highlighted below:
The number of different sources and substances: the resulting odour from a combination of different substances can be perceived as more of a nuisance than the odour of substances emitted separately at the same concentration. Furthermore, in combination with other substances, the characteristic odour of a single substance can be modified so as to be unrecognisable.

The olfactory thresholds of emitted substances: at the same concentration (or distance from the source), some substances will be strongly perceived as others will have disappeared. In case of a mixture, the combined odour will change as the mixture becomes diluted, until the concentration of each component falls below its own threshold.

The individual olfactory ability and subjective reaction of exposed persons: odours can be judged as acceptable or unacceptable depending on the physical sensitivity to it, as well as on psycho-sociological factors which can influence personal preferences. For the same person, an odour can be pleasant when the substance is diluted and become offensive when concentrated.

In general, the human nose is very sensitive to certain substances or components that are typically emitted by oil and, into a lesser extent, by gas refining activities. Table 3.112 gives a selection of values according to different sources. It should be noted that most of these substances, and especially sulphur compounds, generate odours that are generally perceived as very unpleasant or aggressive.

<table>
<thead>
<tr>
<th>Substances or compounds</th>
<th>Odour thresholds</th>
<th>Reported ranges(1) (ppm weight)</th>
<th>Typical(2) (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylmercaptan</td>
<td></td>
<td>0.00007 – 0.004</td>
<td>0.0021</td>
</tr>
<tr>
<td>Ethylmercaptan</td>
<td></td>
<td>0.0000087 – 0.002</td>
<td>0.00277</td>
</tr>
<tr>
<td>Hydrogene sulphide</td>
<td></td>
<td>0.00041 – 0.002</td>
<td>0.0253</td>
</tr>
<tr>
<td>Dimethylsulphide</td>
<td></td>
<td>0.0022 – 0.3</td>
<td>0.0058</td>
</tr>
<tr>
<td>Diethylsulphide</td>
<td></td>
<td>0.002 – 0.4</td>
<td>0.00146</td>
</tr>
<tr>
<td>Dimethyamine</td>
<td></td>
<td>0.033</td>
<td>0.153</td>
</tr>
<tr>
<td>Diethylamine</td>
<td></td>
<td>0.048</td>
<td>0.567</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>1.5 – 4.7</td>
<td>11.8</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td></td>
<td>0.17 – 2.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>0.33 – 50</td>
<td>5.95</td>
</tr>
<tr>
<td>o-, m-, p-Xylene</td>
<td></td>
<td>0.08 – 3.7</td>
<td>1.43 – 3.77</td>
</tr>
<tr>
<td>Lighter alcanes</td>
<td></td>
<td>&gt;50</td>
<td>&gt;500</td>
</tr>
<tr>
<td>Mid range alcanes</td>
<td></td>
<td>&gt;2</td>
<td>&gt;30</td>
</tr>
<tr>
<td>Heavier alcanes</td>
<td></td>
<td>&lt;2</td>
<td>&lt;6</td>
</tr>
</tbody>
</table>

(1) [40, Nagata Y 1990] [42, Devos et al. 1990]
(2) [41, ADEME 2005]
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- the smelling ability and subjective reaction of exposed persons: odours can be judged as acceptable or unacceptable depending on the personal sensitivity to it. For the same person, an odour can be pleasant when the substance is diluted and become offensive when concentrated.

Refineries should have an odour management plan as a well identified part of their environmental management system (see Section 4.15.1.1). The odour management plan should include all of the following elements:

a. an odour management strategy;
b. protocols for conducting odour monitoring;
c. a protocol for response to identified odour events;
d. an ongoing odour prevention and elimination programme designed to identify the location, nature, emission and dispersion of on site odours, to characterise the odours, and to implement elimination and/or reduction measures in relation to these odours;
e. an implementation timetable for all actions to be taken within this programme;
f. reporting procedures to regularly advise management on the results of the plan;
g. a review programme for regularly updating the plan.

Because odorous compounds are primarily VOCs and sulphur and nitrogen compounds, various prevention, reduction and abatement techniques already described in Section 4.25, in particular when applied to fugitive emissions, are closely participating to the prevention and limitation of prevent and limit odour pollution. Furthermore, an overview of main odour management and treatment techniques is available in Section 3.4.3 of the CWW BREF [6, EC 2003].

The following sections focus on specific techniques that can be most appropriate to the oil refining sector.

3.28.1.5.1 Dynamic olfactometry with human assessors

Description
Odour concentration is determined by a panel of trained human assessors or panelists. Odour concentration is measured according to the European standard EN 13725-2003. The basis of this measurement method is that odour can be detected by a person if the individual odour threshold is exceeded, independently from the preliminary knowledge on the odorous substance concerned.

The gaseous sample of odorants is collected on site using special bags to prevent the sample from being polluted by the pumping system used to collect it. The odour concentration is determined by olfactometry, that is by presenting a panel of selected and screened human subjects with that sample, varying the concentration by diluting the sample with odour-free gas in order to determine the dilution factor at the 50 % detection threshold (that is when the odour can just barely be perceived by 50 % of the test panel). The numerical value of the odour concentration is equal to the dilution factor that is necessary to reach the odour threshold. Its unit is the European Odour Unit (ouE). Therefore, the odour concentration at the odour threshold is 1 ouE by definition.

The persons that are members of the panel must fulfil certain requirements, for example regarding their sensitivity to odour perception. The main panel calibration gas used to verify this requirement is n-Butanol. To ensure the required level of accuracy, odour concentration is determined by a panel composed of 6 to 8 members. The laboratory must be ventilated to isolate the panelists from the odours in the ambient environment. Samples must be analysed within 24 hours after sampling.
Achieved environmental benefits
This method provides the necessary input for a well-establish odour management plan (OMP). By recruiting panelists within the people living in the neighboring of the refinery, this technique also improves the preparedness, participation and response of local community potentially exposed to odour pollution.

Cross-media effects
None.

Operational data
No data submitted

Applicability
The technique is fully applicable to new and existing installations.

Economics
The cost reported for one analysis is in the range of EUR 300 – 400. The cost for a complete survey including panelist training is in the range of EUR 50 000 (refinery in Spain).

Driving force for implementation
This technique is used at installations when odour nuisance is an issue or when complaints occur in the vicinity of the industrial site.

Example plants
The technique is reported to have already been used successfully for various public or industrial activities (e.g. municipal waste water treatment plants, waste elimination, animal by-products manufacturing)

Reference literature
[ 41, ADEME 2005 ] [ 43, INERIS 2009 ]

3.28.1.5.2 Odour surveys by a committee of residents

Description
Odour nuisance is assessed by a committee of residents using different questionnaire techniques in order to evaluate the perceived nuisance. Questionnaires are filled in regularly, but always on a voluntary basis. The answers are correlated with meteorological conditions to get a link between actual emission sources and the described nuisance.

At a basic or preliminary step, the respondents are requested to rate the odour perception, the quality, and the level of nuisance on a multi-points scale. As an example, a conventional five-point scale can include the following ratings: 'definitely not annoying', 'slightly annoying', 'annoying', 'highly annoying' and 'extremely annoying'.

As a second step, after specific training, residents can also establish site olfactory imprintings from a collection of odorous molecules organised in accordance with their dominance (e.g. amine, sulphurous, pyrazine) using recognised methodologies. One of these called ‘Le Champ des Odeurs®’ (developed by IAP Sentic) has been used since 1998 around industrial areas of the Seine estuary in France [ 47, AIR NORMAND 2006 ]. Site odour profiles are determined according to individual reference odourers distributed as follows in Figure 3.38.
Conducting a survey requires enough responses to carry out a statistical analysis. Representative sampling observations (in space and time) are obtained by considering, in particular, the population density, and the direction and the velocity of the prevailing winds. The theoretical impact distances (determined by odour dispersion modelling) can also be used for sampling validation.

**Achieved environmental benefits**
This technique allows for a better knowledge and understanding of the conditions under which odour nuisances occur. The results can be used for adjusting plant configuration and operations to reduce odour nuisance and the parameters which have to be assessed to limit olfactory impacts can be determined. Recommendations can be proposed and circulated back to the residents, e.g. specific practices to be avoided under characteristic meteorological conditions, and main sources identified as actually a nuisances and deserving newly adapted prevention measures or abatement techniques. This improves the preparation, participation and response of the local community potentially exposed to odour.

Furthermore, the technique can also play a key role in the control of the effectiveness and efficiency of odour-reducing actions taken from previous monitoring campaigns. As an example, the latest olfactory profile carried out around the ExxonMobil refinery in Port-Jérôme (2006) identified a 20 % odour reduction compared to initial campaigns (1998), enabling for residents to perform by themselves a clear quantification of the results obtained from the odour-reducing action plans implemented by the refinery and neighbouring plants along this period.

**Cross-media effects**
There are no cross-media effects associated with the technique.
Operational data
Investigation campaigns can last quite some time (six months to one year) and require numerous observations and enough residents appropriately sampled on a spatial basis. As a consequence, steering resources should be put in order to ensure:

- having enough volunteers to perform relevant statistical analysis
- motivating respondents during a minimal period lasting from a few month to one year, and ideally even longer in order to keep the same panel for several consecutive campaigns;
- the careful cross-analysis of all data.

In the case of the ExxonMobil refinery in Port-Jérôme (Rouen, France), typical trainings of residents for specific odour identification and site imprintings last 72 hours spread over 4 to 5 months. They involve 30 external voluntary ‘noses’ living in the vicinity, together with 12 internal ‘noses’ from the refinery staff. The odour profile of the refinery has been determined as shown in Figure 3.39.

![Example of olfactory profile of a refinery in Upper-Normandy (France)](image)

Figure 3.39: Olfactory profile of the ExxonMobil refinery in Port Jérôme (France)

Complementary methods (such as the dynamic olfactometry described in Section 3.28.1.5.1 in particular) can be used to qualify and describe the perceived odour in order to determine the odour sources responsible for the annoyance. Implementing this technique involves setting up a training programme for the volunteers and regular debriefings.

Applicability
The technique is fully applicable to new and existing installations. As an example, over 60 industrial companies are due to have their olfactory imprintings defined so far, and have their odourous impact regularly tracked along the Seine estuary industrial area.

Economics
The technique costs are in the range of EUR 20 000 – 30 000 for a 6-month study including the recruitment of volunteers, management of questionnaires (by post, internet or by phone),
analysis of the filled-in questionnaires, and meeting management for the presentation of the results to residents and other stakeholders (specific odour identification trainings excluded). All of this can be managed by an external consulting firm. Equipment needed generally includes a PC, statistical software, and a weather station for a cost of about EUR 10 000.

**Driving force for implementation**
This technique is used at installations when odour nuisance is an acute issue, in order to provide the necessary input for a well-establish odour management plan (OMP). It will help to solve complaints and to build up and maintain constructive relationships between the operator and the residents.

**Example plants**
The technique is reported to be used at several industrial areas in France, where in particular oil and petrochemical plants are in operation.

**Reference literature**
[ 44, INERIS 2009 ] [ 47, AIR NORMAND 2006 ] [ 49, ExxonMobil 2009 ]

### 3.28.2 Monitoring releases to water

Continuous monitoring and flow proportional sampling for releases to water are always preferable but the use of a fixed interval or time proportional sampler for low flow rates (less than 1 litre per second) may be acceptable.

The monitoring of process effluents released to controlled waters and sewers will commonly be made for the following: flow rate, pH, temperature, and TOC (surrogate for COD/BOD). Samples are also being monitored for appropriate other parameters such as COD, BOD, hydrocarbon oil, ammoniacal and total nitrogen, suspended solids, phenols, sulphides, dissolved oxygen, phosphates, nitrates, nitrites, metals (typically Cd, Hg, Cr, Ni, Zn, Cu, As). The periodicity can be typically daily, weekly or monthly depending on risk assessment and on local circumstances.

One problem with water discharge from refineries is analysis, and especially the analysis of oil. There are a number of different methods (e.g. IR one wavelength, IR two wavelengths, gravimetric) which give completely different results. Another problem is the toxic substances used in the COD analysis.

Losses of oil through leaks can also be minimised through the continuous monitoring of the cooling water system. At its simplest, this comprises monitoring of the cooling water separators for oil build-up. If this is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak. A further refinement is to install oil in water monitors at various points in the cooling water system. This allows leaks to be detected rapidly and corrective action to be taken. For this procedure to be effective, sparing of critical heat exchangers will be required.

In case of a once-through system, the cooling fluid outlet system may be divided into a suspect system, where the process pressure is higher than the cooling system pressure and a clean system, where the cooling system pressure is higher than the process pressure. The suspect system needs to be monitored for contamination.
### 3.28.3 Monitoring solid wastes

A recording of the quantity and composition (including prescribed substances) of residues generated is typically done. In addition, the operator typically has written procedures which ensure that releases are handled, treated and disposed of in an approved manner, and which specify how the accumulation and storage of waste are to be controlled. The frequency of analysis of the waste is site and/or process specific.

**Soil Monitoring**

Quoted costs for installation and operation of monitoring wells was highly variable ranging from EUR 25000 for 100 wells (EUR 250 per well) to EUR 140000 for 50 boreholes (EUR 2800 per well) but with a minimal operating cost. Costs of groundwater monitoring systems were quoted as EUR 1400 per year for 18 wells (EUR 78 per well) in one case to an average of EUR 45000 (including EUR 7000 for analysis) for three surveys at intervals of some years.

### 3.28.4 Soil and groundwater monitoring

Text moved from Section 4.15.8. See also Annex 9.8 below

Groundwater is an important resource for drinking water supply and must be protected from deterioration and pollution. In Europe, protecting groundwater is addressed through Water Framework Directive (2000/60/CE establishing a framework for Community action in the field of water policy) and its daughter Directive (2006/118/CE on the protection of groundwater against pollution and deterioration).

As groundwater may be an important way of transfer for pollutants, the implementation of a groundwater monitoring network around industrial sites which could be at the origin of pollutions is essential. Oil refineries are typically of concern. The collection of data on groundwater quality and quantity on a regular basis helps giving the alert in the case of an accidental or chronic pollution at the appropriate time.

Indeed groundwater is an environment integrator and interacts with the overlaying soils and related surface water systems. However, its quality reacts slowly due to a buffering effect from superficial impacts.

An example of soil and ground water monitoring is provided in Annex 9.8 below.
Chapter 4

4 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter section describes techniques (or combinations thereof) considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this document. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers environmental management systems, process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimizing use and reuse are covered. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations).

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 4.1 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied in the sector. Other techniques may exist, or may be developed, which could be considered for the determination of BAT for an individual installation.
<table>
<thead>
<tr>
<th>Type of information considered</th>
<th>Type of information included</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Brief technical description using, as appropriate, pictures, diagrams and flow sheets.</td>
</tr>
<tr>
<td>Achieved environmental benefits</td>
<td>Main potential environmental benefits to be gained through implementing the technique (including energy, water, raw material savings, as well as production yield increases, energy efficiency, etc.).</td>
</tr>
<tr>
<td>Cross-media effects</td>
<td>Potential environmental side effects and disadvantages to other media due to implementing the technique, including details of the environmental effects of the technique in comparison with others (advantages and disadvantages supported by data if available) in order to assess the impact of the technique on the environment as a whole. This may include issues such as: consumption of raw materials and water energy consumption and contribution to climate change stratospheric ozone depletion potential photochemical ozone creation potential acidification resulting from emissions to air particulate matter in ambient air (including microparticles and metals) eutrophication of land and waters resulting from emissions to air or water oxygen depletion potential in water persistent/toxic/bioaccumulable components in water or to land (including metals) creation or reduction of (waste) residues ability to reuse or recycle (waste) residues noise and/or odour risk of accidents.</td>
</tr>
<tr>
<td>Operational data</td>
<td>Actual performance data (including reference conditions, monitoring periods and monitoring methods) on emission levels, consumption levels (raw materials, water, energy) and amounts of waste generated. Any other useful information on how to operate, maintain and control the technique.</td>
</tr>
<tr>
<td>Applicability</td>
<td>Indication of the type of plants or processes in which the technique may or cannot be applied as well as constraints to implementation in certain cases, considering, e.g. plant age (new or existing), factors involved in retrofitting (e.g. space availability), plant size (large or small), techniques already installed and type or quality of product.</td>
</tr>
<tr>
<td>Economics</td>
<td>Information on costs (investment and operating) and any possible savings (e.g. reduced raw material or energy consumption, waste charges) or revenues including details on how these have been calculated/estimated. Economic information relevant to new build and retrofit to existing installations will be included. This should allow for identifying, where possible, the overall economic impact of the technique.</td>
</tr>
<tr>
<td>Driving force for implementation</td>
<td>Specific local conditions, requirements (e.g. legislation, safety measures) or non-environmental triggers (e.g. increased yield, improved product quality) which have driven or stimulated the implementation of the technique to date.</td>
</tr>
<tr>
<td>Example plants</td>
<td>Reference to the plant(s) where the technique has been implemented and from which information has been collected and used in writing the section. Indication of the degree to which the technique is in use in Europe or worldwide.</td>
</tr>
<tr>
<td>Reference literature</td>
<td>Literature or other reference material (e.g. books, reports, studies, websites) that was used in writing the section and that contains more detailed information on the technique.</td>
</tr>
</tbody>
</table>
This chapter describes in detail the techniques that are considered to be most relevant for determining BAT. This chapter should be seen as the main background information for the determination of best available techniques in the refinery sector (Chapter 5). Techniques that are generally seen as obsolete are not included. Moreover, this chapter does not include all the techniques applied in the refinery sector and described in Chapter 2. Only techniques with good environmental performance are included here.

Production, prevention, control, minimisation and recycling procedures/techniques are considered in this chapter. These techniques/procedures can be carried out in many ways, such as using production techniques that pollute less than others, changing the operating conditions, reducing material inputs, re-engineering processes to reuse by-products, improving management practices or employing substitution of toxic chemicals. This chapter provides information on some both general and specific pollution prevention and control advances that have been implemented within industry in general and in the refinery industry in particular.

As in previous Chapters 2 and 3, each section of this chapter deals with a refinery process or activity and contains the process and abatement techniques worth being considered in the determination of BAT. If different techniques may be applicable for one process/activity, they are discussed there in the respective process activity section. Sections 4.2 to 4.22 in this chapter have been structured in the same way. Each of these sections contain first the pollution prevention primary techniques applicable in the process/activity section referred to, and second the end-of-pipe (EOP) techniques that may be applicable for reducing the emissions for the process/activity. The end-of-pipe EOP techniques are grouped into media/pollutant bases to clarify the sequence of techniques applicable. In some cases, the number of EOP techniques that may be used is quite extensive.

At the end of this chapter, three sections appear containing the end-of-pipe (EOP) techniques applied to waste gas, waste water and waste management. These sections contain the descriptions of the EOP techniques that may be applicable to more than a one refinery process/activity, as well as some other EOP processes. Consequently, the descriptions of the EOP techniques that may appear in this chapter are included in Sections 4.25, 4.26 and 4.27 and not in the activities/process sections.

Each technique, both preventive—including process techniques—and control, is well documented and includes information on consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Each technique in this chapter is analysed in the same way in order to give a good solid background for the determination of BAT for the refinery sector, which determination is done in the next chapter. Table 4.1 shows the structure of the information for each technique included in this chapter.

When possible, this chapter provides information from real activities that can be, or are being, implemented by this sector, including associated costs. When possible, information provided gives the context in which the technique can be used effectively.
4.1 General overview of activities considered in this chapter

The following Table 4.2 gives a general picture of the number of techniques considered in the document for each refining activity or process described. These techniques have been split into four categories. The numbers included in this table are only orientative and are not the simple recounting of the subsections that appear in each section. As it will be seen, some subsections include more than one technique. This table is only meant to give an overview of the number of techniques considered in each section of the document. That number can be used as a first indicator of what activities/processes are more important from the environmental point of view (e.g. energy system, storage and handling, integrated management, systems and catalytic cracking, coking). Following the same rationale, it is also easy to see that air emissions are the ones with more abatement techniques.

Note to TWG: Table to be updated for final document

Table 4.2: Number of techniques addressed in Chapter 4 for each described process/unit

<table>
<thead>
<tr>
<th>Chapter section</th>
<th>Activity/process</th>
<th>Production and prevention</th>
<th>Gases and waste gas treatment</th>
<th>Waste water treatment</th>
<th>Solid waste minimisation</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Alkylation</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
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<tr>
<td>3</td>
<td>Base oil production</td>
<td>14</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Bitumen production</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Catalytic cracking</td>
<td>17</td>
<td>13</td>
<td>2</td>
<td>5</td>
<td>37</td>
</tr>
<tr>
<td>6</td>
<td>Catalytic reforming</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Coking processes</td>
<td>9</td>
<td>19</td>
<td>8</td>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>8</td>
<td>Cooling</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>Desalting</td>
<td>13</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td>10</td>
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<td>56</td>
<td>22</td>
<td>2</td>
<td>0</td>
<td>80</td>
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<tr>
<td>11</td>
<td>Etherification</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>Gas separation processes</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>Hydrogen-consuming processes</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>Hydrogen production</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>15</td>
<td>Integrated refinery management</td>
<td>33</td>
<td>0</td>
<td>24</td>
<td>6</td>
<td>63</td>
</tr>
<tr>
<td>16</td>
<td>Isomerisation</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>17</td>
<td>Natural gas plants</td>
<td>0</td>
<td>12</td>
<td>5</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>18</td>
<td>Polymerisation</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>19</td>
<td>Primary distillation units</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>20</td>
<td>Product treatments</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>21</td>
<td>Storage and handling of refinery materials</td>
<td>21</td>
<td>19</td>
<td>2</td>
<td>12</td>
<td>54</td>
</tr>
<tr>
<td>22</td>
<td>Visbreaking</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>23</td>
<td>Waste gas treatments</td>
<td>-</td>
<td>76</td>
<td>-</td>
<td>1</td>
<td>77</td>
</tr>
<tr>
<td>24</td>
<td>Waste water treatments</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>-</td>
<td>41</td>
</tr>
<tr>
<td>25</td>
<td>Waste management</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>58</td>
<td>58</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>207</strong></td>
<td><strong>180</strong></td>
<td><strong>100</strong></td>
<td><strong>101</strong></td>
<td><strong>588</strong></td>
</tr>
</tbody>
</table>

KOM conclusion 1.3: EIPPCB to separate process-related and end-of-pipe techniques in each existing subsection

Note for the TWG: this will be done further on, as far as possible, after agreeing on the changes proposed in Chapter 4). A clear distinction between process-related and end-of-pipe techniques is made in Chapter 5 when setting the BAT conclusions.
4.2 Alkylation

Three alkylation processes are techniques considered in the determination of BAT for the alkylation process are the following: the hydrofluoric acid (HF), the sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) and the solid-acid process. As the third process is still considered an emerging technique, it has been described in Chapter 6.

4.2.1 Hydrofluoric acid alkylation process

Description
A brief description of this process can be found in Section 2.2.

Achieved environmental benefits
The main advantages of the HF-alkylation process in comparison with the sulphuric acid process are the regeneration of HF, which minimises waste formation and disposal, and the lower acid-catalyst consumption as well as the minor consumption of energy and cooling.

Cross-media effects
Effluent gases
A scrubber using alkaline solution (NaOH or KOH) is necessary to remove HF from the incondensable gas stream. The acid relief neutraliser is operated so as to minimise the hydrogen fluoride content of the incondensable gas stream. Concentration of less than 1 mg HF/Nm\textsuperscript{3} can be achieved. The vent gas should be pass to flare not to the refinery fuel gas system. A dedicated flare/stack is normally retained for this used but depending on the composition gases, it is reported to be vented to a non-dedicated flare/stack (e.g. operation at a spanish refinery). Fugitive emissions are also generated by this process.

HF is a very dangerous compound because of its severe corrosive nature and the burning effects of both liquid and fumes to the skin, eyes and mucous membranes. Consequently, storage and handling should comply with all safety rules.

KF (or NaF) is formed during the neutralisation process. The spent solution is stored and then requires regeneration with lime (or alumina). The regenerated KOH (or NaOH) is recycled but typically NaOH is not. CaF\textsubscript{2} is regularly cleaned out and disposed of, usually to a landfill. If alumina is used instead of lime as the neutralising agent, then recovery of the aluminium is possible by the aluminium industry. Fumes can originate in the neutralising basin unit. To prevent the discharge of these odorous gases to the surroundings, the neutralising basins are tightly covered and equipped with a gas scrubber to remove any offensive agents.

Water
HF alkylation effluents are a potential cause of acid excursions in refinery effluents and a high standard of control should be exercised on the neutralisation treatment system, e.g. on-line pH monitoring. The effluent containing HF acid can be treated with lime (CaO-Ca(OH)\textsubscript{2}), AlCl\textsubscript{3} or CaCl\textsubscript{2} or it can be neutralised indirectly in a KOH system to produce the desired CaF\textsubscript{2} or AlF\textsubscript{3} (insolubles) which is separated in a settlement basin. The supernatant liquor flows to the water treatment process. KOH may be regenerated for reuse. After this treatment, the supernatant contains still 10 – 40 ppm F and some hydrocarbons, and is directed to the WWTP. KOH may be regenerated from the aqueous solution for reuse.

Wastes
The HF process also yields tars (polymeric material) but these are essentially free from HF. HF-containing tars are neutralised (with lime or alumina) and disposed of by incineration or blended as a fuel-oil component in small amounts because of its pronounced odours. However, technology and special operating techniques such as internal acid regeneration have virtually eliminated significantly reduced this liquid-waste stream.
Poor operation of the system (excessively cold acid, improper acid settler level, low reactor pressure, excessive acid recycling rate, low i-butane or acid concentration, high reactor temperature and improper mixing) increases the amount of waste generated.

Operational data
The potentially corrosive and toxic properties of HF require special engineering design and special construction materials, advanced process controls and stringent safety, personnel protection and maintenance requirements. These precautions include:

- special seals on acid-containing equipment such as pumps and valve stems;
- special safety clothing which must be worn by personnel entering an acid area;
- extensive operator training;
- special facilities (e.g. sprinkler systems, acid-inventory reduction, HF-detection systems, isolation valves, rapid acid transfer systems) should be included in the design of this kind of system to mitigate the effects of an accidental emission of HF vapour clouds. For leak detection, HF-sensitive colours on pipes and flanges are suitable as alternatives to continuous air analysers and video control. The potential reduction of atmospheric HF acid has also been demonstrated by the addition of additives. Special care should be taken during maintenance and cleaning of the plant, e.g. for major shutdowns not to release odours from the drainage system and/or ponds.

The same developments (such as additives) have been already tested in order to lower the vapour pressure and to minimise the amount of HF released to the atmosphere in case of an accident. The downside of this is that handling and recyling the additive add to the complexity of the process.

Applicability
Fully applicable.

Economics
Table 4.3 shows the investment and production cost summary for HF alkylation. Disposal costs are not included.

Table 4.3: Examples of investment and operational costs for an HF-alkylation unit

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity (kt alkylate/yr)</td>
<td>348</td>
<td>160</td>
</tr>
<tr>
<td>Investment cost (EUR million)</td>
<td>25.6</td>
<td>35</td>
</tr>
<tr>
<td>Operating cost (EUR/tonne alkylate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labour</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>Utilities</td>
<td>0.066</td>
<td></td>
</tr>
<tr>
<td>Chemical consumption, laboratory allowance, maintenance, taxes and insurance</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>Total direct operating costs</td>
<td>0.138</td>
<td></td>
</tr>
</tbody>
</table>

Driving force for implementation
Alkylation plant is a refinery process used to increase gasoline octane. Safety requirements due to HF are the main driver for this process.

Example plants
HF-Alkylation is very widely used.

Reference literature
Chapter 4

4.2.2 Sulphuric acid alkylation process

Description
A brief description of the process can be found in Section 2.2.

Achieved environmental benefits
Sulphuric acid is an alternative process for alkylation, but has the drawback of more spent acid to be disposed of or recycled which must be regenerated, typically outside the plant installation. Efficiency of the process is lower than with the HF alkylation and more cooling is needed.

Cross-media effects
Technologies using sulphuric acid as a catalyst produce very large quantities of spent acid (sulphuric and sulphonic acids) that have to be regenerated. The transport of spent and fresh acid to and from the sulphuric acid regeneration has given rise to some concern and increased pressure on refiners to establish sulphuric acid regeneration plants near the alkylation unit. In some cases this transport to/from the regeneration facility is by pipeline. However, no major new improvements have been introduced in sulphuric acid alkylation technology dealing with the spent acid issue. Fugitive emissions from this process are similar to these from HF alkylation.

Acid-soluble oil should be recycled back into the process. It is continuously generated as a by-product of sulphuric acid alkylation. This oil goes into the acid phase and dilutes the strength of the acid within the unit, unless a portion of the acid is continuously purged (spent acid) and replaced with fresh acid. The spent acid containing the acid soluble oil is sent to the regeneration process (typically off-site), where the acid soluble oil is removed via combustion. Tars from the H₂SO₄ process contain sulphuric and miscellaneous sulphonic acids, which may cause disposal problems. In addition to spent acid, this process generates waste water that should be neutralised before being routed to WWTP, gum, spent acid, caustic solutions from regeneration and fugitive emissions spent caustic and alkaline waste water streams which must be sent to WWTP or possible regeneration (in the case of the caustic). Depending upon BOD and COD requirements at the WWTP, the waste water stream may require a nitrogen stripper to remove dissolved hydrocarbons.

Operational data
The product quality from butylenes (primary feedstock) is higher than in HF alkylation. To produce an equivalent product quality, HF alkylation would require similar energy consumption to sulphuric acid alkylation. This type of alkylation is considered relatively safer when compared with HF catalysed alkylation. As sulphuric acid is less toxic than HF and does not form a vapour cloud if released, this type of process is often consider to be the safer. However, the actual determination of risk level is site-specific and has to be carried out within specific risk assessment methodology.

Table 4.4: Example of utility and chemical consumption for H₂SO₄-alkylation

| Utilities and chemical consumption (based on 716 m³/d alkylate plant) |
|-----------------|----------------|
| Power, kW       | 1779          |
| Compressor      | 1235          |
| Pumps           | 303           |
| Mixers          | 240           |
| Cooling Water, m³/h (°) | 835          |
| Industrial Water, t/d | 39           |
| Steam, kg/h     |               |
| 3.45 barg       | 13            |
| 10.3 barg       | 3             |
| Chemicals       |               |
| Fresh Acid, t/d (°) | 40           |
| NaOH -15 Baume(°), t/d | 1.7          |

(°) Cooling water supply temperature is 26 °C and the average ΔT is 15 °C.
(°) Includes allowance for feed impurities.
(°) 15 ° Baume = 10 % w/w
Chapter 5

The sulphuric acid removed needs to be regenerated in a sulphuric acid plant which is generally not a part of the alkylation unit and is normally located off-site.

Applicability
Fully applicable. On the economical point of view, this type of technique alkylation process is mostly driven by the economics of the proximity of a regeneration facility of sulphuric acid.

Economics
Some data are available in Table 4.4 and Table 4.5.

<table>
<thead>
<tr>
<th>Capacity</th>
<th>Estimated costs</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>290 kt/yr</td>
<td>Material USD12.0 million Labor USD1.7 million</td>
<td>USA Gulf Coast, second quarter 1993. Operational data correspond to this plant.</td>
</tr>
<tr>
<td>28300 m³/d</td>
<td>USD 14.49 million</td>
<td></td>
</tr>
<tr>
<td>1590 m³/d</td>
<td>USD 22 000 per m³/d</td>
<td>USA Gulf Coast, 4th quarter, 1998</td>
</tr>
</tbody>
</table>

Driving force for implementation
Alkylation plant is a refinery process used to increase the gasoline octane.

Example plants
Sulphuric acid alkylation is widely used.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [330, Hommeltoft, 2000], [268, TWG, 2001].

4.2.3 Solid-acid alkylation process

Note to TWG: As no full-size commercial unit of solid-acid alkylation is in operation at the time of writing (2011), the text has been moved to Chapter 6 on Emerging techniques (see Section 6.2.1.3)

4.2.4 Upgrade feedstock by selective hydrogenation or isomerisation

Description
More information about the processes can be found in Sections 2.13, 4.13.5, 2.16 and 4.16.

Achieved environmental benefits
The naphtha hydrotreatment or isomerisation (e.g. hydrogenation of butadiene, isomerisation of 1-butene to 2-butene) helps the alkylation units to reduce the acid losses and consequently the waste generation. As a consequence, the amount of caustic consumption is decreased. The reduction in acid and caustic consumption depends on the feed diene content, which varies widely at different refineries.

Cross-media effects
Drawbacks for the implementation of such a technique include the increased fuel/energy consumption, the increased fugitive emissions and the need for spent catalyst handling to be used in such a process. More information about these issues can be found in Sections 4.13 and 4.16.

Operational data
This technique requires hydrogen and consumes energy.
Applicability
There are no restrictions for the application of this technique.

Economics
See Sections 4.13 and 4.16.

Driving force for implementation
Because of increased demands for higher octane gasoline and the increased conversion of heavier crudes to lighter products, there has been a relative decrease in the quality of alkylation feed throughout the industry.

Example plants
Note for TWG: Please provide updated information. No additional data provided

Reference literature
[113, Noyes, 1993], [268, TWG, 2001]

4.3 Base oil production

As described in Section 2.3, several types of processes can be found in the base oil production. They include the deasphalting unit, aromatic extraction, high pressure hydrogenation unit, dewaxing, hydrofinishing and wax processing. All of these processes are covered here and good techniques from the environmental point of view are discussed in this section. Techniques applicable for the storage of the solvents used in base oil production (e.g. furfural, NMP, MEK, MIBK) are also included here. The storage of products and intermediates appearing in base oil production is included here as well.

Useful information may also be available in the WT BREF [87, EC 2006].

4.3.1 Multiple-effect extraction process

Description
Solvent-based processes used in the manufacture of base oils are energy intensive because large volumes of solvent must be recovered by flash distillation for recycling back to process. The number of stages used for evaporation of the solvents has a significant effect on the energy cost for these processes and as many as five evaporation stages were used in some early liquid SO₂ extraction units in Europe.

Achieved environmental benefits
Heat efficiency can be improved (less water and steam usage) by applying ‘double and triple effect configurations’, especially in the deasphalting and aromatic extraction units. Energy saving for triple-effect evaporation is 30 – 33 % compared with double-effect evaporation.

Cross-media effects
None in particular.

Operational data
Utilities needed in the process are listed in the economic section below. The energy saving for the triple effect system is on the low-level heat side only (in most cases LP-steam) where refineries often already have a surplus. This means that the actual savings depends on the local circumstances and a retrofit/change should be evaluated for each individual location.
Chapter 5

Applicability
Multiple effect evaporation requires both a pressure and a temperature driving force. In some instances, the increase in pressure and temperature required to go from double to triple effect is not feasible and could result in higher emissions and energy consumption because of larger residual amounts of solvent left in the oil leaving the evaporation section and entering the stripping section.

Triple effect systems are typically used for non-fouling feedstocks only (e.g. wax) as they are known to be more vulnerable in this respect, so their application is restricted.

Economics
An order of investment cost (based on a 318 – 6360 m³/d capacity range) was around USD 5000 –18900 per m³/d (4th Q 1998, US Gulf). An example of comparative costs for single, double and triple-effect options is given in Table 4.6.

Table 4.6: Economics related to energy savings for three multiple-effect deasphalting options

<table>
<thead>
<tr>
<th>Type of cost</th>
<th>Single-effect</th>
<th>Double effect</th>
<th>Triple-effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion investment USD (1)</td>
<td>0</td>
<td>1 300 000</td>
<td>1 900 000</td>
</tr>
<tr>
<td>Annual utility cost USD (2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium-pressure steam, USD 8.1/t</td>
<td>91100</td>
<td>91100</td>
<td>91100</td>
</tr>
<tr>
<td>Low-pressure steam, USD6.8/t</td>
<td>931 600</td>
<td>465 200</td>
<td>377 500</td>
</tr>
<tr>
<td>Power, USD 0.04/kWh</td>
<td>218 400</td>
<td>218 400</td>
<td>218 400</td>
</tr>
<tr>
<td>Cooling water, USD 0.018/m³</td>
<td>87 200</td>
<td>47 600</td>
<td>39 200</td>
</tr>
<tr>
<td>Fuel, USD 1.92/net GJ</td>
<td>44 100</td>
<td>44 100</td>
<td>44 100</td>
</tr>
<tr>
<td>Total annual utility costs</td>
<td>1 372 400</td>
<td>866 400</td>
<td>770 300</td>
</tr>
<tr>
<td>Annual utility reduction</td>
<td>0</td>
<td>506 000</td>
<td>602 100</td>
</tr>
</tbody>
</table>

(1) Estimated basis: United States Gulf Coast, third quarter 1995
(2) Based on unit cost provided by SRI International, Menlo Park, CA (US). December 1994
NB: Large savings are shown for low-pressure steam. In most refineries, low-pressure steam is considered ‘free’ since excess is vented to the atmosphere.

Driving force for implementation
The conversion to a multiple-effect unit reduces the utility cost.

Example plants
Multiple-effect extraction is a common technology used in refineries with lubricant oil production. Double effect units are the most predominant type of extraction processes. Units built from 1950-1975 used double effect and a few used single. Because the cost of energy increased rapidly during the 1970s, most new units built since about 1980 have been designed and older units have been converted for triple effect evaporation to reduce the cost of energy consumption.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [319, Sequeira, 1998].

4.3.2 Adjusting the solvent used in the aromatic extraction unit

Description
The selection of the type of solvent used in the aromatic extraction has an impact on the energy consumption of the system process. Moreover, the use of a less toxic solvent, like furfural and or n-methyl pyrrolidone (NMP), can be used instead of the more toxic selective solvent like phenol, cresol and sulphur dioxide.
Achieved environmental benefits
The use of a less polluting solvent (e.g. NMP or furfural) is preferred. As consequence has a positive effect on the reduction of emissions of phenols and sulphur dioxide in the refinery effluents is achieved.

Additional advantages of the use furfural or NMP versus furfural include a higher selectivity leading to a higher raffinate yield and a lower solvent ratio, which both result in a lower energy consumption by some 30 – 40 %.

Cross-media effects
Care should be taken to avoid solvent contamination of aqueous effluents by applying efficient solvent recovery techniques. Some contamination of aqueous effluents occurs, so care should be taken not to upset the activated sludge treatment unit of the waste water treatment. NMP is easier to degrade in the WWTP than furfural, however it is also more corrosive than clean furfural.

Operational data
The performance of NMP and furfural techniques are similar. Well maintained and operated furfural extraction units perform just as well as NMP plants. Similar quantities of furfural, as NMP are required when the plants are run in the correct manner.

Applicability
Some technical difficulty for applicability or change of solvent are the following:

- Phenol is easier to recover than phenol. Furfural is more difficult to recover than phenol. Furfural forms a different ratio azeotrope with water, so a straight switch of solvent of a phenol unit may not be possible, much larger quantities of furfural are used per unit throughput.
- NMP switching of phenol switching to NMP from phenol is also difficult. NMP has a higher boiling point (by 22 ºC), a lower melting point (by 64 ºC) and no azeotrope. For these reasons, furfural is typically used when producing lower boiling point base oils (e.g. transformer oil distillates).

Major modifications would be required for existing units to change from furfural to NMP as the process conditions are different (for example a change from hot oil heat exchangers to a fired furnace to achieve the required temperatures in the solvent recovery section).

Economics
Costs for switching from one solvent to a more favourable one will have to be evaluated on a case-by-case basis. In some cases, the change of solvent used does not entail significant extra costs. On the other hand, in other cases, for instance, the change from a SO2 aromatic extraction to any other solvent requires a completely new unit.

The switch from a furfural to an NMP process requires economic calculations because major modifications may be required. As consequence, the energy saving against the cost of the revamp has to be carried out weighed individually. Changing from furfural to NMP requires significant investment, including, but not limited to the extraction tower, furnaces, metallurgy, etc.

The cost for the conversion of a phenol unit (277 m³ per operating day) to a NMP unit (563 100 m³ per operating day) is estimated at EUR 0.9 4.15 million (cost including solp and solvent tanking example of a 100 M CSZ unit). Other estimates show that the investment costs to switch from a phenol unit to an NMP unit is around 70 % the cost of a completely new unit.

A cost comparison of major base oil refining processes is given in Table 4.7.
### Chapter 5

#### Table 4.7: Basic cost comparison between three aromatic extraction processes

<table>
<thead>
<tr>
<th>Costs</th>
<th>Furfural</th>
<th>NMP</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent, relative</td>
<td>1.0</td>
<td>2.3</td>
<td>0.60</td>
</tr>
<tr>
<td>Investment</td>
<td>Medium</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Maintenance</td>
<td>Medium</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Energy</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
</tbody>
</table>

**Driving force for implementation**
Reduction of energy consumption and the emission of phenols and SO\textsubscript{2} in the refinery.

**Example plants**
Furfural and NMP solvent extraction processes are common technologies.

**Reference literature**
[110, HMIP UK, 1993], [319, Sequeira, 1998], [268, TWG, 2001].

### 4.3.3 Solvent recovery from dewaxing units

**Description**
Information about the process can be found in Section 2.3. The following prevention techniques may be applied to the solvent dewaxing process:

- Including vapours from the wax filters in the inert gas system by circulating the inert gas. In this process, the inert gas is circulating and recovering solvent vapours are recovered by refrigeration as part of the process. Solvent incineration in furnaces should be minimised. An alternative to refrigeration is the pressure absorption of solvents in oil (e.g. fresh feed or finished).
- Using solvents for the process, including propane and mixtures of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK). Toluene (suspected of damaging the foetus) or chlorinated hydrocarbons should be avoided.
- The solvent recovery stage results in solvent-contaminated water, which should be sent to the waste water treatment plant. Sending solvent-contaminated water resulting from the solvent recovery stage to the WWTP.
- Using inert gas, in place of steam for stripping the last traces of solvent from the dewaxed oil and waxes. When chlorinated solvents are used this procedure is typically applied.

**Achieved environmental benefits**
Maximising the recovery of the solvents used in the solvent dewaxing processes reduces the contamination of waste water by toluene or chlorinated hydrocarbons. The benefits of inert gas stripping in solvent dewaxing are the reduction of energy requirements in solvent refining units, the increase of dewaxed oil yields, reduction of the dilution ratios, reduction of solvent losses, decrease of the dewaxing differential, and maintenance cost reduction.

**Cross-media effects**
Large refrigeration systems are used and refrigerant losses from these should be minimised. Energy consumption is increased for refrigeration/pressure and heat. Care should be taken to avoid solvent contamination of aqueous effluents because most of the solvents used in solvent dewaxing are problematic for water micro-organisms and waste water plants. VOC fugitive emissions may be generated during the processes.

**Operational data**
Table 4.8 gives some data on typical utility specific consumption for dewaxing solvent recovery units.
Table 4.8: Typical utility specific consumption for dewaxing solvent recovery units

<table>
<thead>
<tr>
<th>Utilities, typical per m³ feed</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>1856 MJ</td>
</tr>
<tr>
<td>Electricity</td>
<td>290 kW</td>
</tr>
<tr>
<td>Steam</td>
<td>171 kg</td>
</tr>
<tr>
<td>Cooling water (ΔT = 25 ºC)</td>
<td>36 m³</td>
</tr>
<tr>
<td>Solvent make-up</td>
<td>1.7 kg</td>
</tr>
</tbody>
</table>

**Applicability**

Fully applicable.

**Economics**

A new solvent recovery unit cost USD 66 000 per m³/day (based on 44 000 m³/day feed rate capacity, 1998 US Gulf Coast). Data on implementation of inert gas stripping in refineries showed paybacks of 9 – 14 months.

**Driving force for implementation**

Solvent recovery from dewaxing can be used in refineries that have solvent dewaxing units in their lubricant oil production processes to promote the reduction of solvent losses.

**Example plants**

Many refineries with lubricant production contain have these types of processes.

**Reference literature**


### 4.3.4 Wax reprocessing unit

**Description**

Hydrofinishing or clay treating can be used in wax processing.

**Achieved environmental benefits**

Wax hydrofinishing offers several advantages over clay treating which include lower operating costs and the reduction of waste generation.

**Cross-media effects**

When hydroprocessing is used, hydrogen is necessary. Hydrotreatments consume energy, hydrogen and nickel, tungsten or even platinum catalysts are needed for this process. Spent clay results in a disposal problem.

**Operational data**

Hydrogen finishing yields are closed to 100 %, whereas the clay treating product yield ranges from 75 to 90 % for the microcrystalline waxes and as high as 97 % for light paraffin waxes. Hydrogen consumption is around 15 Nm³ per m³ of wax produced. Clay consumption runs from 2 to 45 kg/t of product.

**Applicability**

Hydrofinishing is fully applicable especially when hydrogen is available. However, in some cases, hydrofinishing processes cannot reach certain special product quality specifications.

**Economics**

Investment costs for a wax hydrofinishing process are EUR 1 million for a feed capacity of 20 000 t/yr.
Chapter 5

Driving force for implementation
Hydrotreating offers a lower operating cost.

Example plants
Many examples exist.

Reference literature
[319, Sequeira, 1998], [268, TWG, 2001].

4.3.5 Lube oil clean-up
Useful parts of process description moved to Chapter 2

Description
A short description of the process can be found in Section 2.3. The use of hydrotreating or sulphuric acid and clay treatments are used in lube oil clean-up.

Achieved environmental benefits
The use of hydrotreatment instead of the other cleaning techniques reduces waste generation.

Cross-media effects
Hydrotreatments consume energy, hydrogen and nickel, tungsten or even platinum catalyst needed for this process.

Operational data
In standalone lube oil refineries, the small amounts of H₂S generated due to hydrotreatment are normally incinerated because the erection of a Claus unit is not justified economically.

Applicability
Fully applicable. However, in some cases, hydrotreating processes cannot reach certain very special product quality specifications.

Economics
No data available.

Driving force for implementation
This technique may be used in refineries having lubricant oil production for the production of cleaner lubricants.

Example plants
Sulphuric acid and clay treatments are typically used in old plants.

Reference literature

4.3.6 Storage of base oil intermediates and products

Description
The storage of intermediates and products from base oil production is typically seen in base oil production units.

Achieved environmental benefits
Reduced risk of leaking and VOC emissions.
4.3.7 Storage and benchmarking of solvents

Storage and benchmarking techniques are part of the VOC abatement programme (see Section 4.25.6.1).

Description
Solvents used in the solvent extraction of aromatics should be stored in blanketed tanks to minimise fugitive emissions of furfural, NMP and MEK/toluene. The practice of internal and/or external benchmarking may reduce solvent consumption.

Achieved environmental benefits
Reduced VOC emissions, leakage prevention and reduction of solvent consumption. The leakage prevention of the leakage of solvents that are soluble in water reduces the contamination of soil and groundwater.

Applicability
Storage and benchmarking techniques can be found as part of the VOC abatement programme (see Section 4.25.6.1) or soil contamination prevention programme (see Section 4.27.1).

Driving force for implementation
Toluene and MEK should be routinely nitrogen blanketed, mainly to reduce fire hazard rather than to prevent VOC emissions; higher boiling range solvents, such as furfural and NMP are less prone to VOC releases and may be blanketed mainly to prevent oxidative degradation (furfural) or to reduce odorous nuisance.

Example plants
The benchmarking of solvents for leakage prevention is widely applied in refineries.

Reference literature
[297, Italy, 2000], [268, TWG, 2001].

4.3.8 Sulphur treatment from hydrogenation units

Description
Hydrogenation processes generate H₂S. As a consequence off-gases containing H₂S are recovered in a sulphur recovery plant (See Section 4.25.5) or are incinerated.

Achieved environmental benefits
Reduction of sulphur and H₂S emissions.

Cross-media effects
Amine recovery of H₂S consumes energy and chemicals. Sulphur recovery units consume energy (see Section 4.25.5). Incineration requires fuel.

Operational data
See Section 4.25.5.

Applicability
In standalone lube oil refineries, the small amounts of H₂S generated in this process are typically incinerated. Sulphur recovery is less commonly applied in these specialised refineries.

Economics
For more information on economics, see Section 4.25.5. Data from EU refineries have found that the implementation of SRU in standalone lubricant refineries producing more than two tonnes of sulphur per day is cost-effective.
Chapter 5

Driving force for implementation
Reduction of sulphur oxide and H₂S emissions.

Example plants
At least one specialised European refinery has an SRU which recovers 99.1% of the sulphur in the acid gas.

Reference literature
[147, HMIP UK, 1995], [268, TWG, 2001].

4.3.9 Stripping of waste water from aromatic extraction

Stripping techniques applicable to aromatic extraction waste water are addressed in Section 4.26.

Description
This technique involves the stripping of waste water from aromatic extraction prior to sending it to the waste water treatment plant. Another technique to consider is dehydration/settling.

Achieved environmental benefits
Reduced content of organic and sulphur compounds of waste water produced in the aromatic extraction. Other benefits are reduced energy requirements, increased dewaxed oil yield, decreased dewaxing differential, reduced dilution ratio, reduced solvent losses and reduced maintenance costs.

Cross-media effects
Stripping consumes energy.

Operational data
None available. Note for TWG: please provide information when available

Applicability
Fully applicable.

Driving force for implementation
Energy consumption reduction and reduction of solvent losses are the driving forces for the implementation of this technique.

Example plants
Applied in some refineries.

Reference literature
[147, HMIP UK, 1995], [319, Sequeira, 1998], [268, TWG, 2001]

4.3.10 Common hot oil system

Description
A common hot oil system coming from a single source may be used for heat transfer to all the solvent recovery units. When the base oil production units have a single energy system, the introduction of clean-up facilities in the flue-gases is more cost-effective. (See Section 4.25)

Achieved environmental benefits
The reduction of SOₓ, NOₓ and particulate emissions from a single energy system compared to several individual furnaces.
Cross-media effects
See different cross-media effects for the abatement of SO$_x$, NO$_x$ and particulates in Section 4.25.

Operational data
See Section 4.25 for waste gas treatments.

Applicability
Generally applicable. This technique may nevertheless be very difficult to apply to existing refineries.

Economics
See Section 4.25.

Driving force for implementation
Reduction of SO$_x$, NO$_x$, particulates emissions from the energy system.

Example plants
Some standalone lubricant refineries have already applied this concept and have switched to a common single heating source to reduce emissions coming from the burning of liquid fuels.

Reference literature
[268, TWG, 2001].

4.4 Bitumen production

4.4.1 Storage of bitumen products

Description
Bitumen should be stored in proper storage tanks normally under heating conditions and insulated. Bitumen is generally not handled as a solid, because it is too difficult and is very intensive in man-power. Loading and unloading of the tank is typically done as follows: when the tank is filled, nitrogen does not flow to the tank, and the pressure is lowered by letting part of the gas go to the atmosphere; when the tank is unloaded on a low speed, a small amount of nitrogen is led to the tank; however, when the speed of unload is higher, higher amounts of nitrogen must be used. If the tank is equipped with a cleaning system, it must be is mechanically very simple and easy to clean. More information on storage is available in Section 4.21.

Achieved environmental benefits
For safety reasons, bitumen tanks containing oxidised bitumen are equipped with nitrogen blanketing and pressure/vacuum safety valves. These valves need maintenance due to the slime. In some cases, these valves may be removed and a gaseous overhead treatment scheme is used. As an example see new unit (2010) in CEPSA Huelva (Spain).

Cross-media effects
Hydrocarbons and sulphur compounds may emanate from leakages (particularly in overhead systems) and pressure relief valves and in the form of liquid droplet-containing aerosol from the venting of tanker top-loading operations.

Operational data
Electricity, hot oil and low pressure steam can be used for heating. The heat exchanger can be inside the tank or outside the tank in which case bitumen is circulated through it. Differences in temperature should not be too high due to the surface temperature and coking.

Applicability
Storage of bitumen products is done in refineries that have bitumen production. Prevention techniques, as mentioned, are typically applied.
Economics
None available. Note for TWG: please provide information when available

Driving force for implementation
For safety, to prevent accidents reasons, bitumen tanks are equipped with nitrogen blanketing and a pressure/vacuum safety valve.

Example plants
Some refineries in Europe use the techniques mentioned here. There is a recent unit (2010) at Huelva (Spain).

Reference literature
[268, TWG, 2001].

4.4.2 Techniques to control emissions to the air

4.4.2.1 Treatment of the gaseous overheads

Description
Oxidiser overheads can be routed to a scrubber rather than direct water quenching for contaminant removal prior to incineration. The off-gases are condensed in a scrubber where most of the hydrocarbons are eliminated. The water vapour (sometimes after fully condensation) is left in the air stream to incineration at a temperature of approximately 800°C.

Achieved environmental benefits
Reduction of H₂S, SO₂, SO₃, CO, VOC, particulates, smoke and odour emissions.

Cross-media effects
Additional contaminated water. Scrubber water is dirty and requires oil and solids separation prior to reuse as desalted wash water and/or biotreatment. The sour water from the scrubber is routed to a sour water stripper and stripped prior to reuse and/or purification.

Applicability
Typically applied to overheads from the bitumen blowing systems.

Example plants
Many plants in Europe, e.g. recent unit (Biturox design - 2010) in CEPSA Huelva (Spain), use a gaseous overhead treatment scheme.

Reference literature
[147, HMIP UK, 1995].

4.4.2.2 Use the heat from incondensible products and condensates

Description
Both incondensible products and condensates from the separator, hydrocarbon and aqueous, can be burnt in a purpose-designed incinerator, using support fuel as necessary or in process heaters. Oxidiser overhead slop oil can also be treated in the sludge processing or recycled in the refinery slop oil system.

Achieved environmental benefits
Reduction of emulsion of light oil, water and particulates. Another environmental benefit is the removal of foul smelling odorous incondensables which are difficult to treat elsewhere.
Cross-media effects
On scrubbing, aerosols can give rise to plugging. Additional contaminated Water streams can become contaminated In a well-operated unit, SO₂ or odour from the incineration of bitumen-blowing incondensables do not pose any problem.

Operational data
The incinerator should operate at a temperature of at least 800 ºC and the combustion chambers should have a residence time of at least 0.5 seconds. The oxygen concentration at the combustion chamber outlet should be greater than 3 % v/v. Low-NOₓ burners can be fitted in these incinerators.

Applicability
Widely used to get rid of bitumen fumes. Incondensable and/or condensates can be burnt in process heaters. However, they should be treated or scrubbed to remove compounds of sulphur or combustion products that may cause odours or other environmental problems.

Driving force for implementation
Reduction of odours, sludge and oily waste.

Example plants
Many bitumen oxidisers have associated facilities to handle gas and liquid wastes.

Reference literature
[147, HMIP UK, 1995]

4.4.2.3 Treatment of vents from the storage and handling of bitumen materials

Description
Techniques that may be applied to prevent VOC emissions and odours include:
- venting of odorous gases vented during the storage of bitumens and the venting of tank blending/filling operation can be vented to an incinerator;
- the use of compact wet-type electrostatic precipitators which have been proven capable of successfully removing the liquid element of the aerosol generated during the top-loading of tankers.

Achieved environmental benefits
Reduction of emissions of sulphur compounds, VOC, particulates, smoke and odour emissions.

Cross-media effects
Energy consumption and, in case of wet ESP, waste generation.

Operational data
In the waste gas of a cleaning unit, a mass concentration of VOC of a total of 150 mg/Nm³ can be complied with. In the waste gas of a incineration plant, a mass concentration of VOC, given as total C, of a total of 20 mg/Nm³ can be complied with (half-hourly mean values attainable in operations).

Applicability
Fully applicable.

Driving force for implementation
Reduction of emissions and nuisances.

Reference literature
[147, HMIP UK, 1995], [117, VDI, 2000]
4.4.2.4 Sulphur dioxide abatement and sulphur recovery units

Description
SO\textsubscript{x} abatement techniques and sulphur recovery units (SRU) are techniques to reduce sulphur emissions. They are extensively documented in Section 4.23.5.

Achieved environmental benefits
Reduction of sulphur emissions

Cross-media effects
See corresponding information in Section 4.23.5.

Operational data
See corresponding information in Section 4.23.5.

Applicability
The implementation of vent treatment techniques are extremely linked to the rest of the refinery. In standalone bitumen refineries, their application is more restricted.

Economics
See corresponding information in Section 4.23.5.

Driving force for implementation
Reduction of sulphur emissions.

Example plants
Vent treatment techniques are applied in many refineries. However, fewer applications are found in standalone bitumen production refineries.

Reference literature
[268, TWG, 2001].

4.4.3 Techniques to control emissions to the Waste water pretreatment techniques

Description
Oxidiser overhead waste water accumulated in the overhead condensate collection drum can be sent to a sour water stripper prior to sending it to the effluent water treatment facilities. In some particular schemes, water from the oxidiser is not suitable for the SWS and is directly sent to the WWTP. More information on waste water treatment is available in Section 4.26.

Achieved environmental benefits
The stripping reduces the \text{H}_2\text{S}, oil, aromatics, volatile PAHs, sulphuric acid and odorous oxidation products (ketones, aldehydes, fatty acids) in the sour waste water reducing the charge to the central waste water system of the refinery.

Cross-media effects
An increase in oil and particulates load to the sour water stripper.

Operational data
None available. Note for TWG: please provide information when available

Applicability
Typically applied to waste water from bitumen blowing.
Chapter 4

Economics
None available. Note for TWG: please provide information when available.

Driving force for implementation
Reduction of the pollutant charge to the refinery waste water.

Reference literature
[147, HMIP UK, 1995], [268, TWG, 2001].

4.4.4 Techniques for prevention of generation of waste

Description
In bitumen production facilities, including storage, leakages can be produced. These leakages typically generate waste when mixed with other components such as sand.

Achieved environmental benefits
Reduction of waste production.

Operational data
Techniques for preventing waste generation can be seen as part of a waste management programme described in Section 4.25.1.

Applicability
Fully applicable.

Driving force for implementation
Reduction of waste and cleaning

Example plants
Many refineries apply these type of systems

Reference literature
[268, TWG, 2001].

4.4.5 Hot oil system

Description
When the bitumen production units have a single energy system, the introduction of clean-up facilities in the flue-gases is more cost-effective. More information is available in Section 4.25 and 4.3.10.

Hot oil systems using oil as a medium by heating coils are used for maintaining bitumen fluid during storage.

Achieved environmental benefits
Reduction of SO\textsubscript{x}, NO\textsubscript{x}, and particulate emissions from the energy system.

Cross-media effects
See the different cross-media effects for the abatement of SO\textsubscript{x}, NO\textsubscript{x}, and particulates in Section 4.23.

Operational data
See Section 4.23

Applicability
Hot oil systems may be very difficult apply to existing refineries.
Chapter 5

**Economics**
See Section 4.23.

**Driving force for implementation**
Reduction of $SO_x$, $NO_x$, and particulate emissions from the energy system.

**Example plants**
Some standalone bitumen refineries have already applied this concept to reduce emissions coming from the burning of liquid fuels.

**Reference literature**
[268, TWG, 2001].

4.5 Catalytic cracking

Several types of techniques are considered in this section. The first group of techniques (Sections 4.5.1 to 4.5.3) corresponds to the types of catalytic cracking processes. These sections give the emission values that can be achieved without the use of abatement techniques (where data is available). The remaining sections correspond to process-related and end-of-pipe techniques applicable to cat crackers.

Note to TWG: As proposed in Draft1 and agreed during commenting period, sections 4.5.1 to 4.5.3 have been deleted and useful part of this information has been moved to Chapters 2 and 3. See process descriptions in Section 2.5

4.5.1 Full combustion mode in the regenerator

**Description**
This section gives emissions information from the FCC when it is run under favourable conditions and with the regenerator in total combustion mode. Operational techniques that affect the emissions from the FCC are also discussed here. A description of the process can be found in Section 2.5.

**Achieved environmental benefits**
Some operating modes that can reduce in the full combustion mode, the following precautions should be taken in order to optimise the emission of pollutants from the FCC are the following:

- When operating a FCC in full combustion mode, the following precautions should be taken in order to optimise the emission of pollutants from the FCC are the following:
  - When operating a FCC in full combustion mode, and With an excess of oxygen not greater than 2 %, the amount of CO produced can be limited to a range from 35 to 250 mg/Nm$^3$ with an excess of oxygen greater than 2 %, (value attainable in continuous operations). Emissions values as a daily half-hourly average, mean values. Note for TWG: a larger reference period (1/day + 1/year) would be better but no data has been made available.
  - When operating a FCC in full combustion mode, CO oxidation promoter can be added to the regenerator to catalyse the oxidation of CO. However, this promoter also catalyses the oxidation of the fuel nitrogen in the coke, increasing the NO$_x$ levels (especially NO). A platinum catalyst may promote the generation of N$_2$. Consequently, the amount of CO promoter varies the relationship between the NO$_x$ emissions and CO emissions. However, values of 300 – 700 mg/Nm$^3$ of NO$_x$ (3 % O$_2$) can be achieved.
  - For residual feedstock cracking using antimony addition, NO$_x$ emissions can raise to 1000 mg/Nm$^3$ (3 % O$_2$) if no other reduction technique is used.
  - Minimisation of the use of aeration and purge steam can decrease particulate emissions significantly. Aeration/steam rates are based on achieving a stable catalyst circulation in the catalyst lines between the reactor and the regenerator.
  - Proper loading and pre-sulphiding procedures, good reactor temperature control and good flow distribution can reduce catalyst losses.
Stripping of the catalyst before reaction or before regeneration reduce the HC content in coke to be burnt helps to reduce the coke formation.

Temperature adjustment in the riser by injection of a recycle stream above the zone of the fresh feed injection.

Modification of the design and operation of the regenerator especially to avoid high temperature spots that tend to increase the NOx formation.

Cross-media effects

The cat cracker is a major source of SOx and NOx, CO2, CO, dust (particulates), N2O, SO3, metals (in particular V and Ni), hydrocarbons (e.g. aldehydes) and ammonia emissions, as discussed in Section 3.5.

Considering dust emissions, the basic design of an FCC includes two-stage cyclones in the regenerator vessel, which prevent the bulk of the fine catalyst used from escaping from the system. However, smaller catalyst particles, some of which are introduced with fresh catalyst and some mostly created by attrition in the circulating system, are not easily retained by the two-stage cyclone system. Consequently, in many cases, other abatement techniques have to be included to complement the process abatement techniques discussed here.

A reduction of the regeneration temperatures under the usual conditions (700-750 °C) would not have a significant impact in the NOx emissions but could require a CO boiler; it will increase CO concentration in the flue gas and increase coke formation. A change in the design or operation of the regeneration may increase the CO concentration.

When excess O2 is reduced to around 0.5 %, NOx production is dramatically reduced. This is due to the increase in CO from less available O2 which can help reduce NOx back to N2. Additionally, many FCC/RCC units cannot operate at these low O2 levels and still maintain regenerator temperatures within safe operating limits, and low O2 levels will increase CO emissions. Finally, SOx production is typically increased at low O2 when SOx additives are being used since there is not enough O2 for the SO2 to oxidize to SO3 and be captured by the additive. However, SOx production is typically increased, possibly correlated to a higher coke production.

Table 4.9 gives a summary of the lowest emissions of pollutants to the atmosphere due to an uncontrolled cat cracker (when no end-of-pipe technique is used to abate air emissions).

### Table 4.9: Typical emissions from a FCC unit without abatement techniques

<table>
<thead>
<tr>
<th>PM</th>
<th>SOx (as SO2)</th>
<th>COx</th>
<th>HC</th>
<th>NOx (as NO2)</th>
<th>Aldehydes</th>
<th>NH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.267-0.076</td>
<td>0.286-1.505</td>
<td>25-250</td>
<td>0.630</td>
<td>0.107-0.416</td>
<td>0.054</td>
<td>0.155</td>
</tr>
</tbody>
</table>

Emission factors in kg/1000 litres of fresh feedstock

For CO: reported concentration for full burn FCC with O2 level above 2 %. (Source: CONCAWE 4/09)

Operational data

Operational data on the FCC process can be found in Sections 2.5 and 3.5. More operational data about FCCs can be found in [225, Cary and Handwerk] [226, Nelson]. A high severity FCC process enables There are possibilities to adjust this process in order to obtain higher yields of low olefins (C3-C4) that may be used for alkylation, oxygenates production or direct sale to the market. One way is to increase the process severity by increasing This is carried out increasing the temperature at which the cracking process is done and by decreasing the contact time. Another way, which can be more energy efficient, is to use specific additives containing ZSM-5 aluminosilicate synthetic zeolites.
Chapter 5

Applicability:
Total combustion mode is typically applied to vacuum distillate feedstocks. Only low Conradson carbon feeds are typically processed in full combustion FCCs.

Economics
Table 4.10 gives a typical range of investment cost for two examples of FCC units:

<table>
<thead>
<tr>
<th>Investment cost for FCCs in EUR/(tyr)</th>
<th>Basis of calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>48 – 64</td>
<td>1.5 Mt/yr fresh feed including reaction/regeneration system and product recovery. Excludes offsites, power recovery and flue gas scrubbing (1998).</td>
</tr>
<tr>
<td>45 – 50</td>
<td>2.4 Mt/yr fresh feed including converter, fractionator, vapour recovery, and amine treating but not power recovery battery, battery limit, direct material or labor (1994).</td>
</tr>
<tr>
<td>Maintenance</td>
<td>2 – 3 % of investment per year</td>
</tr>
</tbody>
</table>

Table 4.10: Typical investment cost for a FCC unit in full combustion mode

The operating cost for the addition of a CO promoter to a 1.5 Mt/yr FCC (flue gas generation of around \(10^9\) Nm\(^3\)/yr) providing an efficiency of around 30% (700 mg/Nm\(^3\)) is EUR 0.5 million/yr. A major revamp of an FCC to change the design and/or operation is very expensive and typically is not justified for only environmental reasons.

Driving force for implementation
It is a major production process to convert heavy and residual streams to LPG and transportation fuels. Catalytic cracking has largely replaced thermal cracking because it is able to produce more gasoline with a higher octane and fewer heavy fuel oils and light gases. FCC is a very typical operation in medium complexity refineries but RCC units are becoming more prevalent.

Example plant(s)
Common technique: 56 FCC units were installed in the EU-27 in 2008.

Reference literature

4.5.2 Residue catalytic cracking (RCC)

Description
This section gives emissions information from the RCC when it is run under favourable conditions and the regenerator runs in partial combustion mode. Operational techniques that affect the emissions from the RCC are also discussed. A description of the process can be found in Section 2.5.

Achieved environmental benefits
The possibility to upgrade heavier residues than with the FCC (e.g. atmospheric residue, vacuum residue or low added value residues). As a consequence, the RCC can provide positive environmental benefits for reducing the generation of residue in the refinery that otherwise may go to the bunker and other heavy fuels. These fuels may finally be used in combustion processes generating \(\text{SO}_x\), \(\text{NO}_x\) and metals. Other operational benefits of the RCC over the FCC with environmental consequences are:

• the use of two stage catalyst regeneration as an alternative to a catalyst cooler so as to control the heat release due to coke combustion and can process feeds up to 10% w/w Conradson carbon;
stripping of the catalyst before reaction or before regeneration helps to reduce the coke formation;

- temperature adjustment in the rise by injection of a recycle stream above the zone of the fresh feed injection;

Moreover, the benefits of using CO boilers and expanders in RCC are analysed in Section 4.5.5

**Cross-media effects**
Some feedstocks may need hydrotreatment.

**Applicability**
Fully applicable. An FCC can be retrofitted to an RCC. Medium Conradson carbon feeds would need a CO boiler and higher ones a catalyst cooler. Metal content (Ni, V) should be limited; residue demetallisation/hydrotreating may extend the range of residual feedstocks. It can run with a carbon Conradson index lower than 6 – 8 % and the total metal content less than 20 ppm.

**Example plants**
Several examples in Europe. This technique is less common than FCC in Europe: 4 RCC units were installed in the EU-27 in 2008.

**Reference literature**

### 4.5.3 Partial combustion mode in the regenerator

**Description**
FCC regenerators are operated either in a complete combustion mode (considered in this document as the base operational mode) or partial combustion mode. In the partial combustion mode considerable CO is present in the flue gas and it is consumed downstream of the regenerator in a CO boiler, both to recover the energy produced in a CO boiler and to meet environmental requirements. This system can be seen as two stage regeneration in comparison with the total combustion mode, where a single regeneration step is present. Another technique to consider is the modification of the design and operation of the regenerator, especially to avoid high temperature spots that tend to increase the NO\textsubscript{x} formation.

**Achieved environmental benefits**
The use of a partial combustion mode together with a CO boiler (COB) generates less CO and NO\textsubscript{x} emissions compared with full combustion. The use of a COB or with a high temperature regeneration technology can significantly reduce CO emissions. CO achieved emissions are from less than 50 – 100 mg/Nm\textsuperscript{3} and typically below 100 mg/Nm\textsuperscript{3} (2 % O\textsubscript{2}, daily average). In the COB, refinery fuel gas addition is required to incinerate CO (~900 °C). The advantage of Partial combustion coupled with a COB is also achieve lower NO\textsubscript{x} emissions (100 – 500 mg/Nm\textsuperscript{3} at 2 % O\textsubscript{2}, daily average, standard conditions), ammonia and hydrocarbons emissions. Emissions of SO\textsubscript{x} and particulates are not affected by this mode of operation. According to CONCAWE 4/09 report, from 9 FCC units data set, 8 show SO\textsubscript{x} emissions under 500 mg/Nm\textsuperscript{3} and one up to 800 mg/Nm\textsuperscript{3}. In the latter case, the unit was using supplementary fuel and firing heavy residue in the COB.
The emission factors for a cracking unit with an electrostatic precipitator and a CO boiler are shown Table 4.11:

<table>
<thead>
<tr>
<th>Process</th>
<th>PM</th>
<th>SO\textsubscript{x} (as SO\textsubscript{2})</th>
<th>CO</th>
<th>HC</th>
<th>NO\textsubscript{x} (as NO\textsubscript{2})</th>
<th>Aldehydes</th>
<th>NH\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC with ESP and CO boiler</td>
<td>0.020 – 0.428</td>
<td>0.286 – 1.505</td>
<td>Neg</td>
<td>Neg</td>
<td>0.107 – 0.416</td>
<td>Neg</td>
<td>Neg</td>
</tr>
<tr>
<td>Neg, unacceptable.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.11: Emission factors for cracking (units in kg/1000 litres of fresh feed)
Cross-media effects
Fuel gas is needed for the incineration of CO. If fuel contains sulphur, emissions of $SO_2$ may occur. Other benefits are greater throughputs and heat/power recovery.

Operational data
Where a COB is installed, it should be carefully designed and operated to minimise CO and $NO_x$ releases.

Applicability
This mode of combustion is fully applicable. In general it can be said that feed having a Conradson carbon figure up to 2 – 3 % can be processed in a ‘standard’ FCC without a CO boiler as well as partial-burn FCC. A Conradson figure from 2 – 5 % would require a CO boiler and from 5 – 10 % a cat cooler would be needed. It should be noted that the above figures are only indicative and depend also on the severity of the cracking.

Economics
Investment costs necessary to convert a FCC from total to partial combustion mode is around EUR 2.5 – 4 million. A major revamp of an FCC to change the design and/or operation is very expensive and typically is not justified by environmental reasons alone.

Driving force for implementation
Production process. Partial burn is an option which strongly depends on the type of feedstock to be treated, together with the site pre-existing technical configuration and energy balance.

Example plants
Use of a carbon monoxide boiler is normally a standard practice in fluidised catalytic cracking units in the USA. Many examples also exist in Europe and the rest of the world.

Reference literature
[297, Italy, 2000], [316, TWG, 2000], [268, TWG, 2001]. Add Concawe 2009

4.5.4 Hydrotreatment of feed to the cat cracker

Description
Hydrotreatment of feed to the cat cracker operates at similar conditions to as these used for gasoil, fuel oil and atmospheric residue hydrotreatment (see Sections 2.13 and 4.13). In a growing number of refineries in particular, an hydrotreating or hydrocracking unit is added upstream of the FCC unit, mainly for the purpose of producing low-sulphur gasoline and diesel (<10 ppm) and for optimising the process configuration towards the maximisation of heavy residue conversion and middle distillate production. Simultaneously, this additional treatment also proves to be a key opportunity for the reduction of FCC emissions, leading to a substantial abatement of $NO_x$ and $SO_2$. There are also effects on NO, but they will be driven more by regenerator temperature and combustion dynamics.

Achieved environmental benefits
FCC feedstock hydrotreatment can reduce the sulphur content to <0.1 – 0.5 % w/w (depending on the feedstock). Given that around 9 % of this sulphur content is normally emitted in the regenerator flue-gas, as a consequence of the hydrotreatment, emissions of $SO_2$ from the regenerator can be reduced by up to 90 % as a consequence of the hydrotreatment. The resulting flue-gas daily average concentration can remain in the range of 200 – 600 mg/Nm³ (3 % O₂) depending on the feedstock. One refinery reported values over 600 associated with fluctuations of sulphur content around 0.5 %. In most favourable conditions it is reported that the yearly average concentration can be decreased to as low as 89 mg/Nm³ (3 % O₂) [54, Gallauner et al. 2009] and

[297, Italy, 2000], [316, TWG, 2000], [268, TWG, 2001]. Add Concawe 2009
Nitrogen compounds can also be reduced by up to 75 – 85% (smaller percentage for the partial combustion mode), being aware that a certain percentage on reduction of nitrogen compounds does not lead to equivalent NOx reduction (when it occurs, a maximum reduction of approximately 50 – 60% of NOx reduction is obtained from a 70 – 80% nitrogen reduction in the feedstock). The resulting flue-gas daily average concentration can remain in the range 50 – 180 mg/Nm³ (3% O₂) depending on the feedstock, with a yearly average concentration as low as 71 mg/Nm³ (3% O₂) [54, Gallauner et al. 2009].

This process also reduces the metal emissions (e.g. Ni, V) to the air and prolongs the life of the cat cracker catalyst.

Another benefit of this technique is that hydrotreated mercaptan oxidation is not necessary a lower concentration of mercaptans in the products is less. This may impact the next process stage which is mercaptan removal. This reduces the amount of used caustic and emissions into water.

**Cross-media effects**

Cross-media effects include the increase of energy consumption and the consequent increase in CO₂ emissions, due mainly to the hydrogen, as discussed in Section 3.14. As an illustrating example, the overall energy consumption of a refinery increased from approximately 2 to 2.5 GJ/tonne refined after the addition of an hydrocracker (3 Mt/yr) and a complementary steam methane reforming H₂ production plant (220 000 t/yr).

As discussed in Section 4.13, hydrotreatment processes generate catalysts for disposal and increase the H₂S production with direct consequences for the sour water stripper and sulphur recovery units (which may need to be enlarged or replaced). In addition, heavy metals in FCC feedstock will be shifted from FCC to hydrotreater catalyst. Deep hydrotreatment, by reducing metal content, may also lead to reduce performance of ESP (see section 4.5.9.2).

**Operational data**

Installation of cat cracker feed hydrotreatment (or a feed hydrocracker) will reduce the sulphur content in cat cracker products and improve their quality, so that they require less final processing. Hydrogen and energy are required for this process.

The sulphur removal efficiency achieved by hydrotreatment depends on the boiling range of the cat cracker feed. The heavier the feed, the more energy is required for the same sulphur removal efficiency. The water used for the different catalytic sections yields 20 - 40 m³/h of sour water. Data on the effect of the feedstock hydrotreatment on the cracker’s PM emissions have also been provided in Table 3.44.

The following graphs (Figure 4.1 and Figure 4.2 below) show the performance obtained after the commissioning, in mid-2005, of a new 1 Mt/yr hydrocracking unit upstream to a 1.5 Mt/yr FCC unit in a European refinery. The average emission of the FCC unit fell from a yearly average of 1650 to 670 t (-60%) while the corresponding average sulphur content in its feedstock decreased from 1.5 – 1.7% to 0.25 – 0.35%. For this particular application, the related specific consumption of hydrogen is in the range 8 – 9 kg H₂ per tonne of hydrotreated feedstock.

**Applicability**

Fully applicable. This process is more cost-effective when sufficient hydrogen, SWS and SRU capacities are already available in the refinery.
Economics

Table 4.12 and Table 4.13 give examples of costs associated with FCC feedstock hydrotreatment.

Table 4.12: Catalytic feed hydrotreatment (typical feeds being atmospheric residue and vacuum gas oil) Costs updated by CONCAWE, 2010

<table>
<thead>
<tr>
<th>Size/capacity (ktonnes/yr)</th>
<th>Typical capital/installed cost (EUR million)</th>
<th>Operating cost (EUR million/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 250</td>
<td>65 198</td>
<td>9</td>
</tr>
<tr>
<td>2 500</td>
<td>106 303</td>
<td>17</td>
</tr>
<tr>
<td>3 750</td>
<td>150 394</td>
<td>26</td>
</tr>
</tbody>
</table>

NB: The cost assumes that there is adequate space and an existing SRU (sulphur recovery unit) and sour water stripping capacity. If further hydrogen production is needed, a new hydrogen plant for a 2500 kt/yr FCC UNIT feed hydrotreater or hydrocracker would typically cost in the range of EUR 60 - 75 million.

Sources: [112, Foster Wheeler Energy, 1999]
Table 4.13: Cost ranges associated with the hydrotretment of a 1.5 Mt/yr FCC unit according to some typical configurations

<table>
<thead>
<tr>
<th>Cost parameters</th>
<th>Distillate feed desulphurisation</th>
<th>Residue feed desulphurisation</th>
<th>Feedstock hydrotreating to reduce NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity of process</td>
<td>1.5 Mt/yr</td>
<td>1.5 Mt/yr</td>
<td>1.5 Mt/yr FCC UNIT with CO Boiler</td>
</tr>
<tr>
<td>Investment expenses</td>
<td>80 – 100(3)</td>
<td>45 – 50(2,3)</td>
<td>200 – 300(2,3)</td>
</tr>
<tr>
<td>Operating expenses</td>
<td>4 – 9</td>
<td>15 – 25(3)</td>
<td>30 – 50(2)</td>
</tr>
<tr>
<td>(EUR million)</td>
<td></td>
<td></td>
<td>80 – 100</td>
</tr>
<tr>
<td>(EUR million/yr)</td>
<td></td>
<td></td>
<td>4 – 9</td>
</tr>
</tbody>
</table>

(1) Excluding H2 production and H2S handling facilities
(2) [45a, Sema and Sofres, 1991]
(3) [115, CONCAWE, 1999].

A recent example of the hydrotreating of 56% of a 1.5 Mt/yr FCC unit feedstock gives the following costs:

- Total investment (2005): EUR 230 million, including the three treatment units (cumulated capacity of 1.05 Mt/yr), the necessary adaptation of the FCC, and the related SRU unit and acid water treatment plant;
- Energy costs: EUR 7.15/t of treated feedstock (2009);
- Approximate hydrogen costs (annual): EUR 0.5 million (fixed term) + EUR 1420/t of hydrogen supplied (2009), with a specific consumption of 8 – 9 kg H2/t of treated feedstock;
- The total operating cost (including H2 fixed term) is EUR 7.75/t of treated feedstock, and the corresponding specific cost is 6640 EUR/t of SO2 avoided.

In another example, the following data is provided for the hydrotreatment of a 3Mt FCC feedstock:

- SO2 emissions reduced by 3.7 kg/t of treated feedstock
- Related consumptions are 9.6 kg of H2, 30.8 kWh of electricity, and 556 MJ of fuels per tonne of treated feedstock
- The total operating cost is estimated to EUR 19.3 per tonne of treated feedstock, and the corresponding specific cost is 5200 EUR/t of SO2 avoided.

Note: the operating costs of hydrotreatment should also be partly affected to the improvement of the product characteristics as it is its main objective.

Driving force for implementation
The implementation of this technique is typically product-specification driven because higher conversions are achieved with hydrotreated feedstocks. The majority of the products produced by the cat cracker without previous hydrotreatment need further treatment to comply with product specifications. Moreover, the flue-gas from the regenerator contributes significantly to the overall refinery SOx/NOx emissions. Desulphurisation or mild hydrocracking of the feed is an option to reduce these emissions.

Example plants
Many examples: 16 out of the 56 European sites reported by TWG members were said to use it.

Reference literature
[296, IFP, 2000], [115, CONCAWE, 1999], [112, Foster Wheeler Energy, 1999], [45a, Sema and Sofres, 1991], [247, UBA Austria, 1998], [297, Italy, 2000], [268, TWG, 2001], [Specific attachements to Questionnaires n° 31, 32, 36, 39].
4.5.5 Waste heat boiler and expander applied to flue-gas from the FCC regenerator

Description
Heat recovery from the regenerator flue-gas is conducted in a waste heat boiler or in a CO-boiler. Heat recovery from the reactor vapour is conducted in the main fractionator by heat integration with the unsaturated gas plant as well as by feed preheating and by the generation of steam with the residual heat from product rundown streams and pump-around streams. The steam produced in the CO boiler normally balances the steam consumed in the FCC. Installing an expander in the flue-gas stream from the regenerator can further increase energy efficiency. Figure 4.3 gives a simplified scheme of application of a waste heat boiler.

![Waste heat boiler and expander applied to regenerator flue-gas of a cat cracker](image)

**Figure 4.3:** Waste heat boiler and expander applied to regenerator flue-gas of a cat cracker

Achieved environmental benefits
The waste heat boiler recovers the heat from the flue-gas and the expander can recover part of the pressure to be used in the compression of the air needed in the regenerator. An example of the application of an expander saved 15 MW\textsubscript{electric} from the flue-gas generated by a FCC of a capacity of 5 Mt/yr.

Cross-media effects
Significant quantities of catalyst fines are collected in the waste heat boiler (WHB). The newer WHBs avoid catalyst arrival with configuration such as cyclones or have facilities which permanently remove the collected fines (e.g. sonic soot cleaners), but older WHBs are normally soot-blown once per shift. During this operation, the emission of catalyst fines is especially high if the unit is not equipped with an efficient particulate abatement technique. During heating surface cleaning (or soot blowing) in CO boilers, emissions of PM and metal may increase by about 50%.

Examples of three German refineries where ESP are installed downstream the FCC are shown in Table 4.14.
Table 4.14  Examples of soot blowing effects for 3 German refineries

<table>
<thead>
<tr>
<th>Reference</th>
<th>Capacity</th>
<th>Feed Description</th>
<th>Mode</th>
<th>PM</th>
<th>Metals (&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conc (&lt;sup&gt;1&lt;/sup&gt;) (mg/Nm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>Flux (kg/h)</td>
</tr>
<tr>
<td>Refinery 1</td>
<td>82%</td>
<td>Atmospheric residue, unconverted gasoil</td>
<td>Normal</td>
<td>11.7</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Soot blowing</td>
<td>18.7</td>
<td>1.71</td>
</tr>
<tr>
<td>Refinery 2</td>
<td>79%</td>
<td>Atmospheric residue, heavy and light waxes</td>
<td>Normal</td>
<td>6.70</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Soot blowing</td>
<td>10.2</td>
<td>0.80</td>
</tr>
<tr>
<td>Refinery 3</td>
<td>79%</td>
<td>NA</td>
<td>Normal</td>
<td>6.70</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Soot blowing</td>
<td>9.70</td>
<td>1.43</td>
</tr>
</tbody>
</table>

(<sup>1</sup>) Concentrations are mean values (3*30 minutes) in mg/Nm<sup>3</sup> at 3 % O<sub>2</sub> (dry gas), based on the continuous emission monitoring system.
(<sup>2</sup>) Metals include Ni except for Refinery 1 where it includes Ni, Cu, V

Operational data
Power recovery on regeneration gas reduces the CO boiler duty but leads to an overall higher energy recovery from the FCC.

Applicability
Retrofitting of this equipment can be very difficult because of space limitations in the refinery. On small or low pressure units, expanders are not justified economically.

Economics
Applying an expander on the regenerator gas could be costly because of the additional particulate systems under high temperature that is required. Turbo expanders are costly items and so are waste heat recovery units.

Driving force for implementation
Recovery of energy.

Example plant(s)
Energy recovery by utilising an expander in the regenerator flue-gas is only applied in the larger, more recently built units.

Reference literature
[136, MRI, 1997], [268, TWG, 2001]

4.5.6 Catalyst selection
Description
Techniques to consider are included below.

a. Use of a higher quality FCC catalyst. Process efficiency and metal tolerance (to V and Ni in particular) can be increased while catalyst waste can be reduced and rate of replacement reduced.

b. Use of an attrition-resistant catalyst to reduce the frequency of replacing catalysts, the amount of catalyst added on a daily basis and reduce emission of particulates from the regenerator. Emissions reductions result from both a decrease in the small particulate emissions from fresh catalyst, as well as from the catalyst resisting attrition during unit operations. These catalysts are typically alumina-based (Al-sol binder technology) and their particulates are much harder than the silica-based former catalyst generation.
Achieved environmental benefits
A good selection of the catalyst used in the FCC process can:

- increase the FCC efficiency by up to 20 %, coke production can be decreased and catalyst waste can be reduced;
- increase the recyclability of the catalyst;
- reduce the particulate content of flue-gas before treatment to 300 mg/Nm³.

Cross-media effects
None in particular.

Operational data
Switching from a Si-sol catalyst to a Al-sol catalyst can decrease PM emissions (considered at constant % O₂) by up to 50 % after a transitory period of 50 – 100 days.
Applicability
If not yet optimised, a change in the catalyst is usually most of the time favourable. In exceptional cases however, it may have an adverse effect to the performance on the FCC.

Economics
Investment expenses: none.
Operating expenses: negligible.

Driving force for implementation
Process requirements and reduction of finest PM emissions.

Example plants
Most FCC units in Europe have already optimised catalyst selection.
Note for TWG: please give specific information (e.g. site references)

Reference literature
[80, March Consulting Group, 1991], [115, CONCAWE, 1999] [24, Bruhin et al. 2003]

Section proposed to delete (no appropriate information provided)

4.5.7 Waste water management within FCC UNIT
KOM conclusion 3.5: TWG to review Section 4.5.7, in particular on low consuming water techniques (cascading)

Description
Some techniques to consider for waste water management are:
a. Some cat cracker designs contain cascading overhead washing section in cat cracker designed to minimise water usage;
b. Reuse of waste water generated in FCC UNIT within the refinery (e.g. desalters) or ultimately routed to WWTP.

Achieved environmental benefits
Reduction of water usage and reuse of water within the refinery.

Cross media effects
None to be in particular mentioned.

Applicability
Both techniques are fully applicable to cat crackers.

Driving force for implementation
Reduction of water usage.

Economics
No data available. Note for TWG: please provide information when available.

Example plants
Used in some cat crackers.

Reference literature
[80, March Consulting Group, 1991].
4.5.8 Nitrogen oxides abatement techniques

This section includes NO\textsubscript{x} abatement techniques that may be applied to FCCs. Among these are process-related techniques, which are very specific and mostly involve the reduction of NO\textsubscript{x} using or improving various catalysts and additives by acting on the three major sources of nitrogen in the FCC regenerator: nitrogen compounds in the coke resulting from the feed, nitrogen from air admitted in the regenerator, and nitrogen from the combustion air to CO boilers in the case of partial-burn units. A strong relationship is observed between NO\textsubscript{x} and excess O\textsubscript{2} in the flue-gas, and a poor distribution of O\textsubscript{2} in the regenerator bed which can result in large variations of local scale NO\textsubscript{x} formation.

4.5.8.1 Selective catalytic reduction (SCR)

Description
See Section 4.25.3.3.

Achieved environmental benefits
For FCC application, inlet NO\textsubscript{x} concentrations to the SCR may vary from 200 - 2000 mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2}. Inlet NO\textsubscript{x} concentrations to the SCR vary with depending on the type of FCC used (total or partial combustion in combination with a CO boiler) and the type of feed used (heavier feed tends to produce higher NO\textsubscript{x} emissions). A reduction by of up to 85 – 90 % of NO\textsubscript{x} emissions with the outlet concentration of NO\textsubscript{x} reduced to 20 – 250 mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2} can be obtained, depending on the inlet concentration. As an example, these reduction efficiencies provide a reduction of NO\textsubscript{x} emissions of approximately 300 tonnes of NO\textsubscript{x} per year from cat cracker with a capacity of 1.65 Mt/yr (calculation based on an average of 450 mg/Nm\textsuperscript{3} inlet and 50 mg/Nm\textsuperscript{3} outlet with a 0.7 10\textsuperscript{9} Nm\textsuperscript{3}/yr waste gas flow). Another advantage is that some CO oxidation also occur in the SCR process (approximately 40 %).

Most SCR systems include an upstream section with CO oxidation catalyst that shares SCR installation and achieves up to 95 % CO conversion to CO\textsubscript{2}. In SCR systems not equipped with CO oxidation catalyst, small conversions to CO\textsubscript{2} occurs when CO reacts with NO and generates molecular nitrogen.

Cross-media effects
Use of NH\textsubscript{3} (storage/handling), risk of NH\textsubscript{3} emissions when operating outside stoichiometric proportion and depending on the age of the catalyst (< 2 – 10 mg/Nm\textsuperscript{3}) and SCR catalyst regeneration and disposal. Ammonia needed for this technique may be supplied by two-stage sour water strippers (see Section 0). Another disadvantage of SCR is that a few percent of SO\textsubscript{2} is oxidised to SO\textsubscript{3} over the eNOx cat and as consequence it can potentially create plume opacity problems. See Section 4.25.3.3. Concerning, more specifically, FCC units, the application of an SCR may reduce the potential for energy recovery using expander turbines, as it increases the pressure drop over the regenerator overhead circuit and is also prone to a buildup of pressure drop over time, thereby limiting the available operating window for a turbine expander, particularly in existing facilities with fixed pressure profiles. This may lead to lower thermal efficiency.

Operational data
Table 4.15 illustrates the results obtained for four FCC units equipped with SCR treatment. Question to CONCAWE: data traceability is crucial! Please could you provide the EIPPC bureau, on a confidential basis, with the name of the sites concerned so that corresponding questionnaire references could be added? Answer:NO
Table 4.15: Performances reported as obtained with SCR for four European FCC units

<table>
<thead>
<tr>
<th>Data set reference [Questionnaire]</th>
<th>Type</th>
<th>Inlet</th>
<th>Outlet</th>
<th>% NOx abatement</th>
<th>Ammonia slip</th>
<th>SCR shutdown frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONCAWE 1(1)(2)</td>
<td>Full-burn with auxiliary fired boiler</td>
<td>36 – 244</td>
<td>2 – 26</td>
<td>88 %</td>
<td>–</td>
<td>4 years</td>
</tr>
<tr>
<td>CONCAWE 2(1)(2)</td>
<td>Full-burn unit</td>
<td>25 – 211</td>
<td>3 – 13</td>
<td>91 %</td>
<td>–</td>
<td>7 – 17 months</td>
</tr>
<tr>
<td>CONCAWE 3(1)(2)</td>
<td>Partial-burn with CO boiler</td>
<td>318</td>
<td>99</td>
<td>85 % (&lt;70 % at end of run)</td>
<td>–</td>
<td>4 years</td>
</tr>
<tr>
<td><a href="3">n° 27</a></td>
<td>Full-burn unit</td>
<td>–</td>
<td>249.6</td>
<td>79.1 %</td>
<td>–</td>
<td>1351 t avoided (2006)</td>
</tr>
</tbody>
</table>

(1) Daily average in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.
(2) Averages are calculated from the 5th – 95th percentile range of the complete available dataset.
(3) Yearly averages in mg/Nm³ at 3 % O₂ (dry gas), based on the continuous emission monitoring system.

Source: CONCAWE except for n° 27: TWG 2010 data collection

Catalyst performance and the pressure drop of SCR operated on FCC units is expected to deteriorate over time, due mainly to fouling by the dust PM catalyst fines and SOₓ salts. Theoretical expected catalyst lifetime is about four years but could be much different, depending on the PM filtering efficiency upstream of the SCR and the operating conditions. The two following examples are very illustrative on that respect.

- Intensive fouling has been experienced and deeply analysed in one European site: as seen in Figure 4.6, it was mainly due to an excessive inlet gas temperature (most of time above 362 °C and part of time above 370 °C) which drove the operator to increase the NH₃ injection rate up to 120 % of the theoretical stoichiometry in order to compensate the poor conversion.

- However, on the other hand, current examples in Europe have shown lifetimes well over the expected ones, currently reaching six to seven years and even much longer. In one particular case, the first three SCR catalyst layers installed at Preem Lysekil refinery (SE) in 1994 (and a fortiori the 4th one installed in 2003) were still in operation in 2010. Based on the latest test a lifetime of 140 000 to 150 000 hours is expected.

Information from operators claim that not all SCR applied to FCC have operated to SCR applied below design loads and careful de-dusting of inlet gas upstream of the SCR help leading that fact to increase catalyst lifetimes. Some other concern from operators is that SCR catalyst could potentially be fouled by the particulates in the flue-gas stream. Particle size distribution and particulate load of the flue-gas entering the SCR should be evaluated to determine whether there is potential for fouling (high particulate) and/or thermophoretic fouling (small particulates). If necessary, particulate mitigation equipment such as sootblowers may need to be installed. More general operational data for SCRs can be found in Section 4.25.3.3.
Figure 4.6: SCR conversion yield as a function of inlet temperature for a European FCC unit

Applicability
Because the temperature window is wide (300 – 400 ºC), it is very an SCR is relatively flexible for FCC retrofit applications. However, existing auxiliary fired boilers, CO boilers and waste heat boilers may have to be modified for temperature adjustment.

Considerable space is needed for the installation, SCR applications often require a new waste heat boiler (full burn) or a CO boiler (partial burn) if they are not present. Preferably the \( \text{deNO}_x \) reduction unit is integrated with into the waste heat boiler. Because an SCR operates at oxidising conditions, it cannot be installed upstream of a CO boiler (partial burn).

As the SCR catalyst could potentially be fouled by the particulates present in the flue-gas stream, additional filtering might be required upstream of the new SCR unit.

As for an SNCR, the ammonia dosing rate is limited by the potential risk of corrosion downstream of the unit.

Economics
Table 4.16 shows some examples of the economics of the application of SCR to FCCs.

Table 4.16: Economics of SCR applied to FCC units

<table>
<thead>
<tr>
<th>Size of the FCC (Mt/yr)</th>
<th>Efficiency (%)</th>
<th>Outlet NO(_x) concentration (mg/Nm(^3))</th>
<th>Installation cost (EUR million)</th>
<th>Operating and maintenance cost (EUR million/yr)</th>
<th>Specific removal cost((^4)) (EUR/t of NO(_x) removed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65</td>
<td>90</td>
<td>40</td>
<td>3.8 (SEK 33 million)((^1))  (^{(2)})</td>
<td>0.24 (SEK 2 million)(^3)</td>
<td>2103</td>
</tr>
<tr>
<td>1.5</td>
<td>85</td>
<td>120</td>
<td>6.3 - 13</td>
<td>0.4 – 0.8</td>
<td>2023</td>
</tr>
<tr>
<td>1.5</td>
<td>85</td>
<td>37.5</td>
<td>1.2 – 3.6((^2))</td>
<td>0.12 – 0.48</td>
<td>2042</td>
</tr>
</tbody>
</table>

(\(^1\)) Cost in original currency – Built 1994.
(\(^2\)) Including an SCR reactor, ammonia storage and injection facilities and initial fill of catalyst.
(\(^3\)) Operation and maintenance cost including ammonia, steam and replacement of catalyst.
(\(^4\)) Including a CO boiler.
(\(^5\)) Using the same economic analysis presented in following tables.
NB: All costs for a new SCR installation.
A more detailed economic assessment of a SCR in a FCC unit (year 2000) is shown in Table 4.17.

### Table 4.17: Main cost factors for a selective catalytic reduction (SCR) installation (raw gas) after the FCC plant

<table>
<thead>
<tr>
<th>Cost parameters</th>
<th>Quantity</th>
<th>EUR/unit</th>
<th>EUR/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating hours (h/yr)</td>
<td>8 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investment costs (EUR million)</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input factors for annual expenditure:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of years</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate of interest (%)</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual repayment incl. interest (EUR/yr)</td>
<td>150 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proportional investment costs incl. interest</td>
<td>150 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume of catalyst (m³)</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duration (years)</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Renewal of catalyst (m³/yr)</td>
<td>2.5 EUR 15000/m³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average renewal of catalyst (EUR/yr)</td>
<td>36 300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalysts</td>
<td>36 300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (% of investment costs)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (EUR/yr)</td>
<td>29 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure drop (mbar)</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy for reheating (MJ/h)</td>
<td>0 EUR 3.6/GJ</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Electrical energy (kWh/h)</td>
<td>88 EUR 0.065/kWh</td>
<td>46 000</td>
<td></td>
</tr>
<tr>
<td>NH₃ liquid (kg/h)</td>
<td>36.96 EUR 0.25/kg</td>
<td>75 200</td>
<td></td>
</tr>
<tr>
<td><strong>Total costs</strong></td>
<td><strong>336 269</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NB: In a refinery with a volume of exhaust gas of 100 000 Nm³/h achieving a NOₓ emission reduction of 1 000 mg/Nm³ in relation to actual oxygen content and for a clean gas concentration of <200 mg NOₓ/Nm³. Inlet concentration may vary between 200 – 2000 mg/Nm³ at 3 %O₂. The outlet concentration of NOₓ is reduced to 80 – 120 mg/Nm³ by SCR.

See Table 4.20 for cost comparison of various techniques.

Moreover, potential investment and operational costs for implementing this technique in 2007 on two FCC UNITs in Colorado refineries (USA) were estimated in the range of USD 3016 – 3136 (EUR 2 214 – 2 302 based on 0.734 conversion rate on 2/07/2007) per year and tonne of NOₓ avoided saved, assuming a resulting NOₓ emission decrease of 85 – 90 %. (see also Table 4.20 for a cost comparison with other NOₓ reducing techniques).

A preliminary evaluation for the retrofitting of a 57 500 bpd (3Mt/yr) FCC with an SCR gives the following costs (2007):

- Capital cost GBP: 15 million (EUR 22.2 million, based on 1.4801 conversion rate on 2/07/2007)
- Operating cost GBP: 0.54 million per year (EUR 0.80 million per year)
- Estimated quantity of NOₓ abated: 80 t/yr (assumed reduction yield of 50 %)
- Equivalent annual cost: GBP 34079, (EUR 50 442) per t/yr of NOₓ abated (15-year lifetime assumed).

**Driving force for implementation**

Reduction of NOₓ emissions. A NOₓ reduction of 300 tonnes annually is achieved in an FCC unit of 1.65 Mt/yr when 90 % of NOₓ reduction is achieved.

**Examples**

At least six SCRs are in operation in FCCs worldwide and two in Europe (Scanraff Preemraff Lysekil in Lysekil-Sweden and Shell in Pernis. The Netherlands).
4.5.8.2 Selective non-catalytic reduction (SNCR)

Description
See Section 4.25.3.2.

Achieved environmental benefits
These systems reduce the NO\textsubscript{x} emissions by 40–80%. On FCC units, this technique has shown to be able to achieve NO\textsubscript{x} reductions of up to 70% (on a daily basis). The outlet concentrations can be as low as to <200–400 mg/Nm\textsuperscript{3} at 3% O\textsubscript{2} depending on the nitrogen content of the feedstock. Instead of ammonia, urea can be also used. The use of urea has the advantage to be more soluble in water and consequently reduce the risk of handling/storage of NH\textsubscript{3}.

Cross-media effects
Use of NH\textsubscript{3} (storage/handling), risk of NH\textsubscript{3} emissions when operating outside stoichiometric proportion. Ammonia needed for this technique may be supplied by two-stage sour water strippers (see Section 0). The use of urea generates more ammonia (from urea) slip and some N\textsubscript{2}O formation.
See Section 4.25.3.2.

One issue of particular concern with SNCR applications to FCC units is the potential increase in CO emissions. At the lower end of the SNCR operating temperature range, ammonia can inhibit CO oxidation and increase CO emissions from low temperature CO boilers.

Operational data
High temperatures (800–900 °C) of the flue gases are needed.

Table 4.18 illustrates the results obtained for three FCC units equipped with a SNCR treatment. Question to CONCAWE: data traceability is crucial: please can you provide the EIPPC bureau with the name of the sites concerned so that we can eventually add corresponding questionnaires references Answer:NO

<table>
<thead>
<tr>
<th>Data set reference</th>
<th>Type</th>
<th>Inlet</th>
<th>Outlet</th>
<th>% NO\textsubscript{x} abatement</th>
<th>Ammonia slip</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONCAWE 4</td>
<td>Full-combustion with auxiliary-fired boiler</td>
<td>123 – 410</td>
<td>NA</td>
<td>23</td>
<td>&lt;15</td>
<td>–</td>
</tr>
<tr>
<td>CONCAWE 5</td>
<td>Full-combustion with auxiliary-fired boiler</td>
<td>90 – 530</td>
<td>50 – 180</td>
<td>50</td>
<td>8</td>
<td>95th Perc. abatement: 81% (hourly)</td>
</tr>
<tr>
<td>CONCAWE 6</td>
<td>Partial-combustion with CO boiler</td>
<td>318</td>
<td>99</td>
<td>67</td>
<td>10</td>
<td>95th Perc. abatement: 78% (hourly)</td>
</tr>
</tbody>
</table>

NB: Daily average emissions in mg/Nm\textsuperscript{3} at 3% O\textsubscript{2} (dry gas)
Data based on continuous emission monitoring system.
It is reported that % NO\textsubscript{x} abatement is not unique and is dependent on the inlet concentration
Source: CONCAWE
In a German refinery, the following data on a long period of time are reported about an SNCR installed on a FCC unit:

- outlet NO\textsubscript{x} concentration <100 mg/Nm\textsuperscript{3} (online measurements);
- outlet CO concentration <50 mg/Nm\textsuperscript{3};
- FCC unit with CO boiler in partial combustion;
- total nitrogen content of the FCC feed about 1200 ppm (determined by periodic feed analyses);
- ammonium flow 300 l/h (8 – 10 % concentration)

**Applicability**

SNCR is applicable in partial combustion FCCs with CO boilers, and retrofitting in existing CO boilers is relatively simple. It is also applicable to full combustion units, FCCs with auxiliary fired boilers, depending on adequate residence time in such boiler at the required temperature range. SNCR units cannot work properly during boiler shutdowns.

SNCR is also applicable to full combustion FCCs without auxiliary boilers, using hydrogen addition for injection into the regenerator overhead line. In that case, the application should take into account the unit specificity, including the starting process conditions.

Space requirements are mainly related to NH\textsubscript{3} storage.

**Economics**

**Table 4.19: Economics of SNCR applied to FCCs**

Any reference year?

<table>
<thead>
<tr>
<th>Size of the FCC (Mt/yr)</th>
<th>Efficiency (%)</th>
<th>NO\textsubscript{x} in/out concentration (mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2})</th>
<th>Investment (EUR million)</th>
<th>Operating cost (EUR million/yr)</th>
<th>Specific removal costs (\Delta) (EUR/t of NO\textsubscript{x} removed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>60</td>
<td>800/\textgreater 320</td>
<td>5.4</td>
<td>0.6 (\uparrow)</td>
<td>0.1 – 0.4</td>
</tr>
<tr>
<td>1.5</td>
<td>60 – 80</td>
<td>200/40 – 80</td>
<td>0.35 – 1.5(\downarrow)</td>
<td>0.05 – 0.4</td>
<td>1700</td>
</tr>
</tbody>
</table>

\(\uparrow\) Cost data does not include the cost of the CO boiler
Chapter 5

Potential investment and operational costs for implementing this technique in 2007 on two FCC units in Colorado refineries (USA) were estimated in the range of USD 1940 to USD 2533 per year and tonne of NO$_x$ avoided, assuming a resulting NO$_x$ emission decrease of 60 – 80%.

See also Table 4.20 for a cost comparison with other NO$_x$ reducing techniques.

**Driving force for implementation**
Reduction of NO$_x$ emissions with limited space requirements.

**Example plants**
It has been applied in Japan on an FCC UNIT where a CO boiler provides a sufficient temperature window. Several applications are known, including in Japan.

**Reference literature**
[115, CONCAWE, 1999], [45a, Sema and Sofres, 1991], [316, TWG, 2000] [17, Jeavons and Francis 2008] [36, CONCAWE n°4/09 2009].

**4.5.8.3 Low-NO$_x$ CO oxidation promoters**

**Description**
There is little, if any contribution to NO$_x$ from the thermal oxidation of N$_2$ in the catalytic cracking process itself, as the combustion in the regenerator takes place at reduced temperatures of less than 750 °C. In fact, NO$_x$ released into the regenerator flue-gas is directly linked to the nitrogen contained in the feedstock. In the absence of feed nitrogen, no NO$_x$ is formed and Pt-based CO promoters do not increase overall emission of the FCC. Nearly half of the nitrogen in the catalytic cracker feed leaves the reactor as part of the coke layed on the catalyst. Of the nitrogen in coke, about 80% to 90% is converted directly or indirectly to N$_2$ during regeneration, while the remaining nitrogen ultimately forms NO$_x$. Therefore, nitrogen oxides account for 5 – 10% of the nitrogen introduced in the feedstock.

As shown in Figure 4.8, NO$_x$ formation chemistry in the FCC regenerator is complex: the nitrogen in coke is pyrolysed and first appears in the regenerator as HCN or NH$_3$. These products are then oxidised in N$_2$, NO and NO$_2$, while a simultaneous reduction also takes place between NO and the available CO in order to regenerate gaseous N$_2$.

This technique only concerns the full combustion mode, where the aim is to burn the coke as fully and as efficiently as possible, and where conventional platinum-based CO combustion promoters are usually added which lower CO concentration and enhance the oxidation of HCN, NH$_3$ and other reduced nitrogen intermediates to NO$_2$. 
A first control option is to reduce the platinum load in the catalytic bed, either through minimising the addition rate or reducing the platinum content of the Pt-based CO promoter. However, as afterburning needs to be kept under control, this option can be limited.

Another alternative is to use low-NO\textsubscript{x} non-platinum CO oxidation promoters. The non-platinum promoter selectively promotes the combustion of CO only and prevents the oxidation of the nitrogen which contains intermediates to NO\textsubscript{x}. The addition rate of the non-platinum promoter is equal to two times that of the traditional platinum-containing promoter, depending on regenerator operating conditions and excess oxygen level. The amount of non-platinum promoter is hence around 0.3wt % of the fresh FCC additive rate.

**Achieved environmental benefits**

Typical downstream effluent NO\textsubscript{x} concentrations of 40 to 140 mg/Nm\textsuperscript{3} (daily average) at 3 % O\textsubscript{2} are reported for a feedstock nitrogen content of approximately 0.20 %. The amount of NO\textsubscript{x} removed avoided depends on the amount of additive in the unit, but removal efficiency is typically between 40 – 80 %.

When combining both low-NO\textsubscript{x} non-platinum CO oxidation promoters and NO\textsubscript{x} removal additives (see section 4.5.8.4), or when using specific products which combine the two functions, structurally NO\textsubscript{x} reduction of more than 80 % is achievable depending on the added quantity.

**Cross-media effects**

None in particular Note for TWG: No specific information was provided

**Operational data**

See Section 4.5.8.4

**Applicability**

A low-NO\textsubscript{x} non-Pt CO promoter is an option for NO\textsubscript{x} reduction in full-burn FCC units already using a Pt-base CO promoter. It is not applicable at all for partial-burn FCC units. The application of the additives is not specifically dependent on FCC unit design. However, proper
distribution of air in the regenerator is required to obtain the maximum benefit. No significant deterioration in unit performance is reported, any increase or decrease of the catalyst replacement rate. In addition, care must be taken to optimise the dosage of both Pt-based and non-Pt promoters to assure that the unit is not making more NOx.

**Economics**
Table 4.20 gives rough cost estimates reported for various control approaches for a typical 28,000 bpd (1.6 Mt/yr) FCC unit.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Expected efficiency (%)</th>
<th>Installation cost 2008 (USD million)</th>
<th>Operational cost 2008 (USD million/yr)</th>
<th>Specific removal cost (USD/tonne NOx)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCR</td>
<td>85</td>
<td>2.1 – 6.3</td>
<td>0.21 – 0.84</td>
<td>3 600</td>
</tr>
<tr>
<td>SCNR</td>
<td>60 – 80</td>
<td>0.6 – 2.6</td>
<td>0.09 – 0.70</td>
<td>3 000</td>
</tr>
<tr>
<td>Low-NOx promoter(1)</td>
<td>40 – 70</td>
<td>–</td>
<td>0.32 – 1.76 (1)</td>
<td>1 200 – 3 600</td>
</tr>
<tr>
<td>Specific NOx reduction additive</td>
<td>30 – 80</td>
<td>–</td>
<td>0.11 – 0.22</td>
<td>2 400 – 3 600</td>
</tr>
</tbody>
</table>

(1) Incremental cost compared with a Pt-based promoter

The cost for removing NOx with such a low-NOx CO promoter will depend on the regenerator operating conditions and the actual mechanical design of the promoter. It is estimated that on average the cost will vary between EUR 1 to 5 per kg NOx removed.

**Driving force for implementation**
A noticeable reduction of NOx reduction is obtained while no capital expenditure is required.

**Example plants**
Many refineries (around 40 units alone in the USA) have applied non-Pt CO combustion promoters to the catalyst. The method is well established commercially.

**Reference literature**
[ 27, Vierheilig et al. 2003 ] [ 23, Yaluris et al. 2006 ] [ 26, Kramer et al. 2009 ] [ 36, CONCAWE n°4/09 2009 ].

**4.5.8.4 Specific additives for NOx reduction**

**Description**
As a complementary or substitutional approach to non-Pt low-NOx CO promoters, this technique consists of using specific catalytic additives for enhancing the further reduction of NO by CO. These additives capitalise on the inherent concentration gradients of gases maintained in the regenerator, and catalyse the chemical reactions which belong to the third group as displayed in Figure 4.8. So far, they have proved to be efficient only for full-burn mode. The additives can be used alone, in combination with conventional Pt-based promoters, or together with low-NOx CO promoters, depending of the operational conditions of the unit.

**Achieved environmental benefits**
Results are highly variable and depend on the unit design and the achievable oxygen excess. Reductions of NOx emissions up to 80 % are reported when used in favourable conditions, either alone or in combination with a Pt-based conventional CO promoter. However, such reduction levels remain exceptional and typical reductions more often observed range from around 25 – 60 %.
As shown in Table 4.21, results also depend on the initial NO\textsubscript{x} concentration to be abated in the FCC regenerator.

<table>
<thead>
<tr>
<th>Type of additive(^{(1)})</th>
<th>NG-A</th>
<th>NG-A</th>
<th>NG-B</th>
<th>NG-B</th>
<th>NG-B</th>
<th>NG-B</th>
<th>NG-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC design</td>
<td>Model IV</td>
<td>Ortho-flow</td>
<td>UOP stack</td>
<td>UOP stack</td>
<td>HOC</td>
<td>Model III</td>
<td>UOP HE</td>
</tr>
<tr>
<td>Regenerator bed temperature (°C)</td>
<td>710</td>
<td>706</td>
<td>721</td>
<td>718</td>
<td>721</td>
<td>740</td>
<td>740</td>
</tr>
<tr>
<td>Initial NO\textsubscript{x} concentration (ppm)</td>
<td>125</td>
<td>160</td>
<td>65</td>
<td>69</td>
<td>67</td>
<td>137</td>
<td>90</td>
</tr>
<tr>
<td>Final NO\textsubscript{x} concentration (ppm)</td>
<td>30</td>
<td>63</td>
<td>47</td>
<td>45</td>
<td>44</td>
<td>57</td>
<td>45</td>
</tr>
<tr>
<td>NO\textsubscript{x} reduction</td>
<td>76 %</td>
<td>61 %</td>
<td>28 %</td>
<td>35 %</td>
<td>34 %</td>
<td>58 %</td>
<td>50 %</td>
</tr>
<tr>
<td>Additive concentration (^{(2)}) (%)</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{(1)}\) These types correspond to two different technologies based on different chemical actions for affecting NO\textsubscript{x} reduction. They are developed by the same supplier and can be selected after a minimum 8-day real-run trial.

\(^{(2)}\) Expressed in % of the total catalyst addition.

Figure 4.9 gives more details on the NO\textsubscript{x} reduction that was obtained for a high capacity (110,000 barrels/day – 6 Mt/yr) full-burn FCC unit operated in the US, with a NO\textsubscript{x} reducing additive incorporated intermittently during two years of trials, at concentrations never exceeding 1 % of the catalyst inventory. In this specific case, it was observed that when such additive was used in conjunction with a conventional Pt-based CO promoter, the NO\textsubscript{x} reduction was even greater than when used alone [27, Vierheilig et al. 2003].

![Figure 4.9: Full-burn FCC NO\textsubscript{x} emissions as a function of excess O\textsubscript{2} in various catalyst additive configurations](image-url)
When used in combination with a low-NO_x CO promoter as shown in Figure 4.10, a further reduction of up to 40% can be obtained on the residual NO_x level, depending on the mutual additive rates chosen for the given unit. However, the adjustment of such a catalyst mixture CO promoter/additive for a given installation must be carefully evaluated and tested on a case-by-case basis.

**Cross-media effects**
Copper-based NO_x-reducing additives can also promote the production of hydrogen and create difficulties for FCC units operated at their gas compression capacity limits.

**Operational data**
Figure 4.10 gives an overview of the results obtained on a large 4.5 million t/yr FCC unit, operated on a full combustion mode, after pretreatment with a low-NO_x non-Pt CO promoter. As shown, the NO_x-reducing additive is incorporated both by using one-shot monthly doses together with continuous addition at an increasing rate into the fresh catalyst renewal stream. After a three-month trial, NO_x emissions tended to stabilise at around 40% below the original average.

The use of a non Pt low-NO_x-Co promotor was experimented at a refinery in Portugal, at the beginning of 2010. At the end of the test period, it is reported that the replacement of the previous combustion promoter leads to a 80% reduction of NO_x emissions in the flue-gas with 80 ppm NO_x concentration. In addition, the emissions are reported to be stable, and no longer depend on the nitrogen level in FCC feed [89, Galp 2011].

**Applicability**
This technique was efficient only in full combustion mode.
The performances of such additives are naturally sensitive to the available concentration of CO as one of the reactants. Thus, low excess oxygen conditions favour their efficiency.

Even if good results are obtained with a combination of Pt-based conventional promoters, the logical way is to first reduce the generation of NO_x at source as much as possible by using low-NO_x CO promoters, and then using the additives as complementary.
By 2008, there were four commercially available NO\textsubscript{x} reduction additives, among which three were copper-based.

**Economics**
See Table 4.20 in Section 4.5.8.3. The option of using such additives in combination with a low-NO\textsubscript{x} non-Pt CO promoter compared with using them alone is very often the most economically-sound solution, as NO\textsubscript{x}-reducing additives are added at rates of 0.5 – 2 % of fresh catalyst renewal, while CO promoters are added at much lower rates of 5 – 10 kg/day.

**Driving force for implementation**
To achieve a further reduction of NO\textsubscript{x} emissions with little or no additional capital costs.

**Example plants**
According to equipment suppliers, this technique is said to be currently used by around 20 refineries in the US. In Europe, this technique is also used, e.g. at one refinery in Portugal.

**Reference literature**
[27, Vierheilig et al. 2003] [24, Bruhin et al. 2003] [26, Kramer et al. 2009] [30, Sawyer et al. 2009] [36, CONCAWE n°4/09 2009]

### 4.5.8.5 Low-temperature oxidation (SNERT process/LoTO\textsubscript{x} technology)

**Description**
See Section 4.25.3.1.

**Achieved environmental benefits**
The reduction of NO\textsubscript{x} emission from an FCC unit by 85 – 95 %, with an outlet concentration reduced to 10 ppm (14 mg/Nm\textsuperscript{3} NO\textsubscript{x} under EU reference conditions (0 °C -3 %O\textsubscript{2}) 95 % NO-5 %NO\textsubscript{2}).

**Cross-media effects**
The SNERT/LoTO\textsubscript{x} process operates optimally above 150°C and does not require heat input to maintain operational efficiency, enabling maximum heat recovery from the flue-gas.

Nevertheless, SNERT/LoTO\textsubscript{x} is associated with a new or existing scrubbing unit, which generates waste-water to be treated properly. An increase in nitrate load to the existing WWTP may have to be considered.

Nitric acid is produced and needs to be neutralised with an alkali used in the scrubbing section. In order to oxidise the NO\textsubscript{x} to soluble higher oxides, ozone is required and should be generated on-site using an ozone generator, which consumes oxygen and electrical energy.

**Operational data**
NO\textsubscript{x}-removal performance is directly linked to the ozone injection rate and its real-time regulation in relation to the NO\textsubscript{x} outlet concentration target. The outlet NO\textsubscript{x} can be adjusted by varying the set point on the system controller. In Figure 4.11, the set point was set in order to respect the permit conditions of 20 ppm (27 mg/Nm\textsuperscript{3} NO\textsubscript{x}).
Applicability
The first demonstration tests on the FCC unit were conducted in 2002. Between 2007 and 2009, low temperature oxidation units have been implemented in seven FCC units, among which six are operated in the US and one in Brasil. Four of them have been retrofitted on existing scrubbers, one of them was not originally installed by the LoTOx patenting equipment supplier. In the case of retrofitting, a separate tower may have to be built in order to provide the required additional ozone injection and reaction stage. Ozone slip out of the stack will be associated with this technology. Appropriate design for additional processes related to ozone generation and personnel safety have to be taken into account.

Economics
In 2005, potential investment and operational costs for implementing this technology on two FCC units in Colorado refineries (US) were estimated as a range of USD 1900 – 2100 per year and tonne of NOx avoided, assuming a related NOx emission decrease of 85 – 90 %.

Driving force for implementation
The main advantages of the LoTOx process: NOx selectivity, adjustability of NOx-removal performances, absence of interference with the FCC unit chemical process and operating conditions (including O2 concentration in the flue-gas), compatibility with flue-gas energy recovery, and relative ability to handle unit upsets without impacting overall reliability and mechanical availability.

Example plants
US Refineries: BP (Texas City), Flint Hills (Corpus Christi), Lion Oil (El Dorado), Marathon (Texas City), Valero (Houston and Texas City), Western Gaint (Gallup).

Reference literature
[ 17, Jeavons and Francis 2008 ] [ 18, Confuorto 2007 ].

Figure 4.11: Initial results of commercial operation at a Texas refinery FCC unit - 2007
4.5.9 Particulate abatement techniques

The selection of the catalyst can be seen as a particulate abatement technique has an impact on particulate emissions but will not be considered in the present section. That technique has been included in Section 4.5.6 together with other possible effects of catalyst replacement.

4.5.9.1 Additional Third-stage cyclone separators

Description
Highly specialised cyclones are used (third-stage and multicyclones), which are designed to suit the arrangement, dimensions, contours, velocities, pressures and densities of the particles to be removed. This is the natural first choice of clean-up device for particulates.

Third-stage separators (TSS) is a cyclonic collection device or system installed following the two stages of cyclones within FCC unit. The most common configuration of a TSS consists of a single vessel containing many conventional cyclones or new, improved swirl-tube technology (e.g. Shell Global Solutions, or CycloFines™). It corresponds to a common choice of clean-up devices for particulates and as an aid to energy efficiency. The first attempts at power recovery from FCC unit regenerator flue-gas were unsuccessful because the expander blade lifetimes were limited to a few weeks. It was found that particles sizes of 10 micron and larger were particularly harmful to the blades. TSS were introduced to protect power recovery expander turbines from particulate damage. A TSS is a set of these are conventional cyclones, fitted externally to the regenerator but operating on the same principle as the internal first and second cyclones. Recent advances in this technology, as shown in Figure 4.12, favour in particular, the use of a large number of axial flow swirl tubes of relatively small diameter in order to induce a fast rotating motion and handle the large volume of flue-gas in more compact vessels. They are high-velocity devices and the recovered catalyst is returned to a dust hopper. In some cases a new stage of filtration is used and named 4th stage.

Figure 4.12: Scheme of a TSS using multiple-axial swirl-tube technology

Achieved environmental benefits
An The average performance figure outlet concentration for an advanced TSS cyclone separation alone is in the region of 100—400 is <50 – 100 mg/Nm³ (Inlet concentration from...
400–1000 mg/Nm³), depending on inlet particulate concentration and size distribution. Lower concentrations are not achievable because inlet velocities to the cyclones are in the region that causes additional attrition, which produces additional fines that pass through the cyclone.

Depending on the above factors and the type of technology, cyclones are generally efficient at removing particles in the range of larger than 10 to 40 microns and above. Recent swirl-tube devices allow a 50% cut point of about 2.5 microns. Efficiencies can range from 30 to >90%. For inlet concentrations below 400 mg/Nm³, the efficiency can only exceed 75% for a particulate size distribution with a median (by mass) of >5 microns.

By reducing the particulate content in the air, the metal emissions are also reduced. The fine catalyst disposal is typically 300–400 tonnes/yr per unit. Cyclones are more effective for coarser particles and they have been designed essentially to prevent any particles greater than 10 microns from entering downstream facilities.

**Cross-media effects**
Catalyst fines recovered containing some hazardous metals are considered as hazardous industrial waste (300–400 tonnes/yr per unit). Consequently pollution is transferred which have to be properly handled and eliminated in order to avoid any pollution transfer from air to the water and soil.

**Operational data**
The fine catalyst disposal removal is typically 300–400 tonnes/yr per unit. A TSS generates a pressure drop in the flue-gas. Good performance and reliability in many FCCs have been demonstrated.

**Applicability**
TSSs are applicable to any FCC, but their performance will vary considerably, mainly depending on the particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones.

**Economics**

<table>
<thead>
<tr>
<th>Size of the FCC (Mt/yr)</th>
<th>Efficiency (%)</th>
<th>Downstream particulate concentration (mg/Nm³)</th>
<th>Investment (EUR million)</th>
<th>Operating cost (EUR million/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>30 – 40</td>
<td>40 – 250</td>
<td>1 – 2.5</td>
<td>0.7</td>
</tr>
<tr>
<td>1.5</td>
<td>30 – 90</td>
<td>60 – 150 (¹)</td>
<td>0.5 – 1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>1.2</td>
<td>75</td>
<td>50 – 100(²)</td>
<td>1.5 – 2.5</td>
<td></td>
</tr>
</tbody>
</table>

(¹) Initial concentration: 450 mg/Nm³ (300 – 600 mg/Nm³ range)
(²) Initial concentration: 200 – 1000 mg/Nm³
NB: Operating costs include only direct cash operating expenses i.e. They do not include the depreciation of investment, nor financial charges. Investment costs refer to new plant installation. Economics do not include the cost of disposal of the waste generated.

The cost of disposal of the fine catalyst is around EUR 120–300 per tonne, including transportation.

**Driving force for implementation**
TSSs control particulate emissions and are also used to protect downstream equipment such as heat or power recovery units (e.g. expander blades).

**Example plants**
Many FCC units are operating with these systems.
**Reference literature**

### 4.5.9.2 Electrostatic precipitators

**Description**
A short description of an electrostatic precipitator can be found in Section 4.25.4.

**Achieved environmental benefits**
Typical particulate emission levels are usually <20 – 30 mg/Nm³ are usually obtained as a daily average and this level is based on averaged continuous monitoring under normal operating conditions (and e.g. excluding soot blowing in the CO or auxiliary boilers, and end of run conditions).

When available for shorter averaging periods, values of total particulate matter in the flue-gas of the FCC regenerator <50 mg/Nm³ (expressed as an hourly average) are reported or included in permit (e.g. in Germany see infra operational data). As a consequence of the particulate reduction, metals (Ni, Sb, V and their components) can be reduced to less than 1 mg/Nm³ (given as Ni, Sb and V total) and, within that, Ni by itself and its components can be reduced to less than 0.3 mg/Nm³ (given as Ni), all concentrations being expressed as (half-hourly mean values attainable in continuous operation and with soot blowing in the CO boiler).

Particulate emissions from the FCC can thus be reduced to 1.1 – 2.3 kg/h.

Note for TWG:
1/Rest of existing text transferred to operational data
2/Existing reported data (from Questionnaires) are always expressed as averages, but corresponding sampling periods are almost never available! It seems that 50 mg is a high value which should correspond to a much shorter period than the monthly average proposed by CONCAWE
3/Could we agree on CONCAWE proposal to delete the hourly emission mass flow in kg/h (as highlighted in green at the end of this paragraph) which seems more appropriate for local permitting, but only if the PM concentration range quoted above in this paragraph (also highlighted in green) is still expressed as an hourly average? YES.

**Cross-media effects**
Because these systems recover the fine particulates (mainly catalyst) coming from the FCC, the refinery may need extra facilities to manage the fine particulates (catalyst) recovered ESPs also consume electricity that requires disposal. The high voltage in an ESP introduces a new safety risk in refineries and leads to increase operating costs for electricity and maintenance. For some installations, ammonia may be injected to improve ESP performance (as a resistivity attenuation agent). For these installations, ammonia emissions result from ammonia slip through the ESP can be relatively high compared to other filters. Safety concerns are also expressed about the use of ESPs during the FCC start-up process: although very few significant incident seems to have been reported so far, and none in the oil industry sector. Special care must be taken to ensure that uncombusted hydrocarbons are never allowed to enter the ESP itself, as the sparkling environment may result in an explosion [31, BARPI 2009] [36, CONCAWE n°4/09 2009].

**Operational data**
Particulate abatement measure efficiency with ESP in FCC with electrostatic precipitators with efficiency is usually much greater than 99.8 – 90 %. The actual concentration range achieved at the ESP outlet will depend on the residence time (i.e. the ESP size), the type of the properties of the particulate (i.e. catalysts), the mode of FCC operations the flue-gas temperature, and whether other pretreatment techniques are implemented before the use/particulate removal devices are installed upstream of the ESP. In usual conditions, a residence time greater than 30 seconds would be necessary to achieve very low concentrations (<10 mg/Nm³). Efficiency is not...
dependent on particulate size or of flue gas velocity, and the pressure drop is very marginal. Particle size can also affect ESP efficiency, since very fine particulate (<2 \(\mu\)m) is more readily re-entrained during the cleaning cycle (rapping) of the ESP electrodes.

Electrostatic precipitators cause a very slight pressure drop, add a small pressure drop to the system; higher pressure drops may result from the inlet and outlet ducting to the ESP. In some cases a forced draft or induced draft fan may need to be added. The extra energy consumption (electricity) is typically low, but can be significant for ESPs with large residence times. ESPs also require regular maintenance to ensure high capture efficiency. The extra energy consumption is relatively low, but they consume electricity. They also require high maintenance to keep the capture efficiency high. Continuous monitoring of particulates is not amongst the most reliable continuous monitoring systems. Information from some EU refineries shows that the use of deep desulphurisation of the feedstock can have a great impact on ESP performance (because the content of sulphur and metals is lower) reducing the availability of the ESP efficiency to catch these particulates. In these cases, they have reported that the best values achievable are achievable particulate emissions have been reported to be 30 – 35 mg/Nm\(^3\).

Figure 4.13 and Figure 4.14 show a one year evolution of the daily average concentration achieved by two ESPs operated in two German FCC units. These figures deserve the following comments:

- Results for the first FCC displayed in Figure 4.13 are obtained under normal conditions, using a filtering configuration consisting of a conventional set of internal cyclones, an additional external cyclone and a 4-field ESP. The yearly average concentration is 10.94 mg/Nm\(^3\) with a standard deviation of 9.62, and the maximum recorded daily average is nearly 37 mg/Nm\(^3\). The typical daily average concentration is rather variable, mostly within the range 5 – 25 mg/Nm\(^3\).
- In comparison, the results obtained for the second FCC as shown in (Figure 4.14) illustrate performances achieved with a much simpler filtering configuration, with only a set of internal cyclone and a 2-field ESP. Moreover, this 1-year period includes a shutdown/start-up step (well identified on the graph) during which emissions have been significantly higher than the performance obtained for stable conditions. The yearly average is 10.16 mg/Nm\(^3\) (calculated from daily values different from zero) with a standard deviation of only 5.2. Even though the maximum recorded daily average value of 38 mg/Nm\(^3\) is comparable to the first ESP (Figure 4.13), the typical daily average concentration during stable operating conditions is much more uniform, constant, staying mostly within the range 5 – 15 mg/Nm\(^3\).

A degradation of ESP performances after an FCC turn around usually affects the following weeks after the restart up, and are probably linked to the progressive attrition of the new catalyst and the lower metallic content of particulates. Particulate emissions can increase after an FCC turnaround due to higher solids loading to the ESP. This can be attributed to higher attrition of new catalyst that may be loaded after a turnaround.

The following data for a German FCC plant are reported, after ESP (no cyclone) in waste gas of the CO boiler (normal operation):

- emission limits values in the permit:
  - total particulate matter, daily average value: 30 mg/m\(^3\);
  - 30 minutes average value: 60 mg/m\(^3\);

- monitoring data:
  - Total PM: 13 - 23 mg/m\(^3\) (30 minutes, \(O_2= 3.1\%\), 100 % capacity utilisation, feed 80 % atmospheric residues, 20 % heavy wax distillates)
Another similar FCC with cyclone and ESP abatement techniques is reported to achieve PM 9 - 21 mg/m³ (100 % capacity with feed: 50 % vacuum gas oil, 40 % atmospheric residue, 10 % others). Source: TWG 2010-DE

**Figure 4.13:** Daily average PM concentrations achieved by an ESP on a German FCC unit

**Figure 4.14:** Daily average PM concentrations achieved by an ESP on a German FCC unit

**Applicability**

ESPs require high free significant plot space and volume, especially when they are sized to achieve very low PM particulate emissions levels. In the specific case ofBecause the Large plot space is required because FCC outflows to be treated are typically large (a 1.5Mt/yr FCC generates 2.8 million Nm³/day of flue-gas), and ESP requires low internal velocity and therefore
large volumes at typical design residence times to achieve the required performance levels. In order to not exceed the gasflow speed specifications, should be low to increase the capture of particulates, then these systems require a lot of space. ESP performance may be adversely affected if the particulate has a high electrical resistivity, notably in the case of deep hydrotreatment of the FCC feedstock inducing a will lower catalyst metallic content, reduce conditioning agents (SO3) in the flue-gas and therefore reduce collection efficiency. Also worth mentioning is that the performance of ESPs is likely to degrade from the start to the end of the FCC run, notably due to the evolution of catalyst properties (electrical resistivity, granulometry). It may be due to either ESP maintenance issues, which require a shutdown, and/or potential for increased attrition/loss of catalyst particles at end of run. Finally, ESPs cannot reasonably cover start-up and shut down periods and will have to be electrically isolated due to safety reasons already described.

Economics
Available data has been gathered in Table 4.23.

Table 4.23: Economic data of ESPs applied to FCCs – Updating ?

<table>
<thead>
<tr>
<th>Size of the FCC (Mt/yr)</th>
<th>Efficiency (%)</th>
<th>Downstream PM concentration (mg/Nm³)</th>
<th>Investment (EUR million)</th>
<th>Operating cost (EUR million/yr)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>90</td>
<td>30</td>
<td>4 – 6</td>
<td>0.25 – 0.5</td>
</tr>
<tr>
<td>1.5</td>
<td>85 – 95</td>
<td>&lt;50</td>
<td>3 – 5</td>
<td>0.25 – 0.5</td>
</tr>
<tr>
<td>1</td>
<td>95</td>
<td>10 – 20(1)</td>
<td>5.5 Small Negligible(2)</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>90 – 95</td>
<td>&lt;50(1)</td>
<td>4 – 6</td>
<td>0.25 – 0.5</td>
</tr>
<tr>
<td>2.4</td>
<td>&gt;50(3)</td>
<td>&lt;50(3)</td>
<td>15 – 30</td>
<td>0.15 (4)</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>&lt;30</td>
<td>2.05(6)</td>
<td></td>
</tr>
</tbody>
</table>

(*) Operating costs include only direct cash operating expenses i.e. They do not include the depreciation of the investment, nor financial charges. Investment costs refer to new plant installations.
(1) Initial concentration: 250 – 300 mg/Nm³.
(2) Initial concentration: 4 000 mg/Nm³
(3) Disposal of fines not included
(4) Unabated concentration>100 mg/Nm³ –> Abatement target <50 mg/Nm³
(5) 2009 USD respectively 20 – 40 million (installed capital cost) and 0.2 million [ 30, Sawyer et al. 2009 ]
(6) 2008 HUF 1.3 billion for the whole ESP project

Driving force for implementation
Reduction of particulate emissions.

Example plants
17 of 22 FCC European refineries within the 61 sites of the TWG sample use ESPs in their FCC unit. They are also used in many refineries in the USA and Japan. As an example, in particular, TOTAL in Spergau and MIRO in Karlsruhe (Germany) have ESPs operated on FCC units receiving deeply-hydrotreated feedstocks.

Reference literature
4.5.9.3 Other filters

Description
A further option for regenerator exhaust gases are filters (bag or fabric filters, and ceramic or stainless steel filters (See additional information in Section 4.25.4.3).

Reverse flow (blowback) ceramic or sintered metal filters are devices where after retaining the solids elements at the surface as a cake, it is dislodged by initiating a reverse flow. The dislodged solids are then purged from the filter system.

Achieved environmental benefits
Reverse flow (blowback) and fabric filters are both able to achieve higher performance figures (<1 – 10 mg/Nm³) than cyclones and electrostatic precipitators. Furthermore, in the case of ceramic filters, they prove to be particularly efficient for retaining the finest particulates, and to cope with start-up or upset conditions.

Cross-media effects
None identified so far, except for the need for elimination or valorisation of the collected dust which is an issue for all dry filters.

Operational data
Bag or fabric filters are temperature sensitive (<200 – 240 °C) and hence their use is limited. They can also cause a high significant pressure drop which has to be taken into account in order to fit the overall process.

On the other hand, reverse flow (blowback) ceramic filters are more sophisticated systems which have proven to be appropriate for this application. One of them, installed since mid-2004 as a full 3rd stage filter on a 2100 t/day RCC unit, has operated without incident since its start-up. Blowback sequences are triggered in function of the progressive build-up of the pressure drop generated by the filter, which is an important parameter to monitor. The filter system achieved a steady-state recovery pressure differential after approximately 100 blowback cycles (i.e. nearly one month) and the operating pressure drop due to the filter has been low enough to avoid any adverse impacts on the RCC operation. The related environmental performance is much better than any other filtration processes applied to FCC. As shown on Figure 4.15, the PM concentration measured by opacity analysis has always been below 5 mg/Nm³ since the filter commissioning, and the typical filter performance is 1 – 2 mg/Nm³.

![Figure 4.15: Performance of a FCC sinter alloy 3rd stage blowback filter](image_url)
However, besides the filter pressure drop, other variables have to be monitored in order to ensure a stable filter functioning, such as valve operating and closing times, flue-gas temperatures, blowback accumulation pressure and blowback gas temperature.

**Applicability**

Bag or fabric filters can be retrofitted to the underflow of three-stage cyclones. However, bag filters are not favoured for use in the FCC because of the pressure drop, the potential for ‘blinding’ of the bags, the large space required and their inability to cope with upset conditions. On the other hand, 3rd-stage ceramic filters have proved to be applicable to catalytic cracking flue-gas cleaning since 2004. They are even successful in their ability to cope with various FCC upset conditions. Two specific cases have been reported in the available literature so far. The first one is the handling of upstream concentrations up to 20 000 mg/Nm$^3$ during a two week catalyst attrition problem, with a solid load increase from 250 to 1000 – 2000 kg/day, allowing the RCC unit to keep complying with applicable emission standards and avoid shutdown. The second one is a safe operation of such a filter during a torch oil firing in the regenerator in order to maintain its temperature during emptying and urgent repairing. Therefore, it is possible to benefit from the ceramic filter system also during start-up and shutdown, which corresponds to a major improvement compared with ESPs. Scale up to full regenerator flow from more commonly sized European FCC units needs to be clearly demonstrated.

**Economics**

The specific investment cost for blowback ceramic filters will depend on the temperature and the stream capacity. The cost for a 3rd stage (full stream) filter is estimated at USD 80/m$^3$/h for temperatures below 450 °C, and USD 210/m$^3$/h for higher temperatures up to 750 °C. For smaller hot filters concerned in four stage application, this cost is about USD 260/m$^3$/h (all costs expressed for year 2009 and for actual flue-gas volumes). For a generic 2.4 Mt/yr FCC unit, the installed capital cost in 2009 was estimated to be 15 million-20 million (USD 22 million-30 million).

**Driving force for implementation**

**Reduction of particulate emissions**

Recent reverse flow (blowback) ceramic filters are of the highest interest for FCC applications, where PM emission magnitude, considered together with their associated granulometry and chemical content, are likely to raise health and environmental issues. This technique allows a high-performance filtration of catalyst PM emissions, including finest particulates and heavy metals. It is very low-sensitive to start-up and upsets and prevents related adverse effects on dust loads, particle size, or flow rates. Its compactness is also favourable for retrofitting situations.

**Example plants**

At least one successful application in European FCC.

Full-stream 3rd stage ceramic filters are operated in three refineries: the BP refinery in Kwinana (Australia, 2004), the ORL refinery in Haifa (Israel, 2009), and another in the Big West refinery in Bakersfield, California (US) to be commissioned. Around 15 partial-stream (4th-stage) ceramic separators and hopper filters are also operated in Western Europe, North America and the Middle East.

**Reference literature**

[80, March Consulting Group, 1991] [22, Glenny et al. 2008] [30, Sawyer et al. 2009].

Text moved to waste management 4.27.3.1

4.5.9.4 Control and reuse of the catalyst fines

4.5.9.5 Removal of catalyst from slurry decant oil
4.5.10 Sulphur oxides abatement techniques

This section contains sulphur oxides abatement techniques that may be applicable to FCC units.

4.5.10.1 SO\textsubscript{x}-reducing catalyst additives

Description
Sulphur dioxide in the regenerator off-gas of an FCC unit can be reduced by using a metallic oxide catalyst (metal (e.g. Al/Mg, Ce) oxide) which transfers a significant portion of the sulphur associated with the coke on the catalyst back to the reactor, where it is liberated as hydrogen sulphide. This leaves the reactor with the cracked vapour product for capture in the amine scrubbing system of the refinery and hence conversion of sulphur in the SRU.

DeSO\textsubscript{x} reduction is a three-step process:

1. catalytic oxidation of SO\textsubscript{2} to SO\textsubscript{3} catalysed by cerium in the regenerator;
2. adsorption on the additive of SO\textsubscript{3} produced in the regenerator to give a sulphate which, on return to the reactor;
3. reverts to the oxide and releases hydrogen sulphide into the product gas stream for recovery.

Developed in the late 1970s, SO\textsubscript{x}-reducing catalysts were initially alumina-based and very much subject to deactivation. Progressively, the potential for SO\textsubscript{3} picking-up in the regenerator was substantially increased by replacing pure alumina-based binders with magnesium-aluminate binders (1980s: 1 Al mole for 2 Mg mole) and later with hydrotalcite binders (1990s: 1 Al mole for 3 – 4 Mg mole). State-of-the-art catalysts developed since 2000 show performances improved by 35 – 80 % compared with the first hydrotalcite binder compounds. Pick-up factors (PUF – kg SO\textsubscript{2} removed per kg additive introduced) up to 20 can now be theoretically reached.

Achieved environmental benefits
The amount of SO\textsubscript{x} removed is strongly dependent on the SO\textsubscript{x} raw concentration in the regenerator, the amount of deSO\textsubscript{x}-reducing additive added to the unit, and on the type and efficiency of the SO\textsubscript{x}-reducing additive itself. Some available test data also show that the removal performance is highly influenced by the current oxygen concentration and by the additive’s own resistance to attrition in the operating conditions prevailing in the particular plant concerned. But removal efficiency is typically 20 – 60 % in the full combustion mode. This technique can remove up to 30 % of SO\textsubscript{x} when used in the partial combustion mode.

In the full combustion mode, removal efficiencies obtained with state-of-the-art additives are typically >60 % 50–90 %. Even higher removal rates (of up to 95 – 99 %) have been reported in commercial operation. Best performances are associated to most favourable operating conditions, in particular lowest raw sulphur concentrations in the regenerator and optimisation of regenerator and other process variables.

In the partial combustion mode, the typical reduction might be lower than in full combustion mode, and in most cases, more additive is required. Specific partial-burn additives have been recently developed, and have shown to be twice as active as the older additives. State-of-the-art additives are now typically able to remove between >50 % 50–70 % of emitted SO\textsubscript{x}, and even higher reductions (up to 90 – 95 %) have been reported in commercial operation. Here again, best performances are associated with most favourable operating conditions, as above, in particular lowest raw sulphur concentrations, lowest proportions of pre-existing reduced species (COS, H\textsubscript{2}S) in the regenerator before the CO boiler, and longest regenerator residence times as shown graphically in Figure 4.16.
However, the higher the removal rate, the lower the pick-up factor observed.

- In one example, the literature [25, Pham et al. 2009] reports a case where a 85% reduction in \(\text{SO}_x\), resulting in a 50 ppmv residual emission (0 %O\(_2\)) could be achieved with a PUF of 18 kg \(\text{SO}_x\) removed per kg of additive incorporated. A further reduction of emissions to below 25 ppmv (0 % O\(_2\)) decreased the PUF to 14 kg \(\text{SO}_x\) removed per kg of additive. The concentration required to reduce emissions below 25 ppmv was on the order of 5 % by weight of the total catalyst inventory. The relative cost increase from 50 to 25 ppmv was 31 %.

- A second example of it is described in detail as the case study n°1 for a short trial performed on a ‘deep’ partial-burn FCC with 7 – 8 mol % CO in the regenerator [57, Roberts et al. 2009]. It shows a relatively acceptable efficiency for achieving up to 30 – 35 % \(\text{SO}_x\) removal with a PUF >10. However, it confirms that an attempt to reach 50 % \(\text{SO}_x\) removal in such defavourable conditions was technically and economically almost impossible, as the PUF fell below five and the additional energy consumption at constant steam production was increasing by >8 %, leading to specific costs above kEUR 10/ton \(\text{SO}_2\) saved.

![Graphical representation of the influence of \(\text{SO}_x\)-reducing additives in a partial-burn FCC unit for a given initial concentration profile](source)

**Cross-media effects**

Disadvantages of this technique include the following:

- \(\text{SO}_x\)-reducing additive is not really a polyvalent technique implementable to all units as, despite recent progress made, it remains actually more efficient and economically more attractive in fullburn mode. However, full-burn implies more \(\text{SO}_x\) and \(\text{NO}_x\) formation than partial combustion mode

- There is a possibility of poorer yield of products from FCC units and reduced FCC unit operating flexibility, especially when additives are applied at very high rates (>10 – 15 % of fresh catalyst addition).
SO\textsubscript{x}-reducing additives might have a detrimental effect on PM by increasing catalyst losses due to attrition, and on NO\textsubscript{x} generation by participating in the CO promotion activity. When used in partial-burn mode, this can lead to significant increases in the supporting fuel consumption in the CO boiler for an equivalent steam production.

Other impacts are increased energy consumption, additional waste generation, and the possibility of bottlenecks in the H\textsubscript{2}S amine treating handling facilities.

**Operational data**

For an initial concentration of up to 4000 – 4500 mg/Nm\textsuperscript{3} (corresponding to a feedstock sulphur content of around 2 – 2.5 %), typical downstream effluent of an FCC unit using this technique has a SO\textsubscript{2} concentration of 1000 – 3000 mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2}, depending on the additive usage rate and the unit combustion mode.

Figure 4.17 and Figure 4.18 below relate to a full-burn combustion FCC unit, operated under rather unfavourable conditions due to a very low inventory replacement rate (daily additions of only 0.5 % of the unit inventory), together with respective average rises and regenerator temperatures of 508 °C and 673 °C. The two given sets of data illustrate the results achieved in the case of a high average sulphur content (1.6 %) and a low one (0.5 %), for which the removal yield is higher.

![Figure 4.17: SO\textsubscript{x} reducing additive performance with a 1.6 % sulphur FCC unit feedstock](image-url)
These results are consistent with those reported by an European site, as illustrated on Figure 4.19, where a 50% abatement (average concentration from 980 to 450 mg/Nm$^3$ at 3% O$_2$) has been currently achieved since 2009 on a 1.5 Mt/yr FCC with a 0.32 – 0.45 % S feedstock [Questionnaire n°15].

For an additive content of only 3% in the catalyst inventory, a 25% reduction of SO$_2$ emissions is reported even with a typical feed sulphur content of 0.6 – 1.8% [Questionnaire n°50]. The SO$_x$ removal ability of state-of-the-art SO$_x$ reducing additives is determined by the amount in the catalyst inventory rather by the daily addition rate, showing an increased stability.

Figure 4.19: SO$_2$ emissions decrease from a French FCC unit using SO$_x$ reducing additives
Applicability

The outlet SO\textsubscript{x} concentration achievable with this technique is highly dependant on the SO\textsubscript{x} inlet concentration, the amount of additive that can be used, and the unit operation mode.

This technique is sensitive to unit design, especially regenerator conditions. It operates most effectively under full-oxidising burn combustion conditions, where virtually all as much as 50\% of the sulphur in the flue-gases can be removed when the technique can be retrofitted in the most favourable conditions.

FCC unit performance may, however, be affected and the transfer catalyst replacement rate may be significant. A fine retuning of the catalyst system might be required in the case of large quantities of additives being incorporated.

Thanks to its high adjustability, this technique can also be combined together with other process-related or end-of-pipe abatement techniques.

- In association with wet scrubbing, as has been the case since 2006 for a BP refinery in Texas City, where additives help to reduce the operating chemical consumption (e.g. caustic) and energy (e.g. pumping). Another example of this is reported for a Middle East refinery which processes 30 000 barrels per day (around 2 million t/yr) of a 100\% atmospheric residue feedstock with a high-sulphur content of 2.7\% operated in full burn, where it has been decided to use such an additive in order to master corrosion problems due to high inlet SO\textsubscript{x} concentrations in an existing scrubber. In this refinery a 15\% reduction of the scrubber operating cost has been observed, exceeding the cost for the SO\textsubscript{x} reducing additive, which was fully covered [26, Kramer et al. 2009].

- In association with high efficiency filters, the two techniques could also possibly lead to very cost effective conditions [30, Sawyer et al. 2009].

- In order to increase flexibility in the choice of the feed quality (e.g. external inputs), or for decreasing the severity of the upstream feed hydrotreatment.

On the other hand, this technique proves to be less efficient for FCC units operated in deep partial burn combustion modes, at high regenerator temperatures, with low daily replacement rates, or for which very low SO\textsubscript{x} outlet concentrations are required. In North America, SO\textsubscript{x}- reducing catalysts are being used preferably for with wet scrubbing for FCC units in refineries with capacities lower than 150 000 barrels/day (8 Mt/year).

Economics

There are no major investment cost required: for this option save for only minor capital expenses are need for the dosing equipment for introducing the additive to the catalyst system. As an example, the cost reported for a European site is EUR 300 000 including foundation, construction, piping, downstream capacity improvement, and the permit. Operating expenses are around 0.34 – 0.7 EUR/t (EUR 1 million/yr for a 1.5 Mt/yr FCC). Another reference gives a typical cost of EUR 3 million/yr (1997) for the catalyst for a gas flow of 200000 Nm\textsuperscript{3}/h (2.3 Mt/yr FCC). Cost is highly.

Operating expenses are dependent on the unit, the initial SO\textsubscript{2} emissions and the SO\textsubscript{2} target. The cost reported by a European site, for a 264 kg/day injection rate and a 94 t/yr additional waste elimination of spent catalyst is EUR 1.3 million/yr.

Potential investment and operational costs for implementing this technology on two FCC units in the Colorado refineries (US) were estimated in 2005. Data extrapolated to 2007 give USD 500 per tonne year of SO\textsubscript{2} saved, assuming a resulting SO\textsubscript{2} emission decrease of only 35 – 50\%. [17, Jeavons and Francis 2008]. This data is rather consistent with costs reported more recently by other US sources, also for 2007, according to which the cost for obtaining 25 ppmv at 0 \% O\textsubscript{2} (yearly average) and 50 ppmv at 0 \% O\textsubscript{2} (7-day rolling average) is in the range of USD 500 – 880 per tonne of SO\textsubscript{2} removed.
Another cost estimation is given in Figure 4.20, based on a major catalyst manufacturer’s field experience within US refineries. The graph is provided for a reference unit of 50 000 barrels/day (around 3 million t/yr) capacity, with a 150 tonne catalyst inventory. The range reflects a wide variety of FCC unit configurations, with different untreated off-gas SO\(_x\) levels, feed types and regenerator operational conditions (including full and partial burn).

Figure 4.20: FCC SO\(_x\) reduction additives specific cost versus SO\(_x\) overall reduction target

A similar approach has been followed which proposes a summary cost estimation for each full-burn and partial-burn combustion mode, as drawn from the European catalyst market.

Figure 4.21: Economics of SO\(_x\) reduction additives for FCC units-general cost overview

Finally, the available literature also reports the following removal costs reached during particular trials aiming at ultra-low SO\(_2\) emissions, as shown in Table 4.24 below [30, Sawyer et al. 2009].
Table 4.24: Performances and specific removal costs with SO_x reducing additives at a high injection rate

<table>
<thead>
<tr>
<th>Fresh feed rate (t/day)</th>
<th>Refinery A</th>
<th>Refinery B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh feed (API)</td>
<td>24.9</td>
<td>28.5</td>
</tr>
<tr>
<td>Uncontrolled SO2 (vppm)</td>
<td>178</td>
<td>326</td>
</tr>
<tr>
<td>Controlled SO2 (vppm)</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>SO2 reduction</td>
<td>95 %</td>
<td>98 %</td>
</tr>
<tr>
<td>Removal cost(\textdagger) (EUR/t SO2)</td>
<td>780</td>
<td>940</td>
</tr>
</tbody>
</table>

(\textdagger) Respectively USD 0.51 and 0.61 per lb of SO2 (2009 value)

Driving force for implementation
Reduction of sulphur oxide emissions from the FCC.

Example plant(s)
Many More than 60 refineries worldwide are applying deSO_x additives to the catalyst, including several partial combus- tion units in Germany, Japan, and Republic of South Africa. The method is well established commercially.

Reference literature

4.5.10.2 Wet scrubbing

Description
There are several wet scrubbing processes. A brief description of them is included in Section 4.25.5.4. The types of wet scrubbing that are typically used for FCC units are:

- caustic-based or lime sodium or magnesium-based non-regenerative wet scrubbing, using packed towers, plate towers, spray chambers, or Venturi systems;
- these combining conventional scrubbing techniques with the use of a regenerative process (e.g. the widely applied Wellmann-Lord process using sodium sulphate reagent, or the LABSORBTM produced by BELCO using a patented solution containing soda and phosphoric acid or CANSOLV process with an amine solution— see Section 4.25.5.2.3).

Two Venturi systems have been developed successfully by ExxonMobil specifically for FCC application:
- the Jet Ejector Venturi (JEV) scrubber, for lower pressure streams, where the absorbing liquid is sprayed into the flue-gas stream at the inlet of the venturi above the ‘throat’. Gas and liquid then pass through the throat under conditions of high turbulence;
- the High Energy Venturi (HEV) scrubber, for higher pressure streams, which use the kinetic energy of the flue-gas to break the absorption liquid into droplets. This technique requires a greater drop in gas pressure but it has higher removal efficiencies for small particulates compared to Jet Ejector Venturi Scrubbers, in particular for PM_{10} and PM_{2.5}, typically being able to decrease remove to PM_{2.5}.

Another successful system worth mentioning is the Electro-dynamic Venturi (EDV®) developed by BELCO, which combines the techniques used in Venturi scrubbers with electrostatic dust separation. The system houses a spray tower along with forced condensation and water spraying filtering modules and droplet separators. It can be associated, like in the ENI Sannazzaro refinery, with the LABSORBTM regenerative process (see Section 4.25.4.4), or also...
with the LOTOX™ de-NOₓ SNERT process using ozone injection (see Sections 4.5.8.5 and 4.25.3.1).

Achieved environmental benefits
Even if SO₂ removal is the first objective, a suitably designed wet scrubbing process will normally provide a very high effective removal efficiency of both SO₂/SO₃ and particulates, taking into account that SO₃ abatement is typically not as high as SO₂. With the inclusion of an extra treatment tower to oxidize the NO to NO₂, NOₓ can also be removed partially efficiently. Table 4.25 shows the achievable emission levels that can be expected with a wet scrubber.

Table 4.25: Generic achievable efficiency and emission levels for wet scrubbers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Efficiency (%)(1)</th>
<th>Inlet (mg/Nm³) at 3 % O₂</th>
<th>Outlet (mg/Nm³) at 3 % O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>95 – 99.9</td>
<td>600 – 10 000</td>
<td>&lt;10 – 60 – 400(2)</td>
</tr>
<tr>
<td>Particulates</td>
<td>85 – 95</td>
<td>350 – 800</td>
<td>&lt;10 – 30 – 60(2)</td>
</tr>
<tr>
<td>NOₓ</td>
<td>70</td>
<td>600</td>
<td>180</td>
</tr>
</tbody>
</table>

NB: Particulates removal is very much design related and system pressure drop is highly variable. Scrubbers are less effective on reducing submicron particles.

(1) Source: [45]
(2) Based on sample data of non-regenerative scrubbers as shown in Table 4.26.

In the case of regenerative scrubbing, the main additional benefit is obviously the possibility to regenerate the SOₓ absorbing reagent and to recover concentrated SO₂ streams which can be converted and sold/recycled as liquid SO₂, sulphuric acid or elemental sulphur. In correlation to this, a much lower amount of solid residue must be recovered and eliminated. Compared to a non-regenerative process, the energy consumption is also reported to be lower (see infra Operational data and Economics paragraphs) because technical steps for solid recovery from the exhaust solution no longer needed.

Cross-media effects:

- Non-regenerative wet scrubbing systems create secondary problems of aqueous slurry waste disposal and increase the refinery energy consumption. The effluent water purge contains sulphates (e.g. Na₂SO₄). Another drawback is the consumption of a significant quantity of expensive raw material (e.g. caustic soda) which is roughly proportional to inlet SO₂ loadings. They may need Flue-gas reheat may be needed to prevent plume mist. These systems are generally sensitive to other contaminants such as particulates, salts and sulphur trioxide.

- Other typical impacts of regenerative systems are the possible debottlenecking of H₂S-handling facilities (e.g. SRU, amine scrubbers), the production of other eventual by-products as well as the need for raw material supply and handling, however on a much lower scale than non-regenerative systems.

Wellman-Lord system: Increased energy consumption. By-product, raw material supply and handling possible bottlenecks of H₂S-handling facilities.

Operational data
Note for TWG: 1st paragraph has been transferred to Applicability section

Non-regenerative scrubbing
Table 4.26 provides data observed for seven FCC units operated in the US. All of them are Venturi-type [36, CONCAWE n°4/09 2009].
Regenerative scrubbing

A LABSORB™ regenerative scrubbing system has operated since 2004 at ENI refinery in Sannazzaro (Pavia, Italy). It treats all the flue-gas (0.18 million Nm³/h – 300 °C) from the 5500 t/day FCC unit at an inlet concentration of >1700 mg/Nm³ (3 % O₂). Outlet gas (208.000 Nm³/h – 67°C) is released at a concentration of 50 – 250 mg/Nm³ (3 % O₂) with a SO₂ removal efficiency >85 % as a daily average. An extra 250 kg/h concentrated SO₂ stream is sent to the SRU. Liquid waste production is 1t/hr and solid waste production is 19kg/h (compared to 9 t/h and 1000 kg/h in the case of NaOH conventional absorption for the same capacity).

Another regenerative scrubbing system has been in operation since 2006 at VALERO refinery in Delaware City (Delaware, US). It includes a prescrubber, an amine-based regenerative packed-bed absorber, and a caustic polisher. It is designed to treat an inlet flow of 0.75 million Nm³/h with a SO₂ removal rate of >97 %. Since its installation, it has continuously achieved 1 – 2 ppmv SO₂ at 0 % O₂ (i.e. 3 – 6 mg/Nm³ at 3 % O₂) [25, Pham et al. 2009].

Table 4.27 gives the typical performance achieved with a Wellmann-Lord regenerative scrubber.

<table>
<thead>
<tr>
<th>Technique</th>
<th>SO₂ Reductio</th>
<th>Inlet SO₂ concentration</th>
<th>Outlet SO₂ concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%)</td>
<td>(mg/Nm³) @ 3 % O₂</td>
<td>(mg/Nm³) @ 3 % O₂</td>
</tr>
<tr>
<td>Wellmann Lord</td>
<td>98</td>
<td>2 000 – 7 000</td>
<td>100 – 700</td>
</tr>
</tbody>
</table>

More information and comparison with other techniques can be found in Section 4.25.5.4

Applicability

Wet gas scrubbers are generally recognised as flexible and reliable. Day-to-day operating changes can be readily handled. They generate a low-pressure drop and operate at low temperatures, and do not create solid deposition problems. Their performance can be affected by deposition problems occurring in the course of a typical five-year run: the amount of deposition depends on the inlet catalyst and SO₂ load to the scrubber, the quality of the make-up water, the operating pH of the scrubber and the level of purge applied to the scrubbing slurry. The deposits are formed by catalyst dust that settles at low points and by mist eliminators and hard deposits
(e.g. salts of calcium) that precipitate as the operating pH is increased to achieve high SO$_2$-removal efficiency. Some CO$_2$ can will be removed as well by wet scrubbers, however, in that case, it reduces the capability of the media to dissolve SO$_2$. They are compact systems and fully applicable. These systems, in particular when using Venturi scrubbers, are also rather compact: the necessary plot spaces ranges from 93 to 465 m$^2$ for FCC capacities ranging from 55.2 to 276 dm$^3$/s feed rate (1.5 to 7.5 Mt/yr). Recent trends include forced oxidation to process the SO$_2$ in the SRU, reaction with lime to produce gypsum, a commercial product where there is a market. Spin-off application of power plant, equipped with Wellmann-Lord FGD.

More information can be found in Section 4.25.5.4.

### Economics

Table 4.28 provides an indicative order of retrofitting costs for various FCC wet gas scrubber applications. Note for TWG: Could anybody give me the reference year for the older information in black?

#### Table 4.28: Retrofitting costs for FCC wet gas scrubber applications

<table>
<thead>
<tr>
<th>Objective of the process</th>
<th>FCC capacity (Mt/yr)</th>
<th>Investment expenses (EUR million)</th>
<th>Operating expenses (EUR million/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$ reduction</td>
<td>1.5</td>
<td>10</td>
<td>2 – 5</td>
</tr>
<tr>
<td>Particulates reduction</td>
<td>1.5</td>
<td>2 – 5</td>
<td>2 – 5</td>
</tr>
<tr>
<td>SO$_2$ reduction</td>
<td>3</td>
<td>15 – 20</td>
<td>2 – 3</td>
</tr>
<tr>
<td>SO$_2$ reduction (regenerative)</td>
<td>3</td>
<td>24 – 28</td>
<td>1.5</td>
</tr>
<tr>
<td>SO$_2$ reduction</td>
<td>5</td>
<td>13 (¹)</td>
<td>no data</td>
</tr>
<tr>
<td>SO$_2$ and particulate reduction</td>
<td>0.5 – 4</td>
<td>3 – 15</td>
<td>no data</td>
</tr>
<tr>
<td>SO$_2$ and particulate reduction</td>
<td>2.4</td>
<td>17 – 40 (²)</td>
<td>3.5 – 4.2 (²)</td>
</tr>
</tbody>
</table>

(¹) Investment expenses include the water purge treatment unit.

(²) Respectively USD million 25 – 60 and 5 – 6 in 2009. Capital costs will vary considerably from location to location depending on the scrubber type and the need to upgrade infrastructure and WWTP facilities.

### Non-regenerative scrubbers

The 2003 estimated costs for the installation of non-regenerative wet scrubbers in six different refineries were quoted in a 2009 prospective report from the South Cost Air Quality Management District (California, US). Investment costs cover all production and installation expenses within the scrubber battery area. It does not include foundations, external main ductworks to the scrubber inlet, nor external piping and electrical supply equipment which may add 30 – 50 % to the above costs. Results of this estimation are displayed in Table 4.29.

#### Table 4.29: FCC UNIT - Cost estimates for various off-gas non-regenerative wet scrubbers

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Off-gas flow rate (million Nm$^3$/h)</th>
<th>Capital investment (¹) (million USD)</th>
<th>Operating expenses (million USD/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>0.04 – 0.16</td>
<td>10</td>
<td>0.37</td>
</tr>
<tr>
<td># 2</td>
<td>0.34 – 0.36</td>
<td>13.8</td>
<td>0.56</td>
</tr>
<tr>
<td># 3</td>
<td>0.16</td>
<td>10</td>
<td>0.36</td>
</tr>
<tr>
<td># 4</td>
<td>0.37 – 0.47</td>
<td>15</td>
<td>0.57</td>
</tr>
<tr>
<td># 5</td>
<td>0.20 – 0.23</td>
<td>12.23</td>
<td>0.39</td>
</tr>
<tr>
<td># 6</td>
<td>0.15</td>
<td>9.5</td>
<td>0.32</td>
</tr>
</tbody>
</table>

(¹) Investment expenses cover the costs for all design, fabrication, supply, installation of the complete system, including its new stack, associated purge treatment unit, and internal piping and electrical supply equipment within the scrubber battery area - All costs in 2003 value.

With regard to the assumption of a 25-year life assumption for the scrubber, and considering a 4 % annual increase rate, this report gives an overall cost effectiveness average for these six plants at 24600 USD/tonne of SO$_2$ removed, in order to achieve at least 5 ppmv outlet concentration and 90 % abatement.
Regenerative scrubbers
A regenerative wet gas scrubber typically costs more than a non-regenerative unit to install, due to additional complexity. One equipment suppliers mentions an indicative factor of 2.4. However, the regenerative system has a significant advantage in annual operative costs because of the alkaline absorbing reagent saving and, eventually, the cost return related to by products (e.g. elemental sulphur) sales. The annual operating costs of a regenerative system are estimated to be no more than 35 % of these to be afforded for a non regenerative system. A more detailed comparison is provided in Table 4.30.

Table 4.30: Cost comparison between regenerative and non-regenerative wet scrubbers for FCC application

<table>
<thead>
<tr>
<th>Wet scrubbing cost breakdown</th>
<th>Cost of a regenerative system compared with a non-regenerative system (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital costs</td>
<td>240 %</td>
</tr>
<tr>
<td>Operating costs:</td>
<td></td>
</tr>
<tr>
<td>- Electrical power</td>
<td>35 %</td>
</tr>
<tr>
<td>- Steam</td>
<td>10 %</td>
</tr>
<tr>
<td>- Caustic</td>
<td>18 %</td>
</tr>
<tr>
<td>- Phosphoric acid</td>
<td>5 %</td>
</tr>
<tr>
<td>- Make-up water</td>
<td>&lt;5 %</td>
</tr>
<tr>
<td>- Cooling water</td>
<td>&lt;5 %</td>
</tr>
<tr>
<td>- Water discharge and treatment</td>
<td>&lt;5 %</td>
</tr>
<tr>
<td>- Solid waste disposal</td>
<td>&lt;5 %</td>
</tr>
<tr>
<td>- Operating and maintenance staff</td>
<td>20 %</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Even more favourable costs have been reported in the case of the ENI Sannazzaro LABSORB unit, with a 40 % savings in total operating costs compared with a wet conventional process using caustic soda. This includes 95 % savings in absorbing solution make-up and 25 % savings in power consumption.

Driving force for implementation
Abatement of sulphur oxides and particulates from the flue-gas.

Example plants
A considerable operating experience has been achieved. This technique is widely used on FCC unit plants in the USA. The Wellman-Lord system has been successfully applied to power plants. More information can be found in Section 4.25.5.4.

Reference literature

4.5.10.3 Venturi scrubbing
Note for TWG: No use here → all this information is already incorporated in Section 4.5.10.2

Description
Two variants exist, the jet ejector venturi scrubber, and the high-energy venturi scrubber.

Achieved environmental benefits
Reduction of particulate emissions. Moreover, it can also remove most of the sulphur dioxide present in the flue-gases. Tertiary cyclones with venturi scrubber in the FCCU regenerator have reached efficiencies of 93 % in reducing SO2 and particulate emissions.
Cross-media effects
They produce liquid and solid waste and a wet gas plume.

Operational data
These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide etc.

Applicability
The high energy venturi is the design usually favoured by recent installations. Widely applied for the treatment of small emissions flows.

Driving force for implementation
Reduction of sulphur and particulate emissions.

Example plants
Venturi scrubbing, using an alkaline liquid, has been used successfully on a less widespread scale.

Reference literature
[112, Foster Wheeler Energy, 1999].

4.5.10.4 Dry and semi-dry scrubbers
KOM conclusion 3.5: TWG to provide info for updating Section 4.5 with regard to performances cost and cross-media effects of:

- Alkaline scrubbing
  → Info expected from industry and suppliers. No additional info made available

Description
Two types of scrubbing techniques exist: dry and semi-dry. The key component of the semi-dry process is a spray dryer in which the hot flue-gas comes into contact with a spray of fine droplets of lime slurry. The SO$_2$ is absorbed into the droplets, forming reaction products which are dried to a fine powder by the hot flue-gas. Both dry and semi-dry processes require downstream dust arrestment systems, such as an electrostatic precipitator or bag filtration. More information can be found in Section 4.25.5.4.

Achieved environmental benefits
Reduction of the SO$_2$ in the flue-gas. Efficiency of each process is a 90% sulphur removal with semi-dry, and about 50% removal with dry process. Dry process efficiency of 50% is obtained with lime at relatively high temperatures (about 400 °C) when Ca/S=1, or at 130 - 140 °C when Ca/S=2. The Ca/S ratio has a major influence. With a reactant such as NaHCO$_3$, the abatement rate would be much higher. With lime, it is also possible to have a treatment at 900 °C in a reactor large enough to have a reasonable residence time. The abatement in this case is 80% with CaS=2.1 and 90% with Ca/S=3.

Cross-media effects
Deposition of solid waste results in cases where the reaction products cannot fulfil the quality needed by consumers. Other drawbacks are:

- high-pressure drops across the bag filters if used;
- increased dust load in the gas stream; need for dust capture;
- operational difficulties in water/heat balance (spray dryers only);
- possibly significant pressure drops across bag filter dust arrestment plants, e.g. bag filters;
- generation of solid waste: one tonne of SO$_2$ reduction entails about 2.5 tonnes of solid wastes being generated;
- with the dry and semi-dry scrubbers a mixture of CaSO$_3$, CaSO$_4$, fly-ash and lime is produced.
Operational data
These systems are generally sensitive to other contaminants such as particulates, salts, sulphur trioxide, etc.

Applicability
Operates at low-temperature. Waste generated can be difficult to reuse (no market for gypsum), and difficult to landfill (landfill could be severely restricted in the near future).

Economics
The dry process is a relatively low-cost solution. Raw materials for these processes are cheap. Capital cost and operating costs are typically less than wet scrubbing. Investment cost around EUR 15 - 20 million, and operating costs are around EUR 2 - 3 million/yr (lime cost + landfill waste disposal).

Reference literature
[112, Foster Wheeler Energy, 1999], [257, Gilbert, 2000], [45a, Sema and Sofres, 1991], [297, Italy, 2000].

4.5.10.5 Seawater scrubbing

Description
Seawater scrubbing uses the natural alkalinity of the seawater to remove SO₂. More information can be found in Section 4.25.5.4.

Achieved environmental benefits
SO₂ recovery can be as high as 99%. In order to reduce the particulate emissions to the seawater, a particulate abatement technique should be included before the flue-gas is treated in the seawater scrubber. In this way, seawater scrubbing can be seen as a transfer of the remaining pollution from air to seawater. Seawater scrubbing transfers sulphur emissions from air as SO₂ to the sea as SO₄, with a significant reduction in the overall environmental impact.

Cross-media effects
Particulates containing metals (e.g. V, Ni, Sb) and other pollutants from the flue-gas are transferred to the seawater. The sulphur content of the effluent seawater from the process itself is increased by only approximately 3%. Seawater pumping and compression facilities increase the electricity consumption of the plant.

Operational data
The system needs electrical power (seawater pumps, aeration fans and flue-gas fans) and seawater. The seawater flow required for treating the 497 t/h mixed flue-gas stream received from a RCC unit (with CO boiler) and a SRU is 5000 m³/h in the Statoil refinery of Mongstad (Norway). The seawater scrubber outlet temperature must be 25°C. The seawater is further mixed with cooling water and the mixed temperature is around 15°C released in the environment at around.

In Mongstad refinery, SOₓ emissions from the RCC unit (310 kg/h) and the SRU tail gas (521 kg/h) were abated to 31 kg/h (>96% reduction) as a yearly efficiency average in 2008.

It is feasible to use spent cooling water, for example, when seawater is used as cooling water. The need for seawater is around 30 m³/h for treating flue-gas 1000 Nm³/h with a SOₓ concentration from 3000 to 4000 mg/Nm³ roughly 15000—20000 m³/h per tonne of sulphur removed. Special attention should be paid to minimise corrosion and the maintenance costs derived from it.
Chapter 5

Applicability
The feasibility of applying seawater scrubbing depends on site-specific factors. The process requires access to large amounts of seawater at a competitive cost and high seawater circulation in the areas of the inlet and the outlet. It is fully applied for fuels with up to 1.5 % sulphur content. This system shall normally be applied after a high particulate abatement removal technique to avoid minimising as much as possible the contamination of the sea environment by particulates (containing metals).

Economics
Seawater scrubbers annual costs depend on size and SO$_x$ input/output. The cost is comparable to wet scrubbers. Typical investment costs are in the order of EUR 60/net kWe output of the power plant. The main operating cost is the electrical power for operation of the technique.

Driving force for implementation
Reduction of SO$_2$ emissions.

Example plants
This system has been applied to some power plants around the world (e.g. Norway) and one proven commercial application in FCC for the RFCC flue-gas (after an ESP filtration) operated by Statoil in Mongstad (Norway).

Reference literature
[278, Alstom Power, 2000].

4.5.10.6 ——— Wet gas sulphuric acid process (WSA)

Description
See Section 4.25.5.4.

Achieved environmental benefits
99 % reduction of SO$_2$ and some reduction of NO$_x$. In combination with a SCR, simultaneous reduction of NO$_x$ 95 %.

Reference literature
[247, UBA Austria, 1998]

4.5.11 ——— Combined abatement techniques

Description
There are processes on the market that include an ESP, a SCR for NO$_x$, catalytic oxidation of SO$_2$ and production of sulphuric acid. More information about this technique can be found in Section 4.25.3.

Achieved environmental benefits

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Efficiency of removal</th>
<th>Concentration in the outlet (mg/Nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>≥94 %</td>
<td></td>
</tr>
<tr>
<td>NO$_x$</td>
<td>≥90 %</td>
<td></td>
</tr>
<tr>
<td>Particulates</td>
<td></td>
<td>≤10</td>
</tr>
</tbody>
</table>

The integrated system produces also sulphuric acid of 95 % w/w.

Cross-media effects
See each of the particular techniques included in this process.

Operational data
See each of the particular techniques included in this process.
Applicability
Process qualified for treating very high SO$_2$ concentrations in the flue-gas.

Economics

<table>
<thead>
<tr>
<th>Design capacity</th>
<th>1000000 Nm$^3$/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost</td>
<td>100 EUR million</td>
</tr>
</tbody>
</table>

Driving force for implementation
Reduction of emissions of SO$_2$, NO$_x$ and particulates.

Example plants
Applied to FCC and coking flue-gas.

Reference literature
[297, Italy, 2000]

4.5.12 Waste management techniques

See previous sections for selection of catalyst, control of the emissions of particulates and proper management of product and slurry tank bottoms that can reduce the generation of waste.

Description
Waste is generated during the FCC processes. The selection of catalyst used in the FCC, control of the emissions of particulates and the proper management of product and slurry tank bottoms can reduce the generation of waste. Also the implementation of benchmark performance on the waste generation may be an incentive on how and how much the total amount of waste can be reduced.

Achieved environmental benefits
Reduction of waste generation.

Operational data
These techniques can be seen as part of the waste management programme of a refinery.

Applicability
See Section 4.5.6 for applicability restriction of selection of catalyst.

Driving force for implementation
Reduction of waste management cost and losses of catalyst.

Example plants
Applied in many refineries.

Reference literature
[268, TWG, 2001]
Chapter 5

4.6 Catalytic reforming

The first two techniques considered are process techniques and the rest are techniques for the prevention or control of emissions from the catalytic reforming processes.

KOM conclusion 3.3: TWG to provide necessary information to update BREF Section 4.6 notably for:
- PM, PM$_{10}$ and PM$_{2.5}$ emissions and chemical content for CCR systems
- PCDD/F emissions
- PM and PCDD/F prevention and reduction techniques
- energy consumption and efficiency.

Very few data received so far
Info from equipment suppliers to be searched

Note to TWG: The two following sections describing the processes have been moved to Section 2.6

4.6.1 Continuous catalytic reformer
4.6.2 Semi-regenerative reformer

4.6.3 Type of catalyst promoter

Description
During the regeneration of the catalyst, organic chloride is needed for effective reforming catalyst performance: a chloride injection is needed to reestablish the proper chloride balance in the catalyst and to assure the correct dispersion of the metals. Ozone-depleting substances (e.g. carbon tetrachloride) were initially used during the regeneration of the reformer. According to regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer, the placing on the market and use of such substances, particularly carbon tetrachloride, are now prohibited. Emissions of such substances should be avoided or at least minimised by using less harmful substitutes or by using them in confined compartments.

Achieved environmental benefits
Optimisation and reduction of the use of catalyst promoters. Use of substitutes for ozone-depleting substances, such as perchloroethylene.

Cross-media effects
Due to the use of chlorinated compounds, the possibility of emissions of dioxins and furans during generation has been detected. Refer to Section 3.6.

Operational data
Promoters should be handled in enclosed systems.

Example plants
Most refiners have switched to less ozone-depleting substances, such as perchloroethylene, during the regeneration of the reforming catalyst.

Reference literature
[80, March Consulting Group, 1991].
4.6.4 Cleaning of the regeneration flue-gas

Description
Regenerator flue-gas containing HCl, H₂S, small quantities of catalyst fines, traces of Cl₂, SO₂, and dioxins can be sent to a scrubber prior to release to atmosphere. The regeneration vent gas can contain traces of HCl, Cl₂, CO, SO₂, hydrocarbons, dioxins and furans. The storage and handling of organic chlorides used during the regeneration may also lead to releases. In some reformers, a further filter trap of Cl₂ (ZnO/Na₂CO₃ or NaOH over alumina) is installed. In some designs, the regeneration vent gas may be routed over an adsorption bed, through a scrubber, or combined with a basic water wash system.

Achieved environmental benefits
Reduction of particulates and volatile acids (HCl, H₂S). It has been reported that Cl₂ filter also traps dioxins. Adsorption beds, water or caustic scrubbers, and basic water wash systems lead to a reduction of the emissions of trace components in the regeneration vent gas and removal of the majority of the dioxins and furans from air emissions.

Cross-media effects
When the design includes a scrubber, the recirculated and bleed streams from the regeneration flue-gas wash should be sent to the waste water treatment plant. Due to the low pH of this waste water stream, neutralisation prior to biological treatment may be necessary. The use of scrubbers can move some dioxins from air to water emissions.

Applicability
Fully applicable to new units and with general provisions about retrofitting existing units, taking into account the current design (impact on pressure and temperature balances, existing structures, plot space availability, etc). A Cl₂ trap has been used in continuous reformers.

Economics
No data available for this particular application.

Driving force for implementation
Reduction of air pollutants.

Reference literature
[112, Foster Wheeler Energy, 1999], [268, TWG, 2001].

4.6.5 Electrostatic precipitator in the regeneration flue-gas

Description
Regenerator flue-gas containing HCl, H₂S, small quantities of catalyst fines, traces of Cl₂, SO₂ and dioxins can be sent to an electrostatic precipitator prior to release to the atmosphere. Emissions generated by other activities, such as venting during catalyst regeneration or replacement and plant cleaning, may be sent to the ESP.

Achieved environmental benefits
Reduction of particulate content in the flue-gas coming from the regenerator.

Cross-media effects
See Section 4.25.4.2.

Operational data
None available for this particular application. For general data see Section 4.25.4.2.
Chapter 5

Applicability
Emissions from continuous regeneration sections require particular attention. The use of this type of system in semi-regenerative units is less extended because almost no mechanism exists for the generation of catalyst fines.

Economics
None available for this particular application. For general data see Section 4.25.4.2.

Driving force for implementation
Reduction of particulate emissions during the catalyst regeneration.

Reference literature
[112, Foster Wheeler Energy, 1999], [268, TWG, 2001]

4.6.6 Reduction of PCDD/F emissions from catalytic reforming

Description
Referring to Sections 3.6 and Sections in 4.6 on catalytic reforming, dioxins are typically formed in the three types (continuous, cyclic and semi-regenerative) of catalytic reforming during the regeneration of the catalyst.

If the regenerator flue-gas is treated in a water scrubber (e.g. Section 4.6.4), the dioxins appear detectable in waste water from the scrubber, but they are not detected after the WWTP, possibly due to dilution effects.

In some other cases, because the use of other techniques such as fixed-bed filters. There is a combine reduction of chlorine and dioxins. In some cases, activated carbon has been used to remove dioxins. Another technique that has been used includes the recirculation of vent gases, however, it is not clear how it can reduce the emission of dioxins.

The study of dioxins emissions from reformers and how the regeneration conditions may affect these emission can be a good way to start to understand and solve the problem.

Note for the TWG: please provide updating information on this important subject: Received info appears in operational data and in section 3.6

Achieved environmental benefits
Knowledge of the problem and control of the dioxin emissions.

Cross-media effects
Some dioxins from the regenerator gases may be transferred to water via scrubbing.

Operational data
Preem refinery Lysekil (SE) installed a continuous regeneration gas recycling loop in 2001. The waste gas from the regeneration is recycled to the catalyst where chlorides, chlorinated hydrocarbons and dioxins are re-adsorbed. Emissions of dioxins from the reformer was 0.323 g TCDD-eq/yr. before installation. Emission after the abatement technique installation was 0.0045 g TCDD-eq/yr. (average). The following reductions for dioxins and other parameters were achieved:

-ioxins 99 % reduction;
- chlorobenzene 94 %;
- PCB 93 %;
- chlorides 83 %.
A similar technique is applied with a discontinuous regeneration at Preem refinery Gothenburg. In that case the gases are treated in a scrubber and after that the scrubberwater is filtered through active carbon.

**Applicability**

Note for the TWG: please provide related updated information on this important subject: No data received

**Economics**

Driving force for implementation

Knowledge of the formation of dioxins in the regeneration of the catalysts.

Example plants

Some EU refineries have already applied and monitored dioxin emissions from catalytic reformers. Techniques such as chlorine traps and the recirculation of vents have not been reported to be applied to semi-regenerative reformers due to the use of basic water wash systems in these designs. Efficient abatement techniques are used at two Swedish refineries (see Operational data paragraph).

Reference literature

[268, TWG, 2001] [77, REF TWG 2010]
4.7 Coking processes

The first four techniques considered in this section are coking processes. The information given is intended to help in assessing how well coking processes can perform from the environmental point of view. The rest of the techniques are related to the cleaning of the coke gas, the use of the coking process to destroy solid residues/sludges and, finally, to these techniques related to the abatement of pollution generated by the coking processes.

4.7.1 Techniques to prevent emissions from delayed coking

Description
A description of this process can be found in Section 2.7. Following is a list of the techniques that may be applied to the delayed coker to prevent emissions.

1. Preventing uncondensable vapours generated in the coking processes from passing to the flare system by sending them to a gas separator unit to be sent to the refinery FG network.
2. Passing pressure reliefs from the coke drums to a closed blowdown system, e.g. the quench tower.
3. Techniques for coke drum quench tower pollution control include carrying final venting to gas flare gas compressor to recover as refinery fuel gas, rather than flaring, and sending condensed water to WWTP arrestment train to include consideration of venting the final emission to a flare header with the possible elimination of the second tower and blowdown pond.
4. Using water in the delayed coker as described in Section 4.7.7.
5. Using the steam generated in this process to heat up other refinery processes.
6. Improving heat integration: the delayed coking process itself has a low-level of heat integration. The heat to maintain the coke drums at coking temperature is supplied by heating the feed and the recycle stream in a furnace. However, the atmospheric residue and/or vacuum residue can be fed straight into the delayed coking unit without intermediate cooling, which results in a high heat-integration level between the different units and saves a considerable amount of capital on heat exchangers.
7. Using coking gas. The energy efficiency of the coker can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined cycle units appears in Section 4.10.

Achieved environmental benefits
Reductions of VOC emissions, recovery of products and a reduction of H₂S emissions are achieved when applying some of the above-mentioned techniques. Water reuse is also promoted by the application of these techniques.

Cross-media effects
Note for TWG: please provide appropriate information

Operational data
Some operational data of delayed cokers can be found in Section 3.7.

Applicability
Delayed coking is fully applicable. It is normally applied when the production of petroleum coke has a market or when high-quality coke is required to produce anodes for the non-ferrous metals industry.
Chapter 4

Economics
The typical investment of a full delayed coker (based on 1 Mt/yr straight run vacuum residue feed, US Gulf Coast, fuel grade coke, including vapour recovery) was estimated at USD 136 250 – 218 000 per t/yr in 1998.

Driving force for implementation
Production process.

Example plants
Many delayed processes exist in Europe even if, coking process in general are more commonly used in the US. In 2011, 67 as well as in the rest of the world, delayed coking units are installed worldwide, is the most commonly used technique in the refinery sector.

Reference literature

4.7.2 Techniques to prevent emissions from fluid coking

Description
A description of this process can be found in Section 2.7. General abatement techniques, such as ESP, … (see Section 4.25) are applicable to coking units. Another technique that can be used to prevent emissions or increase energy integration in the fluid coking is to use the coking gas in a gas turbine of a combined cycle unit. Extra information on the application of refinery fuel gas in combined-cycle units appears in Section 4.10.

Achieved environmental benefits
Emission factors for fluid coking (units in kg/1000 litres of fresh feed) are given in Table 4.31.

Table 4.31: Emission factors for fluid coking
Note for the TWG: please provide all useful complementary information and data – No data

<table>
<thead>
<tr>
<th>Process</th>
<th>PM</th>
<th>SOx (as SO2)</th>
<th>CO</th>
<th>HC</th>
<th>NOx (as NO2)</th>
<th>Aldehydes</th>
<th>NH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid coking units uncontrolled</td>
<td>1.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Fluid coking with ESP and CO boiler</td>
<td>0.0196</td>
<td>NA</td>
<td>Neg</td>
<td>Neg</td>
<td>NA</td>
<td>Neg</td>
<td>Neg</td>
</tr>
</tbody>
</table>

NB: Neg: negligible
NA: not available

Cross-media effects
Note for the TWG: please provide information and data

Operational data
This system operates under fluidised-bed conditions.

Applicability
Fully applicable. Although the coke from fluid coking is of a higher grade than the coke from delayed coking, it is not suitable for some specialist applications (e.g. carbon graphite electrodes).

Economics
Investment (US Gulf Coast 1996): USD 10 000 – 13 200 per m3/d.
Driving force for implementation
Production process.

Example plants
Some examples A number of fluid coking units exist around the world.

Reference literature
[136, MRI, 1997].

4.7.3 Techniques to prevent emissions from the calcination process

Description
A brief description of this process can be found in Section 2.7. Certain techniques can be applied to the calcination process to prevent emissions and some of those considered to be beneficial are included in the following list.

1. The kilns can be directly fuelled by coke gas or coke fines, driving off volatile matter and burning it within the kiln.
2. The hot stream of waste gas from the calcination of petroleum coke in rotary kilns contains considerable quantities of particulate matter, which, possibly after heat recovery from the waste gas, is separated with suitable filter devices, e.g. high efficiency multi-cyclones, bag filters and electrostatic precipitators (see also Section 4.7.8). During calcination in multiple-hearth furnaces, particulate abatement techniques are not usually used because of the comparatively low emissions in the waste gases.
3. The unburnt gases from the calcinator are burned in an incinerator, then passed through a waste heat boiler before being released to the atmosphere via a dust collection system.
4. The SCR technique (as described in Section 4.10.4.6) and the SNCR technique (as described in Section 4.10.4.7) may be applicable to these calcination off-gases for an efficient NO\textsubscript{x} reduction.
5. The calcined coke discharges to the rotary cooler where it is cooled by direct water injection. Off-gases from the cooler pass to gas cleaning by multi-cyclones and a wet scrubber.
6. Collected fines from the dust abatement techniques should be conveyed to a silo with exit air filters. Collected cyclone fines may be recycled to product, or may be used within the refinery, or may be sold as product.

Achieved environmental benefits
Some of the techniques mentioned above increase the heat integration of the calciner, reducing the consumption of fuel in the refinery. Others just decrease the amount of particulates emitted to the atmosphere, re-using the coke fines generated during the calcination process. The emission values for petroleum coke production plants attainable in continuous operation are presented in Table 4.32. These values can be achieved by applying the techniques mentioned above.

Table 4.32: Emission values for petroleum coke production plants (calcination of green coke)

<table>
<thead>
<tr>
<th>Emission component</th>
<th>Values attainable in continuous operation (Emissions values as half-hourly mean values in mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate (dust) emissions</td>
<td>20 - 100</td>
</tr>
<tr>
<td>Particulate (dust) components: Ni, V and their components (given as Ni and V total)</td>
<td>3 - 15</td>
</tr>
<tr>
<td>NO\textsubscript{x} (as NO\textsubscript{2})</td>
<td>450 – 875 (No NO\textsubscript{x} abatement technique included)</td>
</tr>
<tr>
<td>SO\textsubscript{x} (as SO\textsubscript{2})</td>
<td>(1000 - 3000) (No SO\textsubscript{x} abatement technique included)</td>
</tr>
<tr>
<td>(100 – 2300(\dagger))</td>
<td></td>
</tr>
<tr>
<td>(300 – 700(\ddagger))</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>100</td>
</tr>
<tr>
<td>HC (given as total carbon)</td>
<td>20</td>
</tr>
<tr>
<td>NB: (\dagger) as daily average</td>
<td></td>
</tr>
<tr>
<td>(\ddagger) as daily average for low sulphur coke</td>
<td></td>
</tr>
</tbody>
</table>
Taking into account the energy-saving additional devices and relevant temperature window availability, a further significant reduction of NO\textsubscript{x} can be achieved using SCR or SNCR.

Operational data
Some operational data of petroleum coke calciners can be found in Sections 2.7 and 3.7. Flue-gas flow rates from calciner (3 % O\textsubscript{2} dry gas) are typically between 1.8 and 3 Nm\textsuperscript{3} per tonne of coke feed (wet feedrate into the calciner). Variation can be connected to the type of coke, and the type of flue-gas (e.g. possible combination of cooler and boiler stacks).

Applicability
Applied to coke produced by delayed cokers and fluid cokers.

Economics
A preliminary very brief evaluation for the retrofitting of an SCR on two calcination kilns gives the following costs that should be taken only as first estimations:

- Design N°1: capital cost EUR 24.24 million, operating cost EUR 0.920 million per year (2007); estimated quantity of NO\textsubscript{x} abated 601 t/yr (EUR 7 450/t for a 15-year life time, rate 12 % assumed) for a 85 % reduction yield;
- Design N°2: capital cost EUR 20.8 million, operating cost EURO 0.71 million per year (2007); estimated quantity of NO\textsubscript{x} abated 563 t/yr (EUR 6 672/t for a 15-year life time rate 12 % assumed) for a 85 % reduction yield.

Driving force for implementation
Production process. For certain applications, green coke produced by the delayed coker should be calcinated before being used or sold.

Example plants
Many examples exist in Europe and around the world. Multiple-hearth furnaces have been extensively applied to waste incineration. The majority of facilities that calcine coke utilise a rotary kiln. The last two calcining facilities built were rotary kilns.

Reference literature
[117, VDI, 2000], [147, HMIP UK, 1995], [268, TWG, 2001], [347, Services, 2001]. [Site questionnaire n°42] [90, EIPPCB 2011].

4.7.4 Flexicoking

Description
A brief description of this production process can be found in Section 2.7. Some techniques that may be applied to prevent emission from the flexicoker are the following.

1. The flexicoking process has a high level of heat integration. The only source of heat in the Flexicoker process is the gasifier, where the coke is partially oxidised. The remainder of the heat in the coker gas is recovered by generating steam. The energy efficiency can be further increased if the coke gas is combusted in a gas turbine of a combined cycle unit. See Section 4.10.

2. As coke cutting from drums is not needed, emissions and dirty effluent generation are avoided as opposed to delayed coking. Moreover, the sulphur components from the coke gas are easy to eliminate. Some 84 – 88 % w/w of the hydrocarbon feed is recovered as hydrocarbon product, the remainder is converted into CO, CO\textsubscript{2} and H\textsubscript{2}O.

3. The coke gas from the heater is passed through a cyclone set to remove the coarser coke particles and is subsequently cooled by generation of high-pressure steam and by preheating boiler feed water. About 75 % of coke fines which pass through the two stages
of heater cyclones are recovered in tertiary cyclones. Almost all the coke fines which escape the tertiary cyclones are scrubbed out in the venturi scrubber. The water slurry from the venturi scrubber is steam-stripped to remove absorbed hydrogen sulphide and ammonia.

**Achieved environmental benefits**
The environmental benefits from the described techniques include:

1. an increase in the energy efficiency of the flexicoking process;
2. less waste generated than delayed coking;
3. prevention of particulate, hydrogen sulphide and ammonia emissions.

**Cross-media effects**
Note for TWG: Please provide specific information available

**Operational data**
Some operational data for flexicokers can be found in Sections 2.7. and 3.7.

**Applicability**
Fully applicable. However, because the products from flexicoking are different than other coking processes (e.g. no coke is produced), refinery product requirements should be considered when implementing this option.

**Economics**
Typical investment (based on US Gulf Coast 1996): USD 15100 – 19500 per m³/d.

**Driving force for implementation**
Production process - The implementation is mainly driven by the site production strategy.

**Example plants**
Many examples exist in Europe, USA and the rest of the world.

**Reference literature**
[212, Hydrocarbon processing, 1998], [271, Martinez del Pozo, 2000].

### 4.7.5 Use of oily sludges and/or waste as coker feedstock

**Description**
In refineries with a coker, oily sludges, sludges from the waste water treatment and waste can be destroyed in the coker (delayed, fluid or flexicoker). In the case If coke is produced, the coke quality produced should remain acceptable (with respect to further use as fuel within/outside the refinery or as material for other purposes). Many oily sludges can be sent to a coking unit where they become part of the refinery products. In the case of a delayed coker, the sludge can be injected into the coke drum with the quench water, or injected into the coker blowdown contactor used in separating the quenching products.

**Achieved environmental benefits**
Reduction of the amount of sludge and/or waste produced in the refinery. In principle, any A refinery with a coker is able to greatly reduce its oily sludge production. to ‘zero’ with the exception BEING where High-quality coke requirements can, nevertheless, restrict its use.

**Cross-media effects**
Typically there is a reduction of the quality of the coke produced.
Moved from applicability If sludges from the waste water treatment are included as feedstock to the coker, part of the water needs to be eliminated (e.g. by vacuum evaporation or in the blowdown system) if the amount of residues are to be maximised.
Applicability
A balance must be achieved between the amount of The quantity of sludge or waste that can be sent to the coker is restricted by and coke quality specifications which may limit the amount of solids in the coke. Coking operations can be upgraded, however, to increase the amount of sludge that they can handle.

The quantity of solids injected depends on the solids content of the slurry, typically being two to 10 to 15%. Loading rates exceeding 40 kg of oil-free dry solids per tonne of coke are considered typical have been established. Higher rates are achievable. At this loading rate, the coke is below anode grade specifications, but within fuel grade specifications.

Cokers in general are an attractive process-integrated reprocessing outlet for oily sludges, provided the sludge-on-feed ratio is kept below 1 – 2 %, depending on the required coke quality. If that ratio is not achieved, neither the operability nor the coke quality is affected.

If sludges from the waste water treatment are included as feedstock to the coker, part of the water needs to be eliminated (e.g. by vacuum evaporation or in the blowdown system) if the amount of residues are to be maximised.

Economics
Typical applications recycle 2 to 16 t/d of oil-free dry solids at a total programme cost of EUR 0.6 – 2.5 million/yr.

Driving force for implementation
Reduction of waste generation in the refinery.

Example plants
The use of sludge as a feedstock has increased significantly in recent years and is at the time of writing (2010) commonly carried out by most refineries where no high quality coke is produced.

Reference literature
[147, HMIP UK, 1995].

4.7.6 Cleaning of the coking gas
Text moved to 4.7.9.4

4.7.7 Water use in the cooling/cutting process

Description
The water used in the cutting/cooling operations is continuously recirculated with a bleed-off to the refinery waste water treatment. Settling and filtering over a vacuum filter enables the reuse of this water, resulting in a ‘closed-water loop’. For water make-up to the quenching and for cutting the water loop, various effluent streams can be used. For this duty-task treated effluent could be used. Collected water from any condenser, and from the draining of wet green coke should be reused for coke drum quenching or drilling. This type of cooling is not used in any other process in the refinery because of environmental concerns. More information about direct cooling (quenching) is found in Section 2.8.

Achieved environmental benefits
Reduce consumption of water in the refinery.

Cross-media effects
Cutting and cooling processes result in vapour emissions (partially-recycled in the main fractionator), significant energy losses, large water use and severe water pollution. Bleeding of cutting water to the desalter has the potential to add solids to the effluent, so it is best to keep coker waters separate.
Operational data
The amount of required make-up water depends on the evaporation losses, loss with the coke product and the bleed to other processes or to the waste water treatment plant and amounts to about 10 - 20 m³/h for a 10^6 t/yr delayed coker unit.

Applicability
Applicable when delayed coking is used. Reuse of water is subject to restrictions of coke quality.

Driving force for implementation
Technique Water reuse is typically offered by used in the delayed coking process and should be optimised as part of the site water management system.

Example plants
Many examples of this application exist in the world.

Reference literature
[268, TWG, 2001].

4.7.8 Handling and storage of the coke

Description
Several techniques are suitable to reduce particulate emissions that may occur during the handling of coke (green and calcined).

1. Providing Provided the green coke is kept wet, the handling between the discharge and the calciner feed hopper is not problematic. There is the possibility that parts of the receiving pit dry out although this is limited as the coke is very wet and is covered with residual hydrocarbons which tend to make it stick together. The construction of wind-breaks around the pit might be considered. Careful design is essential, as bad design could make the situation worse. Complete enclosure of the pit and associated handling facilities is another possibility. The pits are very large and such an enclosure would be very expensive. A monitoring programme should be carried out to evaluate if this option is in fact necessary or desirable.

2. Cutting the coke into a double-roll crusher, and conveying it to an intermediate storage silo is another technique. The railway wagons are then loaded from the storage silo. This approach would collect, filter, and dewater the coke prior to storage.

3. Another option is spraying the calcined coke with a very fine layer of oil, which sticks the dust fines to the coke. The use of oil is limited by its acceptability in further processing. The oil option has the added advantage of reducing unloading problems.

4. Covered and de-pressurising Covering and de-pressuring conveyor belts.

5. Using aspiration systems to extract or collect dust.

6. Using enclosed, hot blowdown system.

7. Enclosing loading areas and maintaining positive/negative pressures, exhausting through bag filters. As an alternative, dust extraction systems can be incorporated with loading equipment.

8. Conveying pneumatically collected fines from the cyclones to a silo with exit air filters. Dust collection systems are provided for handling, storage and loading, using bag filters. Collected fines are recycled to storage by enclosed means.
Achieved environmental benefits
Eliminates particulates matter releases to air of (containing metals) from this part of the process during routine operation as well as from the storage of the coke. An achievable release level of particulate matter for solids handling is 25 mg/Nm$^2$ (value based on averaged continuous monitoring).

Operational data
The storage silo provides a buffering capacity for process fluctuations and enables a controlled loading of railway wagons.

Applicability
Oiling coke (see Item 3 described above) is sometimes practised in fluid and calcined coke, but is rarely applied with delayed coke.

That technique
Collecting and recycling coke fine (see Item 8 described above) is mostly applicable to calciners, fluid cokers and flexicoking units.

Economics
The investment cost of about EUR 30 million for a typical coking unit with a capacity of 1.5 Mt/yr may be expected for the storage system.

Driving force for implementation
Reduction of coke spillage. If the petroleum coke is cut directly from the coking units into railway hopper wagons, it may cause overfilling of the wagons, degrading the quality of the spilled coke and increasing the amount of solids entering the waste water treatment system. Reduction of particulate emissions from the storage system of the coker is another driving force.

Example plants
Many examples available in European refineries.

Reference literature

4.7.9 Techniques to reduce air emissions
This chapter mentions where the abatement techniques may be used and describes the techniques used for abatement of air pollutants.

4.7.9.1 Particulate abatement in coking processes
Description
Flue-gases and coke gas from coking processes normally contain coke particulates (including metals). Dust collection systems are used in all appropriate sections of the coking processes, in order to ensure the cleaning of:
1. cleaning of coke gas;
2. cleaning of the gas produced during the coke cooling;
3. incinerated exhaust gases from the calciner which also produce contain coke fines. Hot flue-gases pass through a waste heat boiler and gas cleaning by equipped with a dust collection system.

In addition to the particulate abatement technique used in the FCC (cyclones or ESP in Section 4.5.9) that may be also used here, bag filters can also be used in these processes.
Achieved environmental benefits
Achievable release levels of particulate matter (values based on averaged continuous monitoring) from calciners and coolers are 10 - 100 mg/Nm\(^3\). Best-performing plants (e.g. OMV in Burghausen, DE) achieve 10 – 20 mg/Nm\(^3\) with electrostatic precipitators (ESP) [28, Tebert et al. 2009].

Cross-media effects
See Sections 4.5.9 and 4.25.4.

Operational data
See Sections 4.5.9 and 4.25.4. The application of an ESP for the control of particulate emissions from petroleum coke calciners has some difficulties in achieving the lower end of the range. The main reason is that coke is a very good conductor of electricity and consequently its surface is very difficult to electrically charge, and consequently difficult to catch by the ESP.

Applicability
See Sections 4.5.9 and 4.25.4. The application of high-efficiency cyclones are easier to apply than ESPs.

Economics
Bag filters can be used at a cost of about EUR 5 million. Calciner boiler cyclones cost EUR 225000 (1999). Economics for other type of systems are not available. An economic study done in a EU refinery in 1992 showed that the cost for an ESP for a calciner was high.

Driving force for implementation
To reduce the particulate emissions from the calciner.

Example plants
Many examples are available in European refineries: that have coking processes, e.g. 4 cokers are installed in Germany, 4 coking units in Spain.

Reference literature
[147, HMIP UK, 1995] [60a, Balik and Koraido, 1991], [297, Italy, 2000], [272, Shawcross, 2000], [117, VDI, 2000], [268, TWG, 2001] [28, Tebert et al. 2009] [77, REF TWG 2010].

4.7.9.2 SO\(_2\) abatement techniques

Description
Sulphur oxides are emitted during the coking processes, especially during the calcination processes. The principal option to reduce sulphur dioxide releases from the process is the use of the lowest possible sulphur-content feedstocks. In practice, low-sulphur feeds are typically used for product quality reasons, since a substantial part of the sulphur remains fixed in the product. However, this option is not always possible and emissions of SO\(_2\) may be significant, especially during the calcining process. To control these sulphur oxide emissions, the same abatement techniques that may be used in the FCC may be also used in this process (see Sections 4.5.10 and 4.25.5.4) with the exception of the DeSO\(_x\) catalyst additive.

Achieved environmental benefits
SO\(_2\) concentrations of 25 - 300 mg/Nm\(^3\) are achieved when the techniques mentioned in Sections 4.5.10 and 4.25.5.4 are used.

Cross-media effects
See Sections 4.5.10 and 4.25.5.4.

Operational data
See Sections 4.5.10 and 4.25.5.4.
Applicability
Normally applied to calciner flue-gases.

Economics
See Sections 4.5.10 and 4.25.5.4

Driving force for implementation
Reduction of SO₂ emissions.

Example plants
Some examples of these techniques can be seen in European and worldwide refineries.

Reference literature
[297, Italy, 2000] and references in Section 4.5.10

4.7.9.3 NOₓ abatement techniques

Description
As already stated in section 4.7.3, SCR technique (as described in Section 4.10.4.6) and SNCR technique (as described in Section 4.10.4.7) may be applicable to calcination off-gases for an efficient NOₓ reduction. Nevertheless very few example data have been made available on this topic.

Operational data
Very few example data have been made available on this topic.

Applicability

4.7.9.4 Cleaning of the coking gas
Text moved from previous Section 4.7.6

Description
After the coking gas has been cleaned to remove particulates and to recuperate part of its heat, it is heated and passed over a catalyst bed in the COS converter, where COS is converted to H₂S. The gas is then cooled and most of the water is condensed. The H₂S is recovered from the coke gas in an amine treater for ultimate recovery of sulphur (see amine treating of refinery fuel gas in Section 4.25.5.1). Clean low-sulphur coking gas can either be used as a site fuel burned in boilers and furnaces or can be sold as low calorific-value gas. Figure 4.22 shows a scheme of that process.

Figure 4.22: Coking gas treatment
Chapter 5

Achieved environmental benefits
Reduction of emissions of H$_2$S (less than 100 ppm v/v in the range displayed in Table 4.86) and COS.

Cross-media effects
Increased use of the amine scrubbing system and increased energy consumption of the COS converter.

Operational data
For amine scrubbing see Section 4.25.5.1.

Applicability
Amine scrubbing is applied to all types of cokers. COS converters are applied to some units, flexicokers.

Economics
The economics data of the amine absorption of H$_2$S can be found in Section 4.25.5.1.

Driving force for implementation
Cleaning of the coke gas. Coke gas forms a main refinery gas source (after dust removal, COS conversion and amine treating for H$_2$S removal).

Example plants
These systems can be found in many cokers.

Reference literature
[118, VROM, 1999]

4.7.9.5 Combined abatement techniques
The same types of techniques used in the FCC can be used in the coker. More information can be found in Section Error! Reference source not found.

4.7.10 Techniques to prevent emissions to water
This Section analyses ways to prevent emissions to effluents. Techniques used in the final cleaning of the waters generated in the coking processes are found in Section 4.26.

4.7.10.1 Treatment of the waste water
In the coking processes, sour water is generated (steam condensate). Consequently, all water from the coking process is sent to the sour water stripper (Section 4.26) before being sent to the waste water treatment plant.

4.7.10.2 Separation of the oil/coke fines from the coke-cutting water
Description
This proposed pollution prevention alternative was to technique consists of retrofitting the sump where the oil/coke fines are collected with an inclined plate separator to increase the separation efficiency.
Achieved environmental benefits
Coke fines and water generated from the coke-cutting operation enter a sump settled on the ground where the solids and water are separated by gravity. A refinery study indicated that this technique could prevent over twenty-five tonnes a per year of coke fines entering the sewage system from that separator.

Cross-media effects
Additional oil/coke fines collected by the separator must receive suitable treatment or be properly eliminated.

Applicability
The technique is fully applicable.

Economics
The annual cost savings associated with the increased recovery of product (coke) and the reduction in oil/water separation solids was approximately EUR 300000 (7.5 Mt/yr refinery).

Driving force for implementation
Reduces the coke fines entering the sewage system and improves the maintenance of the sewage system and the quality of the raw effluents to the WWTP accordingly.

Example plants
Note for TWG: please confirm if this technique is used and to what extent: No info

Reference literature
[60a, Balik and Koraido, 1991].

4.7.11 Techniques to reduce soil contamination

4.7.11.1 Control and reuse of coke fines

Description
Coke fines are often present around the coker unit and coke storage areas. The coke fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Collection techniques include dry sweeping the coke fines and sending the solids to be recycled or disposed of as non-hazardous waste. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse for collection.

Achieved environmental benefits
Reduced soil contamination by coke particulates (including metals). Coke fines can be recycled for fuel use or can be sold outside (e.g. for cement production).

Cross-media effects
Electricity consumption by vacuum ducts/hoses.

Applicability
Fully applicable.

Driving force for implementation
Reduction of soil contamination.

Example plant(s)
The techniques is already in use in USA refineries.

Reference literature
[60a, Balik and Koraido, 1991].
4.8 Cooling systems

Under the IPPC process, a horizontal BREF on industrial cooling systems (ICS) has been produced. The following topics of relevance to refineries are already described and analysed in the industrial cooling system BREF (ICS) [84, COM 2001]

1. reduction of direct energy consumption
2. reduction of water requirements
3. reduction of entrainment
4. reduction of emissions to water
5. reduction of air emissions
6. reduction of noise emissions
7. reduction of risk of leakage
8. reduction of biological risk

The description and analysis includes an extensive discussion of environmental benefits of systems, cross-media effects, operational data, applicability and economics. To avoid repetition, therefore, this section on cooling addresses only topics not covered by the ICS BREF.

4.8.1 Segregation of cooling and process waters

Description
Because process waters are normally more contaminated than cooling waters, it is important to maintain the segregation of the two. Only in cases where cooling waters need treatment (recirculation systems) should they be mixed, and then only at the right point (after the primary treatment of the process waters).

Achieved environmental benefits
Segregation reduces the contamination of cooling water by oil coming from other waters. It increases the recovery of oil by the waste water plant.

Cross-media effects
No cross-media effects have been found.

Operational data
Note for the TWG: the EIPPCB initial intention here was to establish whether non-segregated situations are still existing. No specific info was made available

Applicability
Waste water treatment plants need to be which were originally sized to jointly handle the process water flow and the cooling water flow may have to be modified after segregation in order to efficiently treat the resulting lower and more concentrated effluent.

Economics
Segregation can be very costly in some parts of existing installations.

Driving force for implementation
Avoid To prevent the contamination of cooling water by process waters, which are usually more contaminated, and to avoid the dilution of process waters before their treatment. Some of the topics dealing with pollution of water from cooling systems have already been studied in the OSPAR and HELCOM processes (North Sea and Baltic Sea region).

Reference literature
[107, Janson, 1999], OSPAR, HELCOM recommendations.
4.8.2 Air cooling

**Description**
See Section 2.8 and ICS BREF.

**Achieved environmental benefits**
The major advantage of using air coolers is that no additional medium is required.

**Cross-media effects**
Air cooling tends to produce more noise than water cooling. Noise production due to an air cooler fan measures 97 – 105 dB(A) at source.

**Operational data**
A major disadvantage is that normally a larger plot is required when compared to water coolers (5 – 30 m²/MWth duty). It requires electricity but minimal maintenance cost.

**Applicability**
Air cooling can be sufficient for the cooling needs in some parts of the refinery process. Ambient conditions restrict the temperature levels that can be attained. Climatic conditions (hot climates or temperatures below 0 ºC) typically restrict its use. However the plant location is independent of water availability. Moreover, air fans cannot be located near buildings because air short-circuiting may occur.

**Economics**
Air coolers can be expensive. Minimal maintenance cost.

**Example plants**
Many examples exists in EU refineries.

**Reference literature**
[316, TWG, 2000], [119, Bloemkolk and van der Schaaf, 1996]

4.8.3 Prevention of oil leakages into cooling water

**Description**
Loses of oil through leaks can be minimised through continuous monitoring, associated with a kind of leak detection and repair system (similar to the reference for VOC in Section 3.28.1.4). At its simplest, this

The first step comprises monitoring the cooling water separators for oil build-up. If this oil is observed, then it will be necessary to trace back through the system to identify the source of the leak so that corrective action can be taken. Detailed system drawings and flow charts are essential for this activity. Fingerprinting of the oil can also speed up identification of the leak. A further refinement This technique is better supported and more efficient when oil-in-water monitors are installed at various points in the cooling water system. This allows leaks to be detected rapidly and corrective action taken. For this procedure to be effective, sparing of critical heat exchangers will be required. More information is given in ICS BREF.

**Achieved environmental benefits**
Reduction of oil leakages into cooling water.

**Driving force for implementation**
Detects and correct oil leakages into cooling water.

**Reference literature**
[316, TWG, 2000], [119, Bloemkolk and van der Schaaf, 1996].
4.9 Desalting

4.9.1 Good desalting practices

Description
A short description of desalters can be found in Section 2.9. Several good desalting designs have been included in this section and include:

1. multistage desalters and the combined use of AC and DC fields providing high desalting efficiencies as well as energy savings;
2. recycling, in multistage desalters, part of the brine effluent water of second desalters to the previous one minimising the wash water quantity;
3. use of a low-shear mixing device to mix desalter wash water and crude;
4. avoid turbulence in desalter vessels by using lower water pressure.

Achieved environmental benefits
Increased efficiency of desalters may reduce wash water usage. Other environmental benefits would be limited to energy savings due to a more efficient electrical field.

Operational data
Two-stage processes achieve 99% or better efficiency (more than 99% of the salts/solids are removed from the crude oil). This high efficiency provides process benefits because it allows less corrosion in the topping units.

Applicability
Two-stage or even three-stage desalting is used either if the crude oil salt content is higher than 0.02 % w/w, or if heavy residue is further catalytically processed.

Driving force for implementation
Increase the efficiency of the desalting process.

Reference literature
[113, Noyes, 1993], [297, Italy, 2000], [268, TWG, 2001].

4.9.2 Enhance the oil/water separation before discharge to the waste water treatment plant

Description
Techniques that may be applied are the following.

1. Transfer of the water effluent from desalting units to a settling drum where a further separation between oil and water can be achieved. The oil can be directly recovered in the slop system.
2. Choice of optimum interface level controllers. As a function of specific gravity and range of crudes processed, it is possible to consider the most accurate level sensors among displacers, capacitance probes or radio wave detectors. The accuracy of interface level control is fundamental for the good operation of a desalter.
3. A good improvement in oil/water separation can be achieved using ‘wetting’ agents, whose aim is to de-oil the solid contaminants that are usually responsible for a significant entrainment of oil in the water.
4. Use of non-toxic, biodegradable, safe to use, non-flammable specific demulsifying chemicals to promote coalescence of the water droplets.
Achieved environmental benefits
The systems described above enhance the oil/water separation, reducing the charge of oil to the waste water treatment and recycling it to the process as well as reducing the oily sludge generation (see Section 4.9.3). With the application of the first technique mentioned above some 10 - 20% less oil is sent to the API separators. The second one can separate off some 5 - 10% oil from the water phase.

Cross-media effects
Some of the techniques proposed require the application of chemicals.

Applicability
Fully applicable.

Driving force for implementation
Enhance the oil/water separation.

Reference literature
[297, Italy, 2000].

4.9.3 Enhance the solid/water-oil separation

Description
Solids entering the crude distillation unit are eventually likely to attract more oil and produce additional emulsions and sludges. The amount of solids removed from the desalting unit should, therefore, be maximised. Then the objective is to minimise solids leaving the desalter with the crude oil. A number of techniques can be used to accomplish this.

1. Use low-shear mixing devices to mix desalter wash water and crude oil.
2. Use low-pressure water in the desalter to avoid turbulence.
3. Replace the water jets with mud rakes. They cause less turbulence when removing settled solids.
4. The water phase (suspension) can be separated in a pressurised plate separator. Alternatively, a combination of a hydrocyclone desalter and a hydrocyclone de-oiler can be used.
5. Evaluate the effectiveness of a sludge wash system. The sludge washing is a batch operation meant to stir the water phase in the desalter to suspend and remove the solids accumulated on the vessel bottom. This cleaning operation increases the efficiency of desalters during a normal run, particularly for long cycle runs.

Achieved environmental benefits
With the application of the techniques mentioned above, the content of oil in the generated sludges can be decreased and the separation of the sludges from the water phase can be enhanced.

Cross-media effects
The application of these techniques increases the sludge generation within the refinery. At a bottom sediment content of the crude of 0.015% w/w, theoretically 1500 t/yr sludge can be collected in a 10 Mt/yr refinery.

Applicability
Where bottoms, sediments and water are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids.

Driving force for implementation
Enhances the separation of solids from the oil and water phase.
Chapter 5

Example plants
Desalters with desludging facilities are scarce. Atmospheric residue desalters are also scarce, but the number is increasing with the increasing complexity of refineries with respect to residue conversion. In a few refineries, desalters have been equipped with a bottom flushing system (See Figure 2.11).

Reference literature
[297, Italy, 2000].

4.9.4 Reuse of water for the desalter

Description
The desalting process plays an important role in the waste water management of a refinery (see Section 4.15.7). The water used in other processes can be reused in the desalter. For instance, if stripped sour water is used as desalter wash water, the ammonia, sulphides and phenols that it contains can be reabsorbed by the crude to some extent.

The following process water streams can be suitable for use as desalter wash water.
1. The accumulated water in the crude distillation unit overhead drum, usually 1 - 2 % w/w on crude feed from steam injection;
2. The (unstripped) steam condensates from the light and heavy gasoil dryers and the vacuum distiller overhead (about 3.5 % w/w on feed);
3. Stripped sour water and also other solid-free process water streams. Scrubber or quench water is dirty and requires oil and solids separation prior to biotreatment and/or reuse as desalter wash water. The sour water is routed to and stripped in a sour water stripper prior to reuse and/or final purification in effluent water treatment facilities;
4. Slowdowns from cooling water and boilers.

Achieved environmental benefits
By using the water in this way, the refinery could reduce the hydraulic loading to the waste water treatment units and reduce the consumption of water.

Cross-media effects
Recycling of water streams that may form emulsions need to be avoided, because it results in deterioration of the oil/water phase separation in the desalter, which in turn leads to excessive oil carry over to water. High total dissolved solids (TDS) streams should not be used as desalter wash water due to reduced driving force to extract salt from the crude into the water.

Operational data
The scrubber water would be hard-piped to the desalter water storage tank without being stripped first, in most cases.

Applicability
Examples of effluents that may form emulsions in the desalter are: bitumen blowing units, hydrocrackers, cokers (fines can stabilise emulsions), other deep conversion facilities (insoluble metal sulphides that can stabilise emulsions) and HF-Alkylation units (corrosive fluoride deposits). This option The possibility to reuse desalter waters is fully applicable to new refineries and more difficult to apply in existing refineries. This option is also limited when the salinity of the waste water may reach values that would negatively impinge on the Biox unit.

Economics
The costs of collecting, treating, pumping and piping these waters need to be considered.
Driving force for implementation
The refinery could reduce the hydraulic loading to the waste water treatment units and reduce the consumption of water.

Reference literature
[79, API, 1993], [268, TWG, 2001].

4.9.5 Stripping of the desalter brine

Description
This technique consists of stripping desalter brine for hydrocarbons, sour components and ammonia removal before sending brine to waste water treatment. Recovered hydrocarbons can be blended with several refinery streams. Acid injection can also be employed to enhance the stripping of oil from emulsions.

Achieved environmental benefits
Reduction of the hydrocarbon, sulphur and or ammonia (depending of pH range) content of the waste water generated within the desalter. For example, phenol emissions by 90 % and benzene emissions can be reduced by 95 %.

Cross-media effects
This technique consumes steam, and eventual added acids and other chemicals.

Applicability
Pretreatment of desalter brine is normally applied when processing a very heavy crude.

Operational data
In one Refinery 8.7 Mt/yr refinery produces a waste water flow in the crude unit of 1.3 m³ per minute containing 90 kg/day of phenols is produced. The water discharge from the desalters contains a maximum of 20 ppm benzene, and the quantity of desalter wash water is equivalent to 4 - 8 % v/v of the crude charge. The discharge from the stripper bottoms, with benzene levels in the 20 ppb range, is then routed to the waste water treatment system. A brine de-oiling vessel is installed ahead of the stripping column to decant any free oil undercarry from the desalter. For the above mentioned

Economics
Driving force for implementation
This technique allows to reduce the reduction of the contamination load received at the WWTP and to recover and valorise more hydrocarbons in downstream refining processes, waste water benzene, thereby reducing VOC emissions of benzene in the WWTP.

Example plants

Reference literature
[113, Noyes, 1993], [79, API, 1993].
4.10 Energy system

KOM conclusion 1.2: NL to propose a list of potential inconsistencies (new/existing situations) with the LCP BREF

As mentioned under in the ‘Scope’, this document does not analyse energy production techniques that use conventional fuels. In other words, emission, consumption, cross-media effects, etc., related to commercial fuels (natural gas, fuel oil, etc) can be found in the LCP BREF [7, EC 2006].

The energy system is an important activity from the environmental perspective. Although heat-producing plants are an essential and integral part of most refining processes, the systems tend to be very similar and they are therefore dealt with in this horizontal section. This section therefore includes a detailed analysis of the energy systems that are specific to refineries, i.e. only energy technologies that run (partially or totally) on refinery fuels. When a refinery uses a commercial fuel that can be found on the open market (e.g. natural gas, fuel oil) the emission levels that can be achieved by a certain energy technique (e.g. gas turbines, boilers) are found in the LCP BREF on Large Combustion Plants. Techniques to reduce the energy consumption of a process or activity are addressed in each of the other sections of this document because the reduction of energy consumption is considered an environmental benefit. However, issues such as how the energy system can be integrated within a refinery and how the different processes/activities may share energy are addressed in this section.

Combustion improvement campaigns, the installation of alternative concepts (gas turbines, CHP, expanders, improved heat integration) and a switch to cleaner-burning fuels are some examples of techniques to consider in the determination of BAT. For example, a switch from liquid refinery fuel to natural gas as refinery fuel will reduce not only SO\(_2\) emissions, but also particulates (including metals) and NO\(_x\). All measures to reduce energy consumption will result in a reduction of all emissions to air including CO\(_2\). When end of pipe techniques to abate emissions lead the operator to higher energy consumption and increase of CO\(_2\), this is addressed as a cross media effect. This section has therefore been structured into four blocks of techniques. The first one includes the energy management systems, including general techniques to reduce energy consumption. The second one includes techniques to consider in the selection and cleaning of fuels that can be used in the refinery. The third block contains the techniques for energy production that can provide a good environmental performance using the different type of fuels as well as the utilities needed to run these techniques. The last block (4.10.4 to 4.10.6) includes the abatement techniques to control air emissions that are applicable to energy systems.

Table 4.33 summarises and shows how the main pollutants impacts which may be affected by connected to the techniques that have been considered in this section.

Table 4.33: Possible effect on the main pollutants emissions of the techniques to consider for the determination of BAT in the energy system

<table>
<thead>
<tr>
<th>Section</th>
<th>Techniques to consider in the energy system</th>
<th>CO(_2) (*)</th>
<th>NO(_x)</th>
<th>PM (**)</th>
<th>SO(_2)</th>
<th>Waste water</th>
<th>Residue</th>
<th>Energy</th>
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<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>5</td>
<td>Particulate abatement techniques</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>6</td>
<td>Sulphur oxides abatement techniques</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
</tbody>
</table>

*NB: ↓ Reduction ↑ Increase

(*) CO\(_2\) emissions depend on the type of energy used but are generally expected to follow energy variations

(**) PM for total particulate matter without specification of size
Chapter 4

4.10.1 Energy management

Good design and management of energy systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal general aim is to continuously match the variable production and consumption of fuels in processes and utilities at the lowest economic and environmental cost. This section should be seen as an integration of all techniques proposed below, since an increase in the energy efficiency of a refinery can be achieved through energy conservation technique and heat integration/recovery techniques.

4.10.1.1 Increasing Energy efficiency management

4.10.1.1.1 Increasing energy efficiency

Description

Some techniques to improve and calculate the energy efficiency within the refinery are mentioned below.

The continuous matching of consumption at lowest cost is to be performed at all organisational levels and to be assured at the highest management level. By the adoption of a This energy management may be When included in the site proper management system., this can be done in a similar way to practice as in a number of other fields, notably in the field of safety. In principle the ISO 14000 system series or EMAS [285, Demuynck, 1999] and EN 16001 on energy management systems provide an adequate framework to develop an adequate Energy Management System. In order to ensure continuous improvement, formal reporting of energy consumption data to the authorities can be instigated. Energy audits are part of such a system and it is further recommended that, in the pursuit of continuous improvement, refineries learn from best practice by participating in ranking/benchmarking activities. An annual investment plan on energy consumption reduction is also to be included as a technique to consider in the determination of BAT.

Another way to match production and consumption is to try to improve the energy intensity within the refinery. More efficient refineries make better use of the energy produced within the refinery. To evaluate that, several methodologies exist, including the Solomon energy efficiency index (the most detailed one), specific energy consumption and (less accurate and more simple) the index relating the energy consumption to the amount of feedstock processed (Methods described briefly in Section 3.10.1). Solomon data are also available in that section. Solomon data are available in a form, that only makes sense in its context, and one needs to understand certain underlaying (benchmarking) concepts that are proprietary to Solomon.

Achieved environmental benefits

An increase in the energy efficiency of a refinery has a direct impact on reducing air emissions and indirectly on the generation of waste water and waste. Less Lower consumption of fuels or more energy conservation increase the likelihood that the refinery gas supply will be sufficient for the whole refinery.

Cross-media effects

Some difficulties have been identified in the collection of Solomon energy intensity data from refineries. The main reason is that the figures are considered confidential by both refineries and the provider of the market study (Solomon Associates). Furthermore, Solomon Associates has not provided the TWG with data on the methodology used to calculate the figures. Moreover, it was identified that not all refineries participate in this benchmarking exercise because for different reasons (e.g. cost, confidence in their figures was not high). Also, and not all refineries participate every year.
Chapter 5

Applicability
Fully applicable. The wide range of energy consumption in refineries means that in certain refineries, a considerable reduction in energy consumption can be realised. A concerted and well-managed effort based on an integrated approach in reducing energy use, improved operations, good housekeeping, adequate management and selective investment are good practices that are worth highlighting in this context.

Economics
Energy consumption may account for some 50-65 % of the total operating cost of refineries (50 % typical value for US operating costs on energy, 65 % is reported for some EU countries refining sector). As a consequence a reduction in the energy consumption, or an increase in the refinery efficiency reduce the total operating cost.

Driving force for implementation
Increasing the energy performance of the refinery is typically done in refineries because this reduces their operating cost.

Example plants
Many refineries have installed an energy management system; they issue annual reports on energy consumption performance and participate in benchmarking of energy consumption. Worldwide market studies of a wide variety of refineries (configurations/capacities) on the basis of Equivalent Distillation Capacities has proved useful in helping refineries compare their performance.

Reference literature
[118, VROM, 1999], [316, TWG, 2000], [77, REF TWG 2010], [68, Worrell et al. 2005].

4.10.1.1.2 Energy conservation techniques

Note to TWG: Relevant parts of the text have been moved to section 4.15.1.2

4.10.1.2 Heat integration/recovery techniques

KOM conclusion 3.4: TWG to provide necessary information to update BREF Section 4.10 notably for:

- New practices for improved energy recovery/integration
  - Any additional info from industry still expected NO EXTRA INFO RECEIVED

The following section has been restructured under 1. Design and 2. Process/maintenance techniques by moving relevant text

4.10.1.2.1 Design techniques

Description
Actions that can be taken to improve integration and recovery of heat within a refinery to and increase efficiency are addressed as a general matter in the Energy Efficiency (ENE) reference document [66, EC 2009]. More specifically, techniques applicable to refineries include (non-exhaustive list):

- General measures to reduce refinery CO₂ emissions energy consumption, such as optimised heat integration and improved furnace efficiency combined with computer-controlled combustion. This will lead to lower fuel consumption per tonne of crude processed.
- Installation of waste heat boilers in heaters.
Installation of expanders/power recovery e.g. in FCC unit (see section 2.5).

Expanded heat exchanger areas in which cold streams are preheated by warm product streams directly from processes.

Direct feed of ‘semiproducts’ to processes without cooling and storage. It is always useful, from an energy conservation point of view, to recover the waste heat of hot products of the crude distillation unit, for instance, by later feeding them directly to the downstream units, rather than cooling them for storage and later feeding the downstream units from tankage.

Balancing of vapour and refinery fuel gas systems.

The following part of the bullet list has been moved to section on other techniques

- Use of high-efficiency pumps and compressors.
- Use of heat pumps.
- Decreased film temperature and increased turbulence on heat transfer surfaces.
- Waste heat delivery to adjacent buildings. The identification and use of opportunities for synergy outside the refinery fence (e.g. district/industrial heating, power generation) may reduce the cooling needs within the refinery and will reduce the consumption of fuel somewhere else elsewhere.
- Application of advanced process control to optimise energy utilisation use.
- Insulation of buildings and process units (minimisation of heat losses by thermal radiation).
- Optimisation of energy production (within see Section 4.10.3).
- Optimise recycle gas rates, operating temperatures and pressures and steam pressure levels.
- Minimising or even avoiding slops production and their necessary reprocessing.
- Keeping heat exchanging surfaces clean or cleaning them regularly (good housekeeping) (see a particular example of such a technique in Section 4.10.3.1)
- Repairing leaks and leaking steam traps (see Section 4.10.1.2.2.1).
- Increasing of heat exchanger surface area of new sections of existing plants (so called 'add-ons'). In the cases where more add-ons have been added to an existing plants: re-routing of intermediate process streams and re-definition of the number of steam pressure levels and steam duties.

Achieved environmental benefits

Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled. In a refinery, it is important to maximise heat integration in a plant to minimise heating and cooling duties. This way, substantial amounts of products can be sold instead of being burnt. Heat integration/recovery techniques directly result in lower emissions of CO₂, NOₓ, particulates and SO₂ (see Section 3.10.3 for air emissions from energy system).

Cross-media effects

The interchange of heat between processes implies the transference of disturbances from one process to another. This can affect safety, so stability control systems may be required.

Applicability

Waste heat is abundant at refineries, and so is low/medium-pressure, low-temperature steam. Any effort to recover waste heat as low-pressure/low-temperature steam is pointless if there is no additional use for the extra steam produced. Options for using that heat need to be carefully quantified and qualified. Heat exchangers require space. The identification and use or opperatives or synergy for sharing use of energy outside the refinery fence is sometimes difficult and requires to find partners. compromise commitment and compromises not only by the refinery but also by the other part.
Chapter 5

Economics
It makes economic sense to maximise heat integration in a plant, and as a result minimise heating requirements and the cooling system burden. Heat integration/recovery offers an opportunity for energy cost savings (50% of total operating cost of refineries), but the cost of heat exchangers and piping need to be considered when heat integration is analysed.

Table 4.34 gives various examples of investments for increasing heat exchange surface areas (‘add-ons’) on existing units and, when available, related payback times.

**Note for TWG:** reporting and validation in progress.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Type of units</th>
<th>Energy recovery</th>
<th>Investment cost (year) (EUR)</th>
<th>Payback time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>Atmospheric distillation</td>
<td>10 t/h of steam</td>
<td>1.2 million</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>Debutaniser overhead</td>
<td>5.3 MW</td>
<td>200 000 (2003)</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>39</td>
<td>Diesel hydrotreating</td>
<td>2000 TEP/yr</td>
<td>2.5 million (2006)</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Diesel hydrotreating</td>
<td>400 TEP/yr</td>
<td>400 000 (2006)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Crude oil distillation</td>
<td>6600 TEP/yr</td>
<td>3 million (2006)</td>
<td>6</td>
</tr>
</tbody>
</table>

(*) Site Questionnaire reference number.

Driving force for implementation

Economics: Cost savings by because they reduce reduction of the fuel consumption.

Example plants

Techniques are widely applied in refineries.

Reference literature

[107, Janson, 1999], [118, VROM, 1999], [268, TWG, 2001]. [66, EC 2009].

4.10.1.2.2 Process control and maintenance techniques

4.10.1.2.2.1 Steam Management and reduction of steam consumption

Description

Several techniques have been considered:

Steam used for stripping, vacuum generation, atomisation and tracing is usually lost to waste water and to the atmosphere. Steam used for mechanical and/or electrical energy generation and heating is usually recovered as condensate in the HP-, MP-, and LP-condensate systems and collected in the condensate storage tank. Several techniques can be implemented for optimising the use of steam and reducing steam consumption.

- Reducing the amount of steam stripping when not strictly necessary is not only part of a sound energy management, but also an option to reduce the generation of waste water. Stripping steam is normally used to meet flash point specification and to improve front end fractionation and yields distribution. In order to reduce the sour water loads to SWS strippers and reduce chemical treatments in the overhead systems, an option would be to strip sidedraw products, particularly the lighter cuts, using reboiled sidestrippers instead of steamed strippers. However, the majority of steam is used to strip the column bottom, which could not be reboiled by any other means, so the reduction of condensed steam would be limited anyway; besides, the stripping is far better under vapour stream than under reboiling conditions, because the more volatile fraction distillates off.

- Where inert gas as N₂ is available at an economic price, it can be an alternative to steam for stripping operations, especially for the lighter ends.
• Optimising steam production can also be achieved by waste heat recovery in waste heat boilers (WHB or CHP) from hot flue-gases (e.g. stacks) and hot product streams (related to the techniques shown in Section 4.10.1.2).

• Some sites report interesting initiatives related to systematic programmes for the verification of the very large number of steam condensate drain valves which are usually installed in refinery sites. These programmes consist of the ranking of all valves with regard to induced steam consumption, and the evaluation of all critical valves made on the process and economical points of view. Activities for leakage detection and repair are associated with the programme (‘steam traps’).

**Achieved environmental benefits**
Reducing steam consumption stripping reduces the overall energy consumption, and minimises condensates with a positive impact on waste water generation. The reduction of energy use in steam production will lead to a reduced energy requirement and therefore to lower emissions to air.

**Cross-media effects**
None in particular.

**Operational data**
On a French site, a 'steam trap' programme including the systematic mapping of drain valve systems was undertaken in 2008 and covers 20 000 pieces of equipment. At the date of writing (2010) around 30 tonnes of steam per hour have been saved since the programme started. The same approach has been followed on a British site, involving since 2008 a dedicated team which has managed to reduce steam losses to atmosphere by around 50 000 t/yr ea.

**Economics**
The programme mentioned corresponds to a total annual investment estimated at EUR 450 000.

**Driving force for implementation**
Environmental driving force aimed at energy saving and related decrease of air and water emissions.

**Example plants**
Applications are found in some refineries.

**Reference literature**
[297, Italy, 2000] [Questionaires n° 16 and 45]

4.10.1.2.2.2 Other techniques
Relevant text moved from bullet list at the beginning of the section
• Use of high-efficiency pumps and compressors.
• Use of heat pumps.
• Decreased film temperature and increased turbulence on heat transfer surfaces.
• Application of advanced process control to optimise energy utilisation use.
• Insulation of buildings and process units (minimisation of heat losses by thermal radiation).
• Optimise recycle gas rates, operating temperatures and pressures and steam pressure levels.
• Minimising or even avoiding slops production and their necessary reprocessing.
• Keeping heat exchanging surfaces clean or cleaning them regularly (good housekeeping) (see a particular example of such a technique in Section 4.10.3.1)
• Repairing leaks and leaking steam traps (see Section 4.10.1.2.2.1).
• Increasing of heat exchanger surface areas of new sections of existing plants (so called ‘add-ons’). In the cases where more add-ons have been added to an existing plants: re-routing of intermediate process streams and re-definition of the number of steam pressure levels and steam duties.

4.10.2 Refinery fuels: types and cleaning

As mentioned above, this document offers a detailed analysis only of refinery fuels produced in the refinery. Whilst the use of marketable fuels such as LPG, commercial fuel oil and gasoil in refineries is a technique to consider that may be included in this chapter of the BREF, such use is extensively analysed in the LCP BREF [7, EC 2006] which also gives achievable emissions levels using these fuels.

4.10.2.1 Increase the use of gas

Description
An alternative to reducing SO\textsubscript{2}, NO\textsubscript{x}, CO\textsubscript{2} and metals emissions from a refinery would be to replace or decrease the use of liquid refinery fuel with LPG (often produced on site), refinery fuel gas (produced by some conversion techniques) or natural gas (from external supply). This increase of the use of gas is typically accompanied with by a balance and control of the RFG system between suitable pressure limits to give the system flexibility, with RFG make-up available from clean fuels such as LPG or imported gas. In these cases, state-of-the-art controls optimise the performance of the RFG are necessary.

Achieved environmental benefits

Note for TWG: this 1st paragraph is from the current text but has been transferred from 4.10.3.1. Fired boilers and furnaces generate substantial CO\textsubscript{2}, SO\textsubscript{2}, NO\textsubscript{x}, and particulate emissions, particularly when heavy fuel oil is used. Gas-fired boilers generate hardly any dust and low SO\textsubscript{2} emissions when the refinery gases are cleaned in amine scrubbers. NO\textsubscript{x} emissions are also much lower than these of oil-fired boilers.

Because of the low SO\textsubscript{2} concentrations in the flue-gases of gas-fired boilers, the emission temperatures at the stack can be lowered to 150 °C (dew point corrosion is less of or no longer a constraint). The lower flue-gas temperature represents a difference in energy efficiency and inherent CO\textsubscript{2} emission reduction.

A full switch to a 100 % gas-fired refinery would drastically reduce SO\textsubscript{2}, CO\textsubscript{2} and NO\textsubscript{x} emissions, by up to 90 %, by 30 – 50 %. Releases of heavy metals would also be slashed. Furthermore, the use of gas generates very little dust and very low SO\textsubscript{2} emissions, as part of the refinery gases are usually cleaned in amine scrubbers (see next section). Sulphur emissions are significantly lower when clean refinery fuel gas is used instead of a distillate such as automotive gasoil, i.e. 10 - 20 times better than low-sulphur (1 %) conventional fuel oil. Because of the low SO\textsubscript{2} concentrations in the flue-gases of gas-fired boilers, the emission temperatures at the stack can be lowered to 150 °C. The lower flue-gas temperature represents a difference in energy efficiency and inherent CO\textsubscript{2} emission reduction.

Gaseous fuels typically release less NO\textsubscript{x} per unit of energy compared to liquid fuels, especially liquid refinery fuels. For gaseous fuels, usually only thermal NO\textsubscript{x} is relevant; however NO\textsubscript{x} emissions will depend on the gaseous fuel composition. Oil burning normally leads to higher levels of NO\textsubscript{x} releases for several reasons, especially due to fuel NO\textsubscript{x} arising from the nitrogen content (see section 4.10.2.3), the need to balance NO\textsubscript{x} and particulate releases and the frequent design requirement for firing in combination with gas. More detailed information for achievable emission values can be found in Table 4.37 and Table 4.43.
As a matter of summary, the benefits for a switch to a 100% gas-fired refinery are given below.

- **SO\textsubscript{2} emissions from the energy system will be drastically reduced to nil for the single unit and for.** These emissions will be very low from the refinery gas, and virtually equal to zero for the natural gas. Contributions to the refinery bubble will be mostly attributed to emissions from other sources (very small from refinery gas, from the SRU, from the FCC unit, the flares, etc);
- Particulate emissions including heavy metals will be reduced.
- NO\textsubscript{x} will be reduced to levels close to the levels those typical for natural gas firing for energy production techniques, and consequently other sources such as cat crackers will become predominant emitters in the refinery.
- CO\textsubscript{2} emissions reduction is achieved mainly because of the lower carbon content of gas, its higher calorific value and in addition because of a higher attainable efficiency (stack gases can be cooled further).

**Cross-media effects**

It is acknowledged that the residual fuel replaced by gas results in a further surplus of residue, which has to be considered in any integrated solution for the fuel system of a refinery. It can be the case that those residual fuels could be burned improperly outside the refinery, so emissions produced by that way can be seen as merely an emission shift to outside the refinery rather than an elimination. Furthermore, the conversion of heavy fractions into light products and the targets for lower sulphur specifications of fuels require considerable extra energy. This will lead to an inevitable increase in CO\textsubscript{2} emissions, unless the CO\textsubscript{2} could be captured.

As a first approximation, NO\textsubscript{x} emissions can be magnified by the use of hydrogen, heaviest gaseous hydrocarbons, and residual fuels containing fuel-bound nitrogen. High-hydrogen fuels result in higher flame temperatures, which typically lead to higher NO\textsubscript{x} levels. Although not all the fuel nitrogen ends up as NO\textsubscript{x} emissions, the fuel NO\textsubscript{x} contributions can range from non-existent, as in the case of natural gas fuelled equipment, to several times the thermal NO\textsubscript{x} contribution of the equipment for refinery fuels. Refinery fuel gas may contain amines (nitrogen compounds) and other compounds. Adjustment factors for NO\textsubscript{x} emissions as a function of the bound nitrogen content of heavy fuel oils are available in the literature. A well-recognised reference on this subject is provided by the ‘Besluit Emissie-Eissen Stookinstallaties Milieubeheer A’ (BEES) guidance document published by the Dutch competent authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed in Figure 4.23.
The adjustment factor proposed by the BEES document is made up with the combination of two factors multiplied together. The first accounts for the hydrogen content and the second is attributed to hydrocarbons having a carbon number greater than three.

Further information on conversion techniques of heavy fractions to refinery fuel gas can be found in Section 4.10.3.5: the coking sections and the hydroconversion processes sections.

**Applicability**
The move from liquid to gas fuel would require process upgrades and gas grid connections. Some gases are used locally, i.e. in the process of origin or an adjacent process, but most refineries operate a common RFG mains into which most RFG is fed and transferred to the gas users. In a modern refinery, the RFG mains is carefully ‘balanced’ with respect to supply and demand; necessary flexibility is obtained by control of production (i.e. reformer throughput, LPG evaporation). The relationship to with the refinery flare system is important and RFG will normally include gas received from flare gas recovery. It may also release excess gas to flare if the upper pressure limit is exceeded. The application of energy conservation concepts (see Section 4.10.1) can help refineries to meet all their needs with refinery gas produced in-house.

The US EPA has recently reached a number of settlement agreements (referred to as Partnership Civil Judicial Settlements, or Consent Decrees) with major companies at the company or site level, in order to eliminate or minimise the use of solid and liquid fuels in all boilers and heaters operated in the refineries [25, Pham et al. 2009]. According to these settlement agreements, the use of solid/liquid fuels is only allowed during natural gas curtailment periods.

Nowadays, a number of European refineries have also switched to 100 % gas with similar operating conditions.

**Operational data**
On Figure 4.24, a very clear correlation is displayed between the part of gaseous fuels burnt in the site energy mix and the specific NO\textsubscript{x} and SO\textsubscript{2} emissions achieved by a sample of 55 European refineries during the period 2007 – 2008.
Figure 4.24: Relation between the part of gaseous fuels and specific NO\textsubscript{x} and SO\textsubscript{2} emissions for a sample of European refineries.

Figure 4.25 shows the current respective uses of gas and oil in the energy system for a sample of European refineries. From these data, in 2008, the median percentage of gas firing was around 75\% and liquid oil firing close to 25\%. For oil firing, the corresponding average sulphur content was 1.06\%.

This information is consistent with CONCAWE survey on sulphur dioxide emissions (report 1/10) showing a decreasing oil use from 28.5\% in 1998 to 19.1\% in 2006 and an average sulphur content of 1.33\% in 2006.

Figure 4.25: Oil and gas firing in 2008 TWG data sample
Economics
The cost of switching to gas can be up to as high as EUR 30 million per year for a 10 Mt/yr refinery.

For use of LPG in lieu of fuel oil, the approximate capital cost is small (some reburning) and the approximate operating cost per year is EUR 120 per tonne of fuel (cost differential between LPG and fuel oil). However, operating costs can vary significantly, depending on the season of the year and on the price of LPG on the market.

For use of natural gas in lieu of fuel oil, the approximate capital cost of installation is around GBP 4 million. The approximate operating cost per year may vary from below EUR 50 per tonne to above EUR 100 per tonne (cost differential between natural gas and fuel oil). Again, operating cost can vary significantly depending on the season of the year and on the market.

Driving force for implementation
Reduction of CO₂, NOₓ, SO₂ and particulate emissions (including metals).

Example plants
The amount of refinery gas plus natural gas combusted by European refineries typically account from 60 to 100 % (in terms of megawatts fired). However data from some single European refineries shows that the amount of heavy fuel oil fired can approach to 60 %. From 2007 – 2008, the relative part taken by gaseous fuels (refinery fuel gas eventually completed by natural gas) in the site energy mix was above 80 % for nearly 60 % of European refineries. Very few European sites rely upon more than 25 % of heavy liquid fuels for their own energy supply.

Reference literature
[118, VROM, 1999], [292, HMIP UK, 2000], [7, EC 2006] [249, BMUF, 1999], [268, TWG, 2001] [64, CONCAWE 2010].

4.10.2.2 Cleaning of refinery fuel gas

Description
Some refinery fuel gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) or sulphur-containing at source (most other processes, i.e. from crude distillation, cracking and all hydrodesulphurising processes). In the latter case the gas streams are normally treated by amine scrubbing to remove H₂S before being released to the refinery fuel gas system. More information about amine scrubbers can be found in Section 4.25.5.1.

Achieved environmental benefits
As shown in Table 4.86 of Section 4.25.5.1, amine-treated refinery fuel gases can be controlled to levels range depending of amine scrubber pressure, from 2 – 15 to 20 – 200 220 mg H₂S/Nm³. These levels which will achieve lead to a range the release level of between 5 – 25 5-35 mg/Nm³ SO₂ at 3 % O₂ in flue-gases where upper level is H₂S -220 and taking into account a maximum 45 % of hydrogen content (Source: CONCAWE 4/09).

Cross-media effects
Possibility of bottlenecking the amine scrubbing system. More information can be found in Section 4.25.5.1.

Operational data
See Section 4.25.5.1. At the time of writing (2010) the amine cleaning of refinery fuel gases is adjusted to below 25 – 35 ppmv (annual average) in various US refineries [25, Pham et al, 2009] in order to meet the SO₂ standards imposed for furnaces and boilers emissions.
It should be noted that fuel gas may contain other sulphur compounds as mercaptans (from thermal cracking processes) or COS (from FCC units) which are not removed by amine scrubbers.
Applicability
Fully applicable.

Economics
See Section 4.25.5.1.

Driving force for implementation
To reduce the sulphur content of the flue-gas of the refinery.

Example plants
The treatment of refinery fuel gas in amine scrubbers is commonly used in all refineries.

Reference literature
[297, Italy, 2000] [36, CONCAWE n°4/09 2009].

4.10.2.3 Hydrotreatment of liquid refinery fuels

Description
The nitrogen, sulphur, particulates and metals content of the fuel used in refineries are determined by the crude that is used at the refinery and by the process units it has passed through. Liquid refinery fuel streams originate from various processes such as crude distillation units, vacuum distillation, thermal cracking, cat cracking and hydrocracking of residues. Except for the latter, the sulphur content of these residues can only be controlled by feedstock choice. In general, the liquid refinery fuel may comprise one or more of the aforementioned fractions and the sulphur content can vary greatly. Table 4.35 shows the sulphur, nitrogen and metal content of different fractions suitable to be used as liquid refinery fuel.

Table 4.35: Sulphur, nitrogen and metal content of fractions suitable for liquid refinery fuels

<table>
<thead>
<tr>
<th>Fraction suitable to be used as liquid refinery fuel</th>
<th>Crude oil origin</th>
<th>S (%)</th>
<th>N (%)</th>
<th>Metal content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric residue North Sea</td>
<td>0.6 - 1.1</td>
<td>0.03 - 0.32</td>
<td>0.03 - 0.06</td>
<td></td>
</tr>
<tr>
<td>Atmospheric residue Middle East</td>
<td>2.3 - 4.4</td>
<td>0.04 - 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum residue North Sea</td>
<td>1.1 - 1.8</td>
<td>0.18 - 0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum residue Middle East</td>
<td>3.6 - 6.1</td>
<td>0.07 - 0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cracked residue Middle East</td>
<td>3.5 - 6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on hydrogenation reactions, the hydrotreatment of fuels can reduce the sulphur, nitrogen and metal content of the refinery fractions. The hydrotreatment of liquid fuels can reduce the sulphur content to 0.03 – 1 %. For more information on hydrotreatments, see Section 2.13. This technique is a pre-combustion operational change, treating the feed before it is used.

Achieved environmental benefits
Feed hydrotreating of fuels reduces the feed nitrogen, sulphur and metals content, which in turn reduces the SO₂, NOₓ and particulate emissions. It has been calculated that by switching to fuel oil with a sulphur content of 1 % or less, UK refineries can reduce SO₂ emissions by 19 - 64 %. Another advantage of switching to low-sulphur fuel is that it reduces heat loss to the flue-gas stack (investment in extra heat exchangers or heat exchanger surface to be made) because dew point corrosion is minimised or is no longer a constraint.

Cross-media effects
The hydrotreatment of fuels is a very energy-intensive process consuming hydrogen with a consequent increase in CO₂ emissions. Moreover, effluent water and waste (used catalyst) are generated (see Section 3.13).
Operational data

Adjustment factors for NO\textsubscript{x} emissions as a function of the bound nitrogen content of heavy fuel oils are available in the literature. A well-recognised reference on this subject is provided by the ‘Besluit Emissie-Eissen Stookinstallaties Milieubeheer A’ (BEES) guidance document published by the Dutch competent authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed on Figure 4.26.

![Figure 4.26: Effect of bound nitrogen concentration on NO\textsubscript{x} emissions from fuel oil firing (applying only to existing installations)](image)

Other information on the performance and consumption of hydrotreatments can be found in Sections 2.13 and 3.13.

Applicability

Fully applicable.

Economics

An intensive hydrotreatment is very expensive, increasing the cost of the liquid refinery fuel. Table 4.36 shows an example of the costs of liquid refinery fuel desulphurisation processes.

<table>
<thead>
<tr>
<th>Table 4.36: Economics Costs of a liquid refinery fuel desulphurisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity of the refinery</td>
</tr>
<tr>
<td>Fuels used in the refinery</td>
</tr>
<tr>
<td>Volume of flue-gas emitted</td>
</tr>
<tr>
<td>Sulphur emission</td>
</tr>
<tr>
<td>Desulphurisation efficiency</td>
</tr>
<tr>
<td>Investment cost (EUR)</td>
</tr>
<tr>
<td>Operating costs (EUR/yr)</td>
</tr>
</tbody>
</table>
Driving force for implementation
Reduction of sulphur and nitrogen oxide emissions.

Example plants
The amount of refinery gas combusted by refineries compared to liquid fuel, in terms of megawatts fired, is typically 60% refinery gas to 40% liquid refinery fuel. However, data from the public register for 1996 in the UK show that in some refineries, the amount of fuel oil fired can approach 60%.

Reference literature
[45a, Sema and Sofres, 1991], [292, HMIP UK, 2000], [118, VROM, 1999], [248, Ademe, 2001] [36, CONCAWE n°4/09 2009]

4.10.3 Energy production techniques

All types of energy production techniques found in refineries are included here. However, the emission levels associated with each technique are different from those included in Chapter 3 of this document, because in only good performance levels are included in this section. Techniques to prevent emissions from these energy production techniques are also included.

4.10.3.1 Furnaces and boilers

KOM conclusion 3.4: TWG to provide necessary information to update BREF Section 4.10 notably for soot blowing: Info received from DE

Description
The primary measures considered in this section for furnaces and boilers are given below (see also LCP BREF [7, EC 2006].

- Installation of combustion air preheaters, which would increase the furnace efficiency significantly (by more than 5%).
- Optimise furnace operations, and hence combustion efficiency, by an advanced control of the operations variables (air/fuel ratio for the fuel mix, avoiding sensible heat losses by optimising excess air).
- High thermal efficiency heater/boiler designs with good control systems (e.g. oxygen trim).
- Minimisation of heat losses via radiation or exhaust gas (e.g. minimisation of heat losses via unburnt gases (H₂, CO) or unburnt residues, i.e. ignition loss).
- Continuous monitoring of temperature and O₂ concentration of flue-gas for combustion optimisation. Monitoring of CO may be also considered.
- Maintain a high boiler pressure.
- Preheating of fuel charged to the boilers.
- Preheating of boiler feed water with steam (see also Section 4.10.3.2).
- Prevention of the condensation of exhaust gas on surfaces.
- Minimisation of own requirements by high efficiency pumps, vents, and other equipment.
- Optimisation of combustion conditions (see Section).
- Techniques to control CO emissions which are:
Chapter 5

- good operation and control
- constant delivery of liquid fuel in the secondary heating
- good mixing of the exhaust gases
- catalytic afterburning.

- Regular on-line heater hot tube descaling and hot convection cleaning (dry treatment)
- Regular cleaning of heating surface (soot blowing) for liquid fuel or mixed firing
- Ceramic coatings for process tube protection against oxidation and prevention of scale build up.
- High emissivity refractories for radiant heat transfer improvement, e.g. by application of ceramic coatings.

Achieved environmental benefits
Table 4.37 to Table 4.40 provide the achievable emission levels when primary measures are implemented in furnaces and boilers for each air pollutant. Other measures Some specific techniques, such as low-NOx, flue-gas desulphurisation and others are reviewed later in this chapter. Values in the tables are in mg/Nm³, attainable in continuous operation (half-hourly mean values) and are based on a 3 % oxygen volume in the waste gas, except where specified. For gas, the lower values in the ranges given below relate to natural gas firing. Liquid refinery fuel refers to thermal cracked residue, vacuum residue, etc.

Table 4.37: Expected CO emissions from furnaces and boilers with optimal burner and design

<table>
<thead>
<tr>
<th>Source</th>
<th>Gas</th>
<th>Liquid refinery fuel (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process furnaces</td>
<td>5 – 80</td>
<td>20 – 100</td>
</tr>
<tr>
<td>Boilers</td>
<td>5 – 80</td>
<td>20 – 100</td>
</tr>
<tr>
<td>Engines</td>
<td>10 – 150</td>
<td></td>
</tr>
</tbody>
</table>

(*) For liquid firing, a concentration below 50mg/Nm³ is achievable at temperatures above 800°C, with sufficient retention delivery and retention time
Source: [316, TWG, 2000]

Table 4.38: Expected CO₂ emissions from furnaces and boilers with optimal burner and design

See Table 3.68.

Table 4.39: Expected NOx emissions from furnaces and boilers with optimal burner and design

<table>
<thead>
<tr>
<th>Source</th>
<th>Gas</th>
<th>Liquid refinery fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process furnaces</td>
<td>70 – 150</td>
<td>280 – 450</td>
</tr>
<tr>
<td></td>
<td>400 – 500</td>
<td>280 – 450</td>
</tr>
<tr>
<td>Boilers</td>
<td>80 – 120(*)</td>
<td>300 – 450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350 – 600</td>
</tr>
<tr>
<td>Engines</td>
<td>250 – 400</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NA</td>
</tr>
</tbody>
</table>

(*) TWG 2010 data collection (see also Table 4.47 for mixed firing) - Expected emissions result from multi factor including both burning optimisation and burners design
Table 4.40: Expected particulate emissions from furnaces and boilers with optimal burner and design

<table>
<thead>
<tr>
<th>Source</th>
<th>Gas</th>
<th>Liquid refinery fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boilers and furnaces</td>
<td>&lt;1</td>
<td>20 - 250</td>
</tr>
</tbody>
</table>

Table 4.41: Expected metal emissions from furnaces and boilers with optimal burner and design

<table>
<thead>
<tr>
<th>Source of metals</th>
<th>Gas</th>
<th>Liquid refinery fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source of metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(As, Pb, Cd, Co, Ni, V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and their components)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process furnaces</td>
<td>0</td>
<td>5 - 10</td>
</tr>
<tr>
<td>Boilers</td>
<td>0</td>
<td>5 - 10</td>
</tr>
</tbody>
</table>

Table 4.42: Expected SO\(_2\) emissions from furnaces and boilers

Cross-media effects
Air preheating typically increases the production of NO\(_x\). Adjustment factors for NO\(_x\) emissions as a function of preheated air temperature are available in the literature. A well-recognised reference on this subject is provided by the ‘Besluit Emissie-Eissen Stookinstallaties Milieubeheer A’ (BEES) guidance document published by the Dutch authorities in 1987. The correlation factor (applying only to existing installations) proposed in the BEES is displayed in Figure 4.27.

Figure 4.27: Effect of air preheating on NO\(_x\) emissions for fuel gas firing (applying only to existing installations)
This factor is applied directly for units fired with refinery fuel gas and addresses only the increase in thermal NO\textsubscript{x} production. In the case of fuel oil or mixed liquid/gas fuel firing, this factor should be applied after first adjusting the bound fuel nitrogen to zero (see Figure 4.26 in Section 4.10.2.3) in order to avoid double counting the NO\textsubscript{x} increase due to the fuel nitrogen conversion.

**Operational data**
Direct gas-fired heaters and boilers normally achieve thermal efficiencies of over 85 %. If air preheat is applied and the combustion products (flue-gas) are cooled close to their dew point, the thermal efficiency can be as high as 90 - 93 %.

An average fuel reduction of around 3 % has been obtained by retrofitting ceramic coatings on existing process furnace tubes (e.g. on catalytic reforming and vacuum distillation furnaces). A 2 % reduction was also observed after retrofitting high emissivity ceramic coatings on existing refractories of steam reformer furnace walls. In both cases, the related reduction of NO\textsubscript{x} emissions could be estimated to 30 % for furnaces equipped with conventional burners, and 5 % for those equipped with low-NO\textsubscript{x} burners.

**Applicability**
Most of the techniques mentioned in this section are fully generally applicable. However some restrictions to applicability for retrofitting existing units are to be taken into consideration. In the particular case of ceramic coatings, retrofitting this technique to furnaces fired with 100 % heavy liquid fuels is not advised.

**Economics**
The retrofitting of ceramic coatings on tubes and refractory walls of a 0.5 Mt/yr catalytic reforming furnace and a 2.1 Mt/yr vacuum distillation furnace costed around EUR 0.2 – 0.4 million per furnace (2004). The related payback time was estimated 6 months for the increased productivity (capacity and/or cycle run length) and at 2 years as far as energy consumption is strictly concerned.

**Driving force for implementation**
Reduction of energy consumption and related emissions from processes requiring heat or steam production.

**Example plants**
Each refinery contains many furnaces and boilers of different sizes. All techniques mentioned in this section are widely used in numerous process furnaces operated worldwide. In the particular case of tube and/or refractory ceramic coatings, more than 30 process furnaces have been treated since 2000 in Australia, Canada, Germany, Italy, Mexico, Japan and the US.

**Reference literature**
[117, VDI, 2000], [195, The world refining association, 1999], [45a, Sema and Sofres, 1991], [7, EC 2006] [249, BMUF, 1999], [297, Italy, 2000], [118, VROM, 1999], [268, TWG, 2001], [Questionnaire n° 25], [36, CONCAWE n°4/09 2009].

### 4.10.3.2 **Boiler feed water (BFW) production and reuse**

Note to TWG: No data made available: Could we agree to delete this section and, if necessary only keep a reference to CWW?

**Description**
Techniques to consider for the BFW production and reuse are:

1. The condensate tank is generally equipped with an oil detection system and an oil skimming device.
2. To avoid corrosion in the steam and condensate systems, oxygen and carbon dioxide are removed in de-aerators, and oxygen scavengers and corrosion inhibitors are added. For further conditioning of BFW, dispersing, alkaline and sometimes anti-foaming agents are dosed.

3. Minimisation of heat losses via flue-gas (unburnt gases, such as H₂, CO), via residues (ignition loss), via ashes and slags, via thermal radiation.

4. Preheating of boiler feed water (to de-aerator) by waste heat.

5. Reduction of own energy requirement in the BFW production.

6. Production of boiler feed water: common techniques are ion exchange, microfiltration and reversed osmosis. Unlike ion-exchange techniques, membrane processes do not generate waste water containing high loads of salts. Technologies should be preferred which generate recyclable residues (e.g. iron containing cludges). Preferred use of non-toxic chemicals for water preparation, which are easily degraded by micro-organisms. Use of mineral oil free flocculation agents. Use of chemicals with no or only low content of chloro-organic compounds. Rejection of the following compounds: EDTA (and homologous compounds) and its salts; aminopolycarboxylic acids and their salts; metal-organic compounds; chromates, nitrates, organic polyelectrolytes with a monomer content >0.1 % w/w. Treatment of waste water from boiler feed-water preparation in a well-designed WWTP, especially in case of regenerates that contain high amounts of NH₃ derived from condensate recovery applying ion exchange. [317, EIPPCB, 2002].

7. Conditioning of boiler feed water: Good operation is the combined operation with oxygen dosage by addition of ammonia the pH is adjusted to an alkaline milieu and a small amount of oxygen is added. With this measure, the addition of hydrazine (which is considered a carcinogenic carcinogen substance) can be avoided and the demand for ammonia is decreased. Furthermore, a protective layer of magnetite and hematite is formed on the inner surface of the pipes, which is less rough softer thereby decreasing the pressure drop within the pipes and decreasing the energy demand of the pumps. Waste water from water conditioning needs to be neutralised and treated in a well-designed WWTP [317, EIPPCB, 2002].

8. Repeated reheating of steam.

**Achieved environmental benefits**

The BFW condensate has a very low pollutant content. The reduction in water actual use because of reuse is the most significant environmental benefit.

**Cross-media effects**

Biotreatment may be required if anti-foaming inhibitors are used. Corrosion inhibitors are not biodegradable in the waste water treatment plant.

**Operational data**

BFW should not be recycled or routed to the desalter.

**Applicability**

When the reuse of condensate water as deaerated feed water or preheating the BFW is applied, in some instances, where the condensate and the deaerator are located far apart, their integration is not always possible because of economical reasons.

**Economics**

Site-specific availability and economics determine the choice of the BFW source.

**Driving force for implementation**

The production of BFW is necessary for the production of steam in boilers.

**Example plants**

BFW production occurs in all refineries in some measure way.

**Reference literature**

[327, Broughton, ], [317, EIPPCB, 2002], [316, TWG, 2000], [268, TWG, 2001].
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4.10.3.3 Gas turbines

Description
A description of gas turbines can be found in the LCP BREF [7, EC 2006]. A brief description can also be found in Section 2.10. Some techniques that can be applied to gas turbines in order to reduce air emissions are listed below:

- steam injection
- gas turbines with exhaust gas as combustion air
- optimised transformation of steam into electrical energy (highest possible pressure difference in the steam turbine, generation of steam with high temperature and pressure, multiple reheating of the steam)
- other primary techniques such as dry low-NOx burners included from Section 4.10.4 to 4.10.6.
- use high-efficiency turbines by, for example, optimisation of the design of the turbines, reduce as low technically feasible the outlet steam pressure in the back-pressure turbine

Achieved environmental benefits
Table 4.43 summarises the emission levels that can be achieved with the application of the above mentioned primary measures techniques to for gas turbines.

Table 4.43: Expected air emissions from gas turbines with optimal design primary techniques

<table>
<thead>
<tr>
<th>Pollutant (a)</th>
<th>Gas (b) (mg/Nm³)</th>
<th>Liquid refinery fuel (c) (mg/Nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>5 – 100</td>
<td>&lt;50</td>
</tr>
<tr>
<td>NOx (as NO2) at 15 % O2</td>
<td>20 – 50 (new turbines)</td>
<td>250 – 450 (with water injection)</td>
</tr>
<tr>
<td>Particulates (at 15 % O2)</td>
<td>&lt;10 – 100 without abatement</td>
<td>&lt;5 – 30 with abatement</td>
</tr>
</tbody>
</table>

(1) The lower range relates to natural gas firing
(2) Gas oil/jet oil.
(3) Range depends on the gas turbine type
(*) lower range with dry low NOx burners (DLN)

Additional measures to abate NOx emissions as low as 65 mg/Nm³ (15 % O2) with, e.g. SCR are also possible for existing gas turbines. See Section 4.10.4.7.

Cross-media effects
Steam injection typically produces higher emissions of CO and hydrocarbons. Steam should be produced if it is not available in the refinery.

Applicability
Fully applicable.

Economics
Steam injection applied to a 85 MW output turbine. Uncontrolled NOx emissions of 500 mg/Nm³ at 15 % O2. Down to 50 – 80 mg/Nm³ at 15 % O2. Investment cost (1998) EUR 3.4 million (including cost of steam production). Operating cost: EUR 0.8 million (excludes capital charge).

Driving force for implementation
Process technique used for the production of electricity.

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Example plants
Many examples exist in refineries. A number of refineries have or are currently installing combined cycle gas turbines (CCGT) designed to produce steam and power for the refinery. This is usually done to replace in whole or part an old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators. Recent example (December 2011) for upgrading 6 gas turbines at Qatargas LNG plant (Qatar) shows a dry low NOx system designed to achieve emissions levels of 25 ppm (<50 mg/Nm³).

Reference literature
[45a, Sema and Sofres, 1991], [118, VROM, 1999], [115, CONCAWE, 1999], [7, EC 2006].

4.10.3.4 Cogeneration plants (CHP)

Description
A brief description can be found in Section 2.10.

Achieved environmental benefits
For the combination refinery/other power generators (OPG), the energy consumption and CO₂ emissions will be reduced by the application of the CHP concept. At the OPG, fuel consumption and all related emissions will be reduced but, at the refinery, fuel consumption and emissions may increase. A refinery that generates its own steam and electricity (no import from the OPG) can benefit from (enhanced) cogeneration. In these cases, the environmental benefit includes effect of reduced fuel use and its related emissions accrue completely to the refinery.

Cross-media effects
No cross-media effects have been detected.

Operational data
Most turbines require a particularly stable mix of fuel in order to be sure of flame stability and are basically designed to burn natural gas. Refinery fuel gas components can vary considerably, especially when surplus hydrogen is produced, such as when a hydrotreatment unit is temporarily shut down, resulting in excess hydrogen being sent to the fuel gas system. However, these problems can usually be overcome, up to a limit of about 70% hydrogen in the fuel.

Applicability
Generally applicable. The steam and power cogeneration concept can be also be applied to boilers firing, for instance, liquid refinery fuel. They can be designed to generate high-pressure steam and to let the pressure down over an expander/turbo-generator. Economisers and the optimisation of air-to-fuel control are also techniques applicable in cogeneration plants.

Driving force for implementation
For the production of steam and power to be used within or outside the refinery.

Example plants
A number of refineries have, or are currently installing, combined cycle gas turbine (CCGT) or Combined Heat and Power (CHP) plant, designed to produce steam and power for the refinery. This is usually done to replace in whole or part an old oil-fired boiler plant, to reduce operating costs and to decrease reliance on other power generators.

Reference literature
[118, VROM, 1999].
Chapter 5

4.10.3.5 Gasification of heavy oils or coke (IGCC)

Description
Integrated gasification combined cycle (IGCC) is a technique whose purpose is to produce steam, hydrogen (optional) (see Section 2.14) and electric power from a variety of low-grade fuel types with the highest conversion efficiency possible. More information can be found in Section 2.10.

Achieved environmental benefits
Syngas produced in this process has a sulphur content of 0.01 – 0.05 % and could be used, as refinery fuel gas for hydrogen, fuel or chemical production. Water containing the soot particulates is filtered and the filter cake is subjected to a controlled burning process. The process is, in principle, autothermic; the heat of combustion being sufficient to evaporate the moisture content of the filter cake.

The IGCC is a highly-integrated and efficient process which can supply power, hydrogen and steam. Furthermore, it offers, in principle, an acceptable outlet for heavy residues and feedstocks or even refinery sludges, provided the latter are less than 1 % of feed. Hot gas clean-up systems have the potential to increase system efficiency and lower system costs. The achieved emissions to the atmosphere from that system are: SO₂: 50 mg/Nm³, NOₓ: 65 mg/Nm³ at 3 % O₂, particulate matter: 5 mg/Nm³ and carbon monoxide: 10 – 30 mg/Nm³.

The emissions from the IGCC show a significant decrease compared with conventional power/steam plants. The SO₂ concentration in the refinery exhaust is reduced by 80 % but CO₂ emissions increase.

The use of by-product and residual streams to meet the fuel requirement of refineries cannot only be cost-effective, but also is environmentally beneficial in that it makes use of what would otherwise be a waste refinery stream that would be flared without recovering the energy content.

Cross-media effects
In some cases, some difficulties may occur in burning low-calorific-value gas produced. Water effluent is normally sent to the existing waste water treatment plant of the refinery. It may contain significant amounts of metals such as V, Cr or Ni and PAHs.

Operational data
Utility requirements for the gasification processes are 1800 – 4900 kWh/t of power and 1140 kg/t of steam consumption. The soot product is about 50 – 75 % w/w V₂O₅ residue, which can be sold to metal reclaimers. The IGCC complex is also equipped with all the necessary auxiliary systems, including cooling water (mixed system with an open seawater circuit for large users and a closed clean water circuit for the other users), demi-water, air, nitrogen, water and fuel gas networks, fire fighting, flare, storage, electrical distribution, buildings, etc.

IGCC is a technology with high flexibility in start-up, shutdown and part-load operation, depending on the level of integration between the different sections. Typically, systems that use heat exchange equipment are more efficient than those using quench cooling; however, the capital cost of the system with heat exchange is higher and there is a risk of fouling. The handling of the soot and filter cake should be done with care to avoid dust (even at 80 % moisture) due to the toxic properties of the residue.

Applicability
This technique can be seen as an alternative approach to removing sulphur using feed hydrotreatment (see Section 4.10.2.3). During normal refinery operation the gasifiers of the IGCC plant are able to convert almost any refinery residue (atmospheric residues, vacuum residues, visbroken or thermal tars, etc.) to heat and power. These feedstocks can have a high sulphur content.
Economics
Table 4.44 gives the economics of two examples of IGCC applied in European refineries.

Table 4.44: Economics of two IGCC plants of European refineries

<table>
<thead>
<tr>
<th>Refinery capacity</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Some characteristics of the refinery are:</td>
<td></td>
</tr>
</tbody>
</table>
| Fuel used in the refinery | 120 000 liquid  
180 000 gaseous |
| Volume of flue-gas generated in the refinery | 1.68 \(10^9\) |
| \(SO_x\) emissions (as \(SO_2\)) before application of IGCC | 5 000 (for liquid refinery fuels with 3% S) |
| \(SO_x\) emission load | 8 400 |
| Efficiency of the process measured as sulphur content of the gaseous fuel | 0.01 |
| Investment cost | 200 - 400 EUR million |
| Operating costs | 20 - 40 EUR million/yr |

<table>
<thead>
<tr>
<th>Size of the IGCC</th>
<th>280</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net cogeneration efficiency</td>
<td>47.2</td>
<td>%</td>
</tr>
<tr>
<td>Investment cost</td>
<td>648</td>
<td>EUR million</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristics of the feedstock used</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density: 1.05 - 1.1</td>
<td>kg/dm³</td>
</tr>
<tr>
<td>Viscosity: 100 - 3500</td>
<td>cts at 150 °C</td>
</tr>
<tr>
<td>Sulphur: 3.5 - 7</td>
<td>%</td>
</tr>
<tr>
<td>Metals: 300 - 800</td>
<td>ppm</td>
</tr>
<tr>
<td>Heating value: 8800 – 9200</td>
<td>kcal/kg</td>
</tr>
</tbody>
</table>

Example plant(s)
The IGCC concept as such is quite a recent technological application for power stations. The main sections of an IGCC plant, i.e. gasification, air separation, gas cleaning and combined cycle are well known techniques that have previously been used separately for different applications and with different feedstocks. Integration (the ‘I’ in IGCC), though, is a more recent idea. Oil gasification is a process that has been applied for many years. Gasification of heavy residues, according to the principles of IGCC, is rather new. At least 4 IGCC plants are already in operation within European refineries and some others are in the design/construction phase. Coal gasification, also applying the IGCC concept, is new as well and a few plants are in operation.

Reference literature
[45a, Sema and Sofres, 1991], [297, Italy, 2000], [320, Italy, 1996].

4.10.3.6 Fluidised-bed boiler

Description
An alternative method for the disposal use of heavy residual oils or petroleum coke is the combustion in a fluidised boiler with limestone injection for sulphur capture.

Achieved environmental benefits
About 90% of the sulphur content of the fuel is captured and about 50% of the calcium in the limestone is used in sulphur absorption.

Cross-media effects
The resulting calcium sulphate and unconverted calcium oxide together with the nickel and vanadium in the fuel are discharged from the boiler as a solid residue which can be used as road aggregate or disposed of to landfill.
However, such schemes have a lower sulphur capture performance than gasification and they do not provide the option of producing hydrogen. There could also be environmental objections to the mining and transport of limestone and disposal of the residue. For these reasons, gasification may be generally more attractive in the long term.

**Applicability**
A combination of fluidised-bed boilers with upstream solvent deasphalting or delayed coking can be a cost-effective solution for refineries with existing FCCU unit capacity and steam/power deficiencies.

**Economics**
Typically cheaper than gasification.

**Driving force for implementation**
Reduction of solid waste generation.

**Reference literature**
[118, VROM, 1999].

### 4.10.4 Nitrogen oxide control and abatement techniques

Techniques to reduce NOₓ emissions fall into two broad categories. Primary techniques include NOₓ control techniques, such as pre-combustion operational changes and combustion modifications. Secondary techniques include the post-combustion flue-gas treatments or NOₓ abatement techniques. More information about NOₓ abatement techniques can be found in Section 4.25.3. Primary and secondary techniques are considered in this section. The types of NOₓ control and abatement techniques to be considered in the energy systems are summarised in Table 4.45.

#### Table 4.45: NOₓ control and abatement techniques considered to be applied into for energy systems

<table>
<thead>
<tr>
<th>Type of techniques</th>
<th>Fired heaters</th>
<th>Boilers</th>
<th>Gas turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary measures (control</td>
<td>Low-NOₓ burners</td>
<td>Flue-gas recirculation</td>
<td>Dry low-NOₓ combustors</td>
</tr>
<tr>
<td>techniques)</td>
<td>Ultra-low-NOₓ</td>
<td>Ultra-low-NOₓ</td>
<td>Steam injection</td>
</tr>
<tr>
<td>(control)</td>
<td>burners reburning</td>
<td>burners reburning</td>
<td>Water injection</td>
</tr>
<tr>
<td>Secondary measures</td>
<td>SCR</td>
<td>SCR</td>
<td>SCR</td>
</tr>
<tr>
<td>(abatement techniques)</td>
<td>SNCR</td>
<td>SNCR</td>
<td></td>
</tr>
</tbody>
</table>

#### 4.10.4.1 Low-NOₓ burners and ultra-low-NOₓ burners

**Description**
Low-NOₓ burners, either air-staged or fuel-staged, have the aim of reducing peak temperatures, reducing the oxygen concentration in the primary combustion zone, and reducing the residence time at high temperatures, thereby decreasing thermally formed NOₓ. Staging of fuel addition is also thought to provide a reburning effect further reducing the NOₓ. Moreover, in the case of fuel-staged burners, the under-stochiometric conditions created by the secondary flame after the fuel complementary addition creates a further chemical reduction of NOₓ in N₂ by NH₃, HCN and CO radicals.

Ultra low-NOₓ burners add the internal or external recirculation of flue-gases to the features of the basic low-NOₓ burner design, enabling the decrease of the oxygen concentration in the combustion area and a further abatement of NOₓ reductions acting in particular on fuel-bear. Further information on various burner designs and features can be found in Section 3.4.1.6 of the BREF on Large Combustion Plants [7, EC 2006].
Achieved environmental benefits
When successfully implemented, low-NOx burners can achieve NOx reduction performances of 40 - 60 % for gaseous fuels and 30 - 50 % for liquid fuels compared to conventional burners of the same thermal capacity. Respectively, ultra low-NOx burners successfully applied to gas-fired process heaters and boilers can achieve a 60 - 75 % reduction of NOx emissions.

Table 4.46 shows a summary of the achievable emission levels that can be found when the different types of fuel are fired in different types of combustion techniques and when low-NOx burners are applied.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Natural and forced draft heaters (T)</th>
<th>Boilers (T)</th>
<th>Gas Turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>30 - 150 (15 - 50)</td>
<td>30 - 150 (15 - 50)</td>
<td>NA</td>
</tr>
<tr>
<td>Liquid refinery fuel (0.3 % N)</td>
<td>100 - 250 (25 - 70)</td>
<td>100 - 250 (25 - 70)</td>
<td>NA</td>
</tr>
<tr>
<td>Liquid refinery fuel (heavy)</td>
<td>150 - 400</td>
<td>150 - 400</td>
<td>NA</td>
</tr>
</tbody>
</table>

Note: Units in mg/Nm^3 at 3 % O_2 (within brackets in mg/MJ)

Table 4.46: NOx emissions achieved with low and ultra low-NOx burners for different type of equipment

Replacement of many of old burners with new low-NOx burners may have also a positive effect on:
- process energy efficiency because new burners are generally more fuel efficient;
- noise generated by the combustion plant as a global improvement opportunity.

Cross-media effects
For heavy liquid fuel oil firing, there is a direct link between NOx and particulates, i.e. reduction in NOx as the flame temperature falls will lead to an increase in particulates. For low-NOx fuel oil burners, as with conventional fuel oil burners, a further reduction of thermal NOx results in an increase in carbon particulates. CO emissions are also increased.

In all cases, an improper control of the flame volume after retrofitting can lead to excessively hot gases impinging on key heater internal components (e.g. tubes in the radiant or the convection section), causing corrosion, deposits or other material damage, and reducing the run length of the process. Therefore, no burner replacement project should be contemplated unless it is proven to be technically feasible, using notably CFD modelling to confidently predict the heat firebox characteristics that would be seen once new burners are installed.

Besides the flexibility limitation (see comments on applicability below), Low NOx burners can be subject to flame instability and increased tip plugging and coking problems, with other potential incidences on process safety. As technology expands and operation is pushed further and further to the limits (e.g. decreasing the diameter of individual fuel injectors), fuel filtering (e.g. using coalescent filters), fuel heat tracing and thorough maintenance are essential for a proper burner operation.

Operational data
Refinery gas firing with ultra low-NOx burners in both forced or natural draft conditions may show signs of instability at some points, particularly at low turndown and low excess air. Care needs to be taken during the installation of these burners. Burner testing to explore the limits of combustion prior to site installation is highly recommended for reliable operation and to evaluate that this technique is applicable in specific case.

Table 4.47 gives a selection of results reported by various European refineries within the data collection process launched for the BREF review.
### Table 4.47: Reported performance of low-NO\textsubscript{x} burners in TWG site-level questionnaires

<table>
<thead>
<tr>
<th>Reference [Questionnaire]</th>
<th>Type of fuel/burner</th>
<th>Emissions (daily average)</th>
<th>Available comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mixed-fired LNB</td>
<td>317 (monthly)</td>
<td>Max (spot): 400</td>
</tr>
<tr>
<td>[no 20]</td>
<td>Gas-fired LNB</td>
<td>100</td>
<td>Average ranges obtained on 2 RFG-fired and 1 mixed-fired furnaces equipped with first generation LNB</td>
</tr>
<tr>
<td></td>
<td>Mixed-fired LNB</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>[no 22]</td>
<td>Gas-fired LNB</td>
<td>80 – 120</td>
<td>Average ranges obtained on a large number of furnaces equipped with LNB</td>
</tr>
<tr>
<td></td>
<td>Mixed-fired LNB</td>
<td>200 – 250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixed-fired LNB</td>
<td>301 317 330 – 360 336 469 322</td>
<td>30/70 fuel to gas 34/66 fuel to gas 40/60 fuel to gas 45/55 50/50 58/42 (N content in liquid fuel: 0.6 %)</td>
</tr>
<tr>
<td></td>
<td>Mixed-fired LNB</td>
<td>435</td>
<td>50/50 fuel to gas N content: 2.44 % (liquid)/0.47 % (solid) H\textsubscript{2} in fuel gas: 32 % (mass)</td>
</tr>
<tr>
<td>[no 38]</td>
<td>Mixed-fired LNB</td>
<td>30 – 45(1)</td>
<td>LNB burners Last generation of burners: 2000 Achievable with low throughput and low oxygen demand</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 – 50</td>
<td></td>
</tr>
<tr>
<td>[no 39]</td>
<td>Liquid-fired LNB</td>
<td>&lt;125</td>
<td>Obtained with ULSG burners</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;250</td>
<td>Mixed-fired LNB 340 Best boiler – 50/50 fuel to gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mixed-fired LNB 220 Best furnace – 50/50 fuel to gas</td>
</tr>
</tbody>
</table>

\(^{(1)}\) 15 mg/MJ
\(^{(2)}\) 20 mg/MJ

NB: Units in mg/Nm\textsuperscript{3} at 3 % O\textsubscript{2} (except no39)

Extensive work has been undertaken to develop correlations that help explain how NO\textsubscript{x} emissions relate to changes in operational parameters, e.g. fuel type and composition (in particular fuel bound nitrogen), combustion air preheat temperature, and fire box temperature. A good example is given by the set of adjustment factors developed in the Netherlands and provided as a national guidance for permit writers in 1987 [36, CONCAWE 2009 (Appendix 1)].

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Table 4.48 shows a summary of typical ranges of NO\textsubscript{x} emissions achieved in real refining operating conditions. These ranges cover a spectrum of different situations resulting from these variable conditions, and are considered for air combustion converted back to ambient air temperature.

Table 4.48:  Typical ranges of emission measured under various refining operating conditions, and converted back to ambient air temperature [36, CONCAWE n°4/09 2009]

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Type of burner</th>
<th>Emissions (daily average)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>Low-NO\textsubscript{x} burner with air or fuel basic staging</td>
<td>80 – 140( ^{(1)} )</td>
<td>For combustion air at ambient temperature</td>
</tr>
<tr>
<td></td>
<td>Ultra low-NO\textsubscript{x} burner</td>
<td>60 – 90( ^{(1)} )</td>
<td>For combustion air at ambient temperature</td>
</tr>
<tr>
<td></td>
<td>First generation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultra low-NO\textsubscript{x} burner</td>
<td>30 – 60( ^{(1)})(( ^{(2)} ))</td>
<td>For combustion air at ambient temperature and firebox temperature &lt;900(^{\circ} )</td>
</tr>
<tr>
<td></td>
<td>Latest generation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixt gas/liquid</td>
<td>Dual fired Low-NO\textsubscript{x} burner</td>
<td>80 – 140( ^{(1)})(( ^{(2)} ))</td>
<td>For combustion air at ambient temperature</td>
</tr>
</tbody>
</table>

\(^{(1)} \) Lower values are achievable with firebox temperature of <800\(^{\circ} \) and <10 \% volume of hydrogen or C3 + in the refinery fuel gas composition.

\(^{(2)} \) Lower values are achievable with fuel gas containing no ammonia or other fuel-bond nitrogen.

\(^{(3)} \) Lower values are achievable with <0.1 \% fuel-bond nitrogen mass content in the liquid fuel burnt.

NB: Units in mg/Nm\(^{3} \) at 3 \%O\(_{2}\)

For the gas refining sector in Norway, the following table shows recent examples of use of ultra low NO\textsubscript{x} burners.

Table 4.49:  Recent example of ultra low NO\textsubscript{x} burners in natural gas plants in Norway

<table>
<thead>
<tr>
<th>Site</th>
<th>Thermal input capacity</th>
<th>Type of burner/fuel/year</th>
<th>NO\textsubscript{x} emissions</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ormen Lange</td>
<td>2 x 42.1 MW</td>
<td>Ultra low-NO\textsubscript{x} burner with fuel gas recirculation Natural gas/2007</td>
<td>20 mg/Nm(^{3} )</td>
<td>Measurements in 2008 in the range 20 – 90 mg/Nm(^{3} ) (30 to 10 MW) – NO\textsubscript{x} emissions vary inversely to the MW of heat applied to the ovens</td>
</tr>
<tr>
<td>Kollsnes</td>
<td>18.4 MW</td>
<td>Ultra low-NO\textsubscript{x} burner Natural gas/2012(^{(2)} )</td>
<td>30 mg/Nm(^{3} )(( ^{(1)} ))</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(1)} \) Value guaranteed by supplier for 60-100 \% operating duty range of the heater

\(^{(2)} \) Heater will be in operation in 2012 and used instead of existing one

NB: Units in mg/Nm\(^{3} \) at 3 \%O\(_{2}\)

Applicability

New installations
Apart from fuel-specific limiting conditions (see below), application is straightforward for new installations of both fired heaters and boilers.

Retrofitting existing installations
Compared to conventional burners, usual low-and ultra low-NO\textsubscript{x} burners of the same thermal capacity tend to stretch the flame length up to 50 \% and the flame diameter up to 30 – 50 \%. They also need more space (internal and external area and volume) for being installed as their footprint is also increased, due to the presence of fuel injectors and/or the incorporation of furnace gas recirculation devices in and outside the burner tile. Finally, they usually offer a lower flexibility (‘turndown’ capability ratio) between the highest and lowest accessible firing rate for given operating conditions, raising operating constraints and potential safety concerns.
Therefore, some older-fired heaters are fitted with large high-intensity burners which cannot be easily retrofitted with new low-NO\(_x\) burners. As an illustration of this, some cases of disappointing results have been reported within the data collection process for the review of this BREF. Another example is the retrofitting of dual-fuel burners theoretically capable of operating with 100% gas fuel, but with a practical restriction on the maximum amount of gas due to tube skin temperature limits in the primary and secondary super-heater section [Questionnaires n° 31, 32, 37, 45]. Retrofitting of low-NO\(_x\) burners will depend on the furnace design and surrounding environment, and may be simple, difficult or, because of the increased flame volume, even impossible without heavily modifying the technical integration of the furnace into the unit, or changing the furnace. For instance the increased length of low-NO\(_x\) burners may restrict applicability in furnaces built low above ground. NO\(_x\) abatement on older furnaces and boilers may also be less effective due mainly to the need to avoid flame impingement on the furnace tubes.

The retrofitting of low-NO\(_x\) burners is possible in general but will depend on site-specific conditions (such as furnace design and surrounding environment). Nevertheless, in some specific cases, it can lead to heavily modifying the technical integration of the furnace into the unit, or to changing the furnace.

Some state-of-the-art burners have been specifically designed for being retrofitted to existing plants, and may be very well adapted to the upgrading of oil refining gas-fueled heaters. They benefit from advanced computational fluid dynamics (CFD) modelling and show a highest compactness associated with an improved turndown capability.

Fuel-specific limiting conditions
Some liquid fuels are not suitable for the latest generation of low-NO\(_x\) burners. The applicability for state-of-the-art gas-fired ultra low-NO\(_x\) burners is limited to fuel gases having a small amount of components heavier than propane and a low olefinic content. NO\(_x\) performance with ultra low NO\(_x\) burners (ULNB) is more sensitive to excess oxygen. Therefore, this performance will depend on the feasibility and reliability of oxygen concentration control in the firebox. Comment for TWG (CONCAWE): it would be useful to precise here related orders of magnitude for these conditions: No data received.

Economics
The following tables show the economics of several applications of low- and ultra low-NO\(_x\) burners in different refineries. Comment for TWG: As proposed in Draft 1, the 2 first original Tables have been deleted and replaced by an updated one. The following table gives different cost examples for the installation of low-NO\(_x\) burners, derived from various retrofitting projects in refineries.
Table 4.50: Cost and Specific cost examples for the retrofitting of low and ultra low NOx burners

<table>
<thead>
<tr>
<th>Applied to Project/reference</th>
<th>Investment cost</th>
<th>More information Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/Reburning a typical crude oil furnace consisting of 40 forced-draught burners Reference?</td>
<td>EUR 3.3 million GBP 2 million (1998) Average per individual burner: GPD 50 000</td>
<td>Including the general upgrading of the furnace air, fuel and control systems likely to be carried out at the same time by a refiner</td>
</tr>
<tr>
<td>2/Retrofit several plants with gas-fired Low-NOx burners as follows: vaccum heaters crude heaters</td>
<td>Total investments: - SEK 11 million (1991) - SEK 41 million (1998)</td>
<td>Assuming a 5-year operation life: - 25 000 SEK per t.y (80 t/yr NOx saved) - 34 000 SEK per t.y (220 t/yr NOx saved)</td>
</tr>
<tr>
<td>3a/Retrofit several process heaters operated within: - a CDU (10 Mt/yr – 20 burnners) - a thermal cracker (3 Mt/yr – 120 burnners) - a HDS unit (12 burnners)</td>
<td>Pre-evaluation step: average for the overall + project involving 152 burnners (early 2007) Cost per individual burner: - GPD 16 200 - GPD 17 200</td>
<td>Does not include the general upgrading of the air, fuel and control systems. For the CDU unit: assumes a 5-year operation life: - GPD 639 per t.y (141 t/yr NOx saved) - GPD 472 per t.y (202 t/yr NOx saved)</td>
</tr>
<tr>
<td>3b/Retrofit several process heaters operated in units including finally: - a CDU (10 Mt/yr – 20 burnners) - an alkylation unit (0.4 Mt/yr – 6 burnners) - a VDU (7 Mt/yr – 16+13 burnners) - HDS units (12 + 12 burnners)</td>
<td>Updated evaluation step from 2A above (preliminary design): average for the overall final project involving 79 burnners (early 2009) Cost per individual burner: - GPD 40 000</td>
<td>Include the general upgrading of the air, fuel and control systems For the CDU unit: assuming a 5-year operation life: - GPD 644 per t.y (202 t/yr NOx saved)</td>
</tr>
<tr>
<td>4/Retrofit 20 low-NOx burners on a visbreaker furnace in 2008</td>
<td>Total burners cost alone: EUR 140 000 (EUR 7 000/burner) Total installation cost: EUR 756 000</td>
<td>Additional cost for burners installation: + EUR 37 800/burner in average (+ 540 % of burner individual cost)</td>
</tr>
</tbody>
</table>

The comparison between examples 2 and 3 show very clearly that given the small cost difference, an ultra low-NOx burner can be an excellent cost-effective option when it is possible to retrofit on a high-power installation, compared to low-NOx burners.

Potential investment and operational cost, expressed as total annual costs, for implementing this technique in 2007 on RFG and natural gas-fired process heaters in the Colorado refineries (US) were estimated as follows:

- For low-NOx burners: EUR(\(^\prime\)) 2818 (USD 3817) per year and tonne of NOx saved, avoided, assuming a resulting NOx emission decrease of 28 – 50 %;
- For ultra low-NOx burners (first generation): EUR(\(^\prime\)) 4087 (USD 5536) per year and tonne of NOx saved, avoided, assuming a resulting NOx emission decrease of 55 %;
- For ultra low-NOx burners (last generation): EUR(\(^\prime\)) 613 to 908 (USD 831 to 1230) per year and tonne of NOx saved, avoided, assuming a resulting NOx emission decrease of 75 – 85 %.

\(^\prime\) Based on currency conversion rate of 0.73822 on 1/07/2007
Driving force for implementation
Reduction of NO\textsubscript{x} emissions in combination with good cost-benefit conditions. When it is proved to be possible, this reduction is most often reached with good cost-benefit conditions.

Example plants
There are many examples of applications in European refineries. At Preem Lysekil (SE), low-NO\textsubscript{x} burners are used in 16 of 21 furnaces and boilers. For the Shell Gothenburg (SE) refinery, 85% of the furnaces are equipped with low NO\textsubscript{x} burners.

Reference literature
[17, Jeavons and Francis 2008] [36, CONCAWE n°4/09 2009].

4.10.4.2 Dry low-NO\textsubscript{x} combustors

Description
More information can be found in the LCP BREF [7, EC 2006].

Achieved environmental benefits
A 90% reduction in NO\textsubscript{x} emissions in natural gas-fired gas turbine applications are possible. Note for TWG: please provide any useful information for updating this table.

Table 4.51: NO\textsubscript{x} emissions achieved with dry low-NO\textsubscript{x} combustors for different types of equipment

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Fired Heaters</th>
<th>Boilers</th>
<th>Gas Turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>NA</td>
<td>NA</td>
<td>[50–100 (40–60)]</td>
</tr>
<tr>
<td>Light fuel oil</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

NB: Data in mg/Nm\textsuperscript{3} at 15% O\textsubscript{2} (g/GJ). n/a: not applicable

(^*) Source [7, EC 2006]

Cross media effects
None in particular.

Operational data
Dry combustors differ from burners as their performance increases with higher loads.

Applicability
Applicable to gas turbines. Dry low-NO\textsubscript{x} combustors are not available for gas turbines fired with refinery blend gas that contains more than 5 to 10% v/v of hydrogen.

Economics
The investment cost is EUR 2.2 million (1998) and the operating cost is nil for an 85 MW\textsubscript{e} output turbine.

Driving force for implementation
Reduction of NO\textsubscript{x} emissions.

Reference literature
[115, CONCAWE, 1999], [316, TWG, 2000].
4.10.4.3 Flue-gas recirculation

Description
External flue-gas recirculation (FGR) is applied to boilers and heaters to increase the diluent effect, hence to reduce combustion temperature. Typically 20 % of the available flue-gas from the boiler stack is ducted to mix with fresh combustion air.

Achieved environmental benefits
Using recirculated flue-gas as part of the combustion air can further reduce NOx formation. Note for TWG: please provide any useful information for updating this table. No info provided.
It is proposed to delete the table.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Fired Heaters</th>
<th>Boilers</th>
<th>Gas Turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Light fuel oil (LCO)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 4.52: NOx emissions achieved with flue gas recirculation for different types of equipment

Operational data
The process is difficult to control especially during turndown.

Applicability
It is applied to boilers and fired heaters. In a boiler retrofit (in particular boilers and furnaces in forced draught mode operation), FGR increases hydraulic loads, and shifts the heat load towards the convective section(s) and may not be practical.

Economics
Higher cost than other primary measures.

Driving force for implementation
To reduce the NOx emissions from boilers and heaters.

Reference literature
[115, CONCAWE, 1999], [316, TWG, 2000].

4.10.4.4 Diluent injection

Description
Inert diluents, such as flue-gas, steam, water and nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NOx in the flue-gases.

Achieved environmental benefits
Control of NOx in gas turbine combustors may be carried out by using steam/water injection, which can achieve reduction performances of 80 - 90 %.
Note for TWG: please provide any useful information for updating this table. No info provided.
It is proposed to delete the table.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Fired Heaters</th>
<th>Boilers</th>
<th>Gas Turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>NA</td>
<td>NA</td>
<td>50 - 80</td>
</tr>
<tr>
<td>Light fuel oil</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

NB: Data in mg/Nm³ at 15 % O₂
Chapter 5

Cross-media effects

Energy required to produce steam, higher emissions of CO and hydrocarbons. When extra energy is required to produce steam, it could result in higher emissions and reduction of the overall system efficiency.

Operational data
The use of steam generates more corrosion in the system than the use of nitrogen.

Applicability
Steam and water injection is widely applied to gas turbines both in new installations and retrofits and is also applicable to fired heaters and boilers (see also Section 4.10.5.2). There are technical difficulties in applying water injection in boilers and furnaces. Nitrogen dilution is only applied when nitrogen is already available in the refinery.

Economics
Capital costs of the steam and water injection is less than that of SCR, making the technology a good first choice for substantial levels of NO\textsubscript{x} reductions, with SCR often added on if higher NO\textsubscript{x} reduction is needed. Substantial recurring operating costs are, however, encountered for producing high-purity steam, and maintenance costs for re-blading may be high.

Note to TWG: It is proposed to delete the table and text if not updated with real current data

<table>
<thead>
<tr>
<th>Cost relates to a 85 MW output turbine</th>
<th>NO\textsubscript{x} control for gas turbines firing refinery blend gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment cost (1998) (EUR million)</td>
<td>3.4</td>
</tr>
<tr>
<td>Operating costs per year (excludes capital charge) (EUR million)</td>
<td>0.8</td>
</tr>
<tr>
<td>Cost-effectiveness</td>
<td></td>
</tr>
<tr>
<td>EUR per tonne NO\textsubscript{x} removed (incl. capital charge at 15 %)</td>
<td>1500</td>
</tr>
</tbody>
</table>

Other sources show that operating costs in a gas turbine using 80 t/h steam injection would cost EUR 0.9 million per year.

Driving force for implementation
Reduction of NO\textsubscript{x} emissions.

Example plants
By-product nitrogen from the air separation plant in refinery residue gasification projects has recently been proven commercially demonstrated as a diluent for gas turbine NO\textsubscript{x} reduction. Within the refining industry, steam injection predominates.

Reference literature
[112, Foster Wheeler Energy, 1999], [115, CONCAWE, 1999], [268, TWG, 2001]

4.10.4.5 Fuel staging (reburning)

Description
Fuel staging, also called reburning, is based on the creation of different zones in the furnace by staged injection of fuel and air. The aim is to reduce NO\textsubscript{x} emissions, which have already been formed back into nitrogen. This technique adds to the flame cooling a reaction by which organic radicals assist in the breakdown of NO\textsubscript{x}. More information is available in the LCP BREF [7, EC 2006].
Achieved environmental benefits
Achievable levels are <100 ppm 200 mg/Nm³ NO₂ equivalent, specially for gas firing for which the lowest levels are more easily achievable.

Cross-media effects
Additional energy consumption (estimated at around 15 % without any complementary energy recovery).

Applicability
This technique is applied at the furnace or boiler burner level but it is strongly connected with the burner technique. It is widely used for gas firing. For mixed or liquid firing, a specific burner design is required.

Driving force for implementation
Reduction of NOₓ emissions.

Reference literature
[112, Foster Wheeler Energy, 1999].

4.10.4.6 Selective non-catalytic reduction (SNCR)
TWG KOM conclusion 5.2: TWG to provide info for updating Section 4.10 on real examples of application of SCR and SNCR for combustion or conversion processes.

Operational data expected from AT, NL, SE.

Italy/AGIP for Gela Refinery

Description
This technique also called THERMAL deNOₓ reduces the NOₓ that has been formed in the combustion process. This process is a non-catalytic process which utilises ammonia or urea to reduce NOₓ to nitrogen and water. More information can be found in Section 4.25.3. See Section 4.25.3.2 below.

Achieved environmental benefits
In oil refining, reductions of NOₓ between 40 % and from 25 % up to 70 % have been demonstrated under favourable conditions for full-size combustion plants.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Fired Heaters</th>
<th>Boilers</th>
<th>Gas Turbines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery fuel gas</td>
<td>150 - 200</td>
<td>150 - 200</td>
<td>n/a</td>
</tr>
<tr>
<td>Light fuel oil (0.3 % N)</td>
<td>150 - 300</td>
<td>150 - 300</td>
<td>n/a</td>
</tr>
<tr>
<td>Heavy fuel oil (0.8 % N)</td>
<td>200 - 400</td>
<td>200 - 400</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 4.54: NOₓ emissions achieved with SNCR for different types of equipment

Cross-media effects
General cross-media effects are described in Section 4.25.3.2 below.

Risk of NH₃ or urea emissions (storage and non-reacted). Turndown is a problem.

The emissions of N₂O may be increased by this technique.

In the particular context of oil refining, effects given below are to be noticed.

- The use of urea causes higher emissions of CO and N₂O and can cause high temperature corrosion.
- A side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphate deposits give rise to the fouling and corrosion of cooler downstream equipment. Ammonium sulphate can also result in aerosol emissions from the stack and contribute to PM emissions.
Chapter 5

The storage and use of gaseous or liquefied anhydrous ammonia has a great hazardous potential. However, the refinery safety management system is normally designed for taking this into account, in addition to hazards generated by other toxic substances (e.g. \( \text{H}_2\text{S} \), or eventually \( \text{HF} \) used for alkylation) and by flammable gases and liquids. If such storage is impossible to avoid, risk assessment should be carried out and appropriate prevention measures are required. When technically possible, a liquid solution of ammonia (25 %) is should always be preferred.

- Flue-gas temperature drops after urea or ammonia injection, which penalise the energy recovery potential.

Operational data

More information can be found in 4.25.3.2.

Table 4.55 gives some illustrating examples of this, for 3 boilers operated in oil refineries.

<table>
<thead>
<tr>
<th>Reference [Questionnaire]</th>
<th>Thermal capacity</th>
<th>Fuel type</th>
<th>% N in liquid fuel</th>
<th>% liquid fuel/total</th>
<th>Inlet concentration</th>
<th>% NO(_x) abatement</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>[no 13] 98 MW Mixed</td>
<td>0.40 – 0.50</td>
<td>30 – 95</td>
<td>244 – 810</td>
<td>25 – 40</td>
<td>-40 % only obtained for specific boiler load</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[no 15] 45 MW Mixed</td>
<td>0.34 – 0.45</td>
<td>80 – 95</td>
<td>667 – 877</td>
<td>25 – 30</td>
<td>Ammonia slip &gt;15 ppm for &gt;30 % abatement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[no 15] 45 MW Mixed</td>
<td>0.34 – 0.45</td>
<td>70 – 90</td>
<td>568 – 780</td>
<td>25 – 30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NB: Emissions in mg/Nm\(^3\) at 3 % \( \text{O}_2 \) (dry gas)

Data based on CONCAWE 4/09 a continuous emission monitoring system for reference No XX

These figures are consistent with a urea test performed from 2008 – 2009 in a French refinery on a 99 MW boiler. In the 104 t/h flue-gas stream containing 600 – 800 mg/Nm\(^3\) (3 % \( \text{O}_2 \) dry) of NO\(_x\), the initial urea injection rate was 150 – 200 l/h, corresponding to approximately 1 kg urea per kg NO\(_x\) to be treated. NO\(_x\) reduction achieved was 35 – 45 % with concentrations in the range 380 – 400 mg/Nm\(^3\). However, after some tube perforations due to corrosion, the injection rate was reduced and then stopped for the injection conditions being modified and optimised.

At the Gothenburg Shell refinery (SE), it is reported that an SNCR operating at one boiler (XX MW) achieves the following reductions:

- from 300 to 150 mg/Nm\(^3\) for gas firing
- from 1 100 to 550 for oil firing.

Applicability

SNCR requires temperatures above 650 °C within the following window:

- 850 – 1000 °C for ammonia and caustic ammonia (optimum 870 °C)
- 800 – 1100 °C for urea (optimum 1000 °C).

The retrofitting to existing boilers and furnaces can be limited as there may not be enough residence time (0.2 to 0.5 s in the region of injection) at the required temperature levels.

Thus, application of the SNCR technique in existing furnaces and boilers requires well chosen injection locations and a mixing region with an appropriate temperature and size to allow for sufficient NO reduction.
Application is also complicated when flue-gases to treat come from the combustion of high sulphur content heavy fuel oil for which ammonia slips can lead to the formation of ammonium sulphate deposits. When retrofitting, new space requirements are very limited and are mainly restricted to ammonia storage and injection equipment.

Economics
Note to TWG: Table 4.56 shows the economics of the application of SNCR for the treatment of flue-gases coming from the combustion processes from different sources. Any update?

Table 4.56: Examples and main cost factors for a Selective Non Catalytic Reduction (SNCR)

<table>
<thead>
<tr>
<th>Values corresponding to a 100 GJ/h installation - retrofit of existing installation</th>
<th>Fired heaters and boilers firing refinery blend gas</th>
<th>Boilers firing residual fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Down to ppm at 3 % O₂</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Investment (1998) (EUR million)</td>
<td>0.4 - 0.5</td>
<td>0.4 - 0.9</td>
</tr>
<tr>
<td>Operating costs per year (excludes capital charge) (EUR million)</td>
<td>0.025</td>
<td>0.05 - 0.07</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Capacity of the refinery</th>
<th>5</th>
<th>Mt/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel consumption</td>
<td>120000 (liquid refinery fuels), 180000 (refinery fuel gas)</td>
<td>t/yr</td>
</tr>
<tr>
<td>Volume of the flue-gas</td>
<td>3 (10^9)</td>
<td>Nm³/yr</td>
</tr>
<tr>
<td>Efficiency of the SNCR</td>
<td>60 - 80.</td>
<td>%</td>
</tr>
<tr>
<td>NOₓ emissions (as NO₂)</td>
<td>200</td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Investment cost</td>
<td>3 – 5</td>
<td>EUR million</td>
</tr>
<tr>
<td>Operating costs</td>
<td>0.2 - 1</td>
<td>EUR million/yr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cost parameters</th>
<th>EUR/unit</th>
<th>EUR/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating hours (h/yr)</td>
<td>8000</td>
<td></td>
</tr>
<tr>
<td>Investment costs (EUR)</td>
<td>1 090 093</td>
<td></td>
</tr>
<tr>
<td>Input factors for annual expenditure:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of years</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Interest rate (%)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Annual repayment incl. Interest (EUR/yr)</td>
<td>112 239</td>
<td></td>
</tr>
<tr>
<td>Proportional investment incl. Interest</td>
<td>112 239</td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (% of investment costs)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (EUR/yr)</td>
<td>21 802</td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear</td>
<td>21 802</td>
<td></td>
</tr>
<tr>
<td>Electrical energy (kWh/h)</td>
<td>40</td>
<td>0.07 EUR/kWh</td>
</tr>
<tr>
<td>Air (Nm³/h)</td>
<td>1200</td>
<td>0.01 EUR/Nm³</td>
</tr>
<tr>
<td>NH₃ liquid (kg/h)</td>
<td>83.15</td>
<td>0.25 EUR/kg</td>
</tr>
<tr>
<td>Total cost</td>
<td>442 774</td>
<td></td>
</tr>
</tbody>
</table>

NB: Installation on a volume of exhaust gas of 250 000 Nm³/h after a power plant in a refinery achieving a NOₓ emission reduction of 500 mg/Nm³ in relation to actual oxygen content and for a clean gas concentration of <200 mg NOₓ/Nm³.
Chapter 5

Potential investment and operational costs for implementing this technique in 2007 on process heaters in the Colorado refineries (US) were estimated at EUR(*) 3 644 (USD 4936) per year and tonne of NO\textsubscript{x} avoided, assuming a resulting NO\textsubscript{x} emission decrease of 43 – 60 %. This seems overvalued with respect to the recent data. Another set of data gathered during an applicability test on a French refinery site (see details under operational data) leads to less expensive costs as shown in Table 4.57 below.

Table 4.57: Cost evaluation for urea SNCR retrofitting of a 99 MW refinery boiler (2009)

<table>
<thead>
<tr>
<th>Urea SNCR retrofitting costs to a 99 MW boiler</th>
<th>Costs (EUR)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Investment cost</strong></td>
<td>500 000</td>
<td></td>
</tr>
<tr>
<td><strong>Operational costs:</strong></td>
<td>539 000</td>
<td></td>
</tr>
<tr>
<td>Including:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urea 200 l/h</td>
<td>376 000</td>
<td>(Excluding capital charges)</td>
</tr>
<tr>
<td>Equipment rental</td>
<td>100 000</td>
<td>EUR 190/t – 1980 t/yr</td>
</tr>
<tr>
<td>Energy for vaporisation (40 % urea in water)</td>
<td>55 000</td>
<td>180 kW estimated</td>
</tr>
<tr>
<td>maintenance</td>
<td>8 000</td>
<td>120 hours</td>
</tr>
<tr>
<td>Inlet concentration: 700 mg/Nm\textsuperscript{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outlet concentration: 420 mg/Nm\textsuperscript{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduction 40 % NO\textsubscript{x}: 330 t/yr</td>
<td>EUR/t of NO\textsubscript{x} 1 935</td>
<td></td>
</tr>
<tr>
<td><strong>Specific cost for 2009</strong></td>
<td></td>
<td>37.7 kg/h</td>
</tr>
</tbody>
</table>

Driving force for implementation
Reduction of NO\subscript{x} emissions.

Example plants
This process has been applied to heaters and boilers of refinery plants. The experience of application of SNCR on oil-fired heaters is more limited. A US study reports that SNCR is less used less frequently than SCR for the control of NO\subscript{x} and that only 12 of the 150 boilers/heater installations of 8 refineries use this type of technique. In the EU, for example, Shell refinery in Gothenburg (SE) operates an SNCR on one boiler.

Reference literature
[107, Janson, 1999], [115, CONCAWE, 1999], [45a, Sema and Sofres, 1991], [250, Winter, 2000], [348, Ashworth Leininger Group, 2001] [17, Jeavons and Francis 2008] [36, CONCAWE n°4/09 2009] [Questionaire n° 13].

4.10.4.7 Selective catalytic reduction (SCR)
TWG KOM conclusion 5.2: TWG to provide info for updating Section 4.10 on real examples of application of SCR and SNCR for combustion or conversion processes
Operational data expected from AT, NL, SE.

Description
Another secondary technique is known as catalytic deNO\subscript{x}. As in THERMAL deNO\subscript{x}, ammonia is used to reduce the NO\subscript{x} to nitrogen and water vapour. The ammonia vapour is mixed with the flue gas and the mixture passed through a catalyst to complete the reaction. More information can be found in Section 4.25.3.
See Section 4.25.3.3 below.

(*) based on currency conversion rate of 0.73822 at 1/07/2007
Achieved environmental benefits

SCR is capable of reducing NO\textsubscript{x} by 90–94 \% in refining boilers and heater applications, as well as for gas turbine flue-gases.

Note for TWG: All other information is transferred to operational data section.

Cross-media effects

Generic cross-media effects are described in Section 4.25.3.3 below.

Risk of NH\textsubscript{3} emissions when operating outside stoichiometric conditions and catalyst disposal. The risk of ammonia emissions during storage of gaseous ammonia can be minimised if ammonia is stored and used as an aqueous solution (25 \%). It may increase the emissions of N\textsubscript{2}O. Operational slip of NH\textsubscript{3} is around 5 ppm, a value that normally increases during the catalyst’s lifetime. A side reaction of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphates give rise to deactivation of the catalyst and to fouling and corrosion of downstream equipment.

In the particular context of oil refining, the effects given below are to be noticed.

- As for the SNCR technique, a side effect of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphate deposits give rise to the fouling and corrosion of cooler downstream equipment. Ammonium sulphate can also result in aerosol emissions from the stack and contribute to PM emissions.
- As for the SNCR, the storage and use of gaseous or liquefied anhydrous ammonia has a great hazardous potential adding to hazards generated by other toxic substances (e.g., H\textsubscript{2}S or eventually HF used for alkylation) and by flammable gases and liquids. If such storage is impossible to avoid, risk assessment should be carried out and appropriate prevention measures are required. The refinery safety management system should take it into account. When technically possible, a liquid solution of ammonia (25 \%) is should be preferred.

Operational data

More information can be found in 4.25.3.2.

At a Shell refinery (SE), an SCR unit has been installed at a 68 MW boiler (1998). The unit was put into operation in October 1998. Fuel oil is used and NO\textsubscript{x} emissions are 16 mg/MJ (55 mg/Nm\textsuperscript{3}, 3 \% O\textsubscript{2}). The NO\textsubscript{x} reduction is about 94 \% and the ammonia slip well below 5 ppm. (68 MW). Preem Lysekil (SE) has an SCR on the FCC (see Section 4.5.8.1). Preem refinery Gothenburg (SE) has two SCRs, on the reformer and one on of the two crude distillation units.

At the STEAG power station (Total Raffinerie Mitteldeutschland in Germany), the three oil-fired heaters (each producing 160 t/h steam -100 bars - 505 °C, consuming 12 t/h of heavy fuel oil at 3.7 \% S) are equipped with an SCR plant (high-dust); they have to reach NO\textsubscript{x} emissions below 150 mg/m\textsuperscript{3}.

Table 4.58 below gives more data concerning the power plant in the Mider refinery this particular example.

<table>
<thead>
<tr>
<th>Parameters (yearly average 2009)</th>
<th>Raw gas</th>
<th>Clean gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue-gas volume, wet (m\textsuperscript{3}/h, 7 % O\textsubscript{2})</td>
<td>171 690</td>
<td>188 249</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>&lt;180</td>
<td>&lt;76</td>
</tr>
<tr>
<td>Dust (mg/Nm\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>220</td>
<td>&lt;10</td>
</tr>
<tr>
<td>NO\textsubscript{x} as NO\textsubscript{2} (mg/Nm\textsuperscript{3}, 3 %O\textsubscript{2})</td>
<td>800</td>
<td>&lt;150</td>
</tr>
<tr>
<td>SO\textsubscript{2} (mg/Nm\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>&lt;4 100</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{2} (mg/Nm\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td>650</td>
<td>&lt;10</td>
</tr>
<tr>
<td>SO\textsubscript{x} as SO\textsubscript{2} (mg/Nm\textsuperscript{3}, 3 % O\textsubscript{2})</td>
<td></td>
<td>&lt;220</td>
</tr>
</tbody>
</table>
Moreover, CONCAWE reports two other datasets on SCR in refineries, one covering a mixed gas/oil fired heater, and the other covering a common stack of four mixed gas/oil fired boilers. In both cases, a 80–82% removal is shown, resulting in a 90–120 mg/Nm$^3$ outlet concentration (3 % O$_2$).

Finally, one recent example of SCR has been reported for a 19 MW refinery gas turbine application in France. After the operation restarted in 2009, first results showed a 80 % NO$_x$ decrease from concentrations registered before (max. 350 mg/Nm$^3$) to new maximum concentrations measured below 65 mg/Nm$^3$ (15 % O$_2$). A 2 % loss was reported on generated power.

**Applicability**

The application of this technology to existing process furnaces can be limited by problems of space, pressure and temperature. However SCR is considered in California technologically feasible in boilers and heaters.

Section 4.25.3.3 below gives general considerations on the usual constraints for the retrofitting of the SCR technique to existing combustion plants, notably in terms of space availability, temperature and pressure drop.

In the particular case of boilers and heaters of refineries fired with heavy fuels, Oil fly-ash contains metal oxides, soot and coke. Unabated fly-ash concentrations for oil firing are in the range of 100 – 600 mg/Nm$^3$ (with the highest values corresponding to vacuum residues). SCR applied under these conditions may suffer from clogging by fly-ash and sulphates (with coal firing, the sandblasting effect of the fly-ash keeps the catalyst clean). The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 – 4 %).

NO$_x$ removal efficiency will also depend on the NO$_x$ inlet concentration to be abated, because even under optimal thermal conditions, there is a lower limit to the technically achievable reduction yield and outlet concentration due to the particular mixing conditions and chemical kinetics.

**Economics**

The costs of SCR range, depending on the fuels, exhaust volume and required NO$_x$ reduction. For new power generation installations, the cost range may be EUR 25 – 110/kW for new power generation installations. Maintenance costs are minimal, the bulk of which are from NH$_3$ consumption.

<table>
<thead>
<tr>
<th>NO$_x$ reduction %</th>
<th>Heaters and boilers firing refinery blend gas</th>
<th>Boilers firing residual fuel oil</th>
<th>Gas turbines firing natural or refinery blend-gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Down to mg/Nm$^3$ @ 3 % O$_2$ (15 % O$_2$ for gas turbines)</td>
<td>90</td>
<td>75</td>
<td>90</td>
</tr>
<tr>
<td>Investment cost (1998) (EUR million)</td>
<td>2.8 – 3.2</td>
<td>2.4 – 3.4</td>
<td>4.9 – 5.4</td>
</tr>
<tr>
<td>Operating costs per year (excludes capital charge) (EUR million)</td>
<td>0.15</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

For retrofitting situations, two examples of the application of SCR in refinery power plants are shown in Table 4.59 and Table 4.60. The use of an SCR unit after for treating the power plant flue-gas has been estimated in raw gas (
Table 4.60) and clean gas (Table 4.59) operation mode. These two cost tables refer to the Total Raffinerie Mitteldeutschland project in the two cases already mentioned, for which performance data are provided in Table 4.58.

Table 4.59: Main cost factors for a Selective Catalytic Reduction (SCR) on clean gas operation

<table>
<thead>
<tr>
<th>Cost details (clean gas operation) in 1998</th>
<th>EUR/unit</th>
<th>EUR/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating hours (h/yr)</td>
<td>8000</td>
<td></td>
</tr>
<tr>
<td>Investment (EUR)</td>
<td>3 270 278</td>
<td></td>
</tr>
<tr>
<td>Input factors for annual expenditure:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of years</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Interest rate (%)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Annual repayment incl. interest (EUR/yr)</td>
<td>336 717</td>
<td></td>
</tr>
<tr>
<td>Proportional investment costs incl. interest</td>
<td>336 717</td>
<td></td>
</tr>
<tr>
<td>Volume of catalyst (m³)</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Endurance (years)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Renewal-Renewal of catalyst (m³/yr)</td>
<td>1.33</td>
<td>14 535 EUR/m³</td>
</tr>
<tr>
<td>Average Renewal renewal of catalyst (EUR/yr)</td>
<td>19 379</td>
<td></td>
</tr>
<tr>
<td>Catalysts</td>
<td>19 379</td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (% of investment costs)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (EUR/yr)</td>
<td>65 406</td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear</td>
<td>65 406</td>
<td></td>
</tr>
<tr>
<td>Pressure drop (mbar)</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Energy for reheating (MJ/h)</td>
<td>343210</td>
<td></td>
</tr>
<tr>
<td>Electrical energy (kWh/h)</td>
<td>319187</td>
<td></td>
</tr>
<tr>
<td>NH₂ liquid (kg/h)</td>
<td>94 001</td>
<td></td>
</tr>
<tr>
<td>Total costs (1998)</td>
<td>1 177 900</td>
<td></td>
</tr>
</tbody>
</table>

NB: Installation on a volume of exhaust gas of 250 000 Nm³/h in the dedusted off-gas after a power plant in a refinery achieving a NOₓ emission reduction of 500 mg/Nm³ in relation to actual oxygen content and for a clean gas concentration of <100 mg NOₓ/Nm³.

Table 4.60: Main cost factors for a Selective Catalytic Reduction (SCR) on raw gas operation

<table>
<thead>
<tr>
<th>Cost details (raw gas operation) in 1998</th>
<th>Quantity</th>
<th>EUR/unit</th>
<th>EUR/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating hours (h/yr)</td>
<td>8 000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investment costs (EUR)</td>
<td>2 180 185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Input factors for annual expenditure:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of years</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interest rate (%)</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual repayment incl. interest (EUR/yr)</td>
<td>224 478</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proportional investment costs incl. interest</td>
<td>224 478</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume of catalyst (m³)</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endurance (years)</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Renewal-Renewal of catalyst (m³/yr)</td>
<td>4.38</td>
<td>14 535 EUR/m³</td>
<td></td>
</tr>
<tr>
<td>Average Renewal renewal of catalyst (EUR/yr)</td>
<td>63 589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalysts</td>
<td>63 589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (% of investment costs)</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear (EUR/yr)</td>
<td>43 604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maintenance + wear and tear</td>
<td>43 604</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure drop (mbar)</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy for reheating (MJ/h)</td>
<td>0</td>
<td>3.63 EUR/GJ</td>
<td></td>
</tr>
<tr>
<td>Electrical energy (kWh/h)</td>
<td>83 753</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₂ liquid (kg/h)</td>
<td>94 001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total costs (1998)</td>
<td>509 425</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NB: Installation (raw gas) on a volume of exhaust gas of 250 000 Nm³/h after a power plant in a refinery achieving a NOₓ emission reduction of 500 mg/Nm³ in relation to actual oxygen content and for a clean gas concentration of <100 mg NOₓ/Nm³.
Table 4.61 illustrates another retrofitting cost example for the reformer furnace of the Swedish Preem refinery, also in 1998.

Note to TWG: Table 4.61 clarified and updated with data from SE

Table 4.61: Investment cost for a SCR retrofitting to a reformer furnace (1998)

<table>
<thead>
<tr>
<th>Data</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>68 MW</td>
</tr>
<tr>
<td>Efficiency (design)</td>
<td>94.90 % Design for low temperature: 185 ºC Ammonia slip of 5 ppm</td>
</tr>
<tr>
<td>Efficiency (operational)</td>
<td>91 % Designed for low temperature: 185 ºC Ammonia slip of 5 ppm</td>
</tr>
<tr>
<td>Investment cost (1998)</td>
<td>EUR 3.2 million</td>
</tr>
</tbody>
</table>

Moreover, potential investment and operational costs for implementing this technique in 2007 on existing boilers and process heaters in Colorado refineries (US) were estimated at a range of EUR(*) 2000 to 6054 (USD 2708 to USD 8201) per year and tonne of NOx saved, assuming a resulting NOx emission decrease of 70 – 90 %.

For retrofitting a 19 MW refinery gas turbine in France, the following costs were reported:

- total construction cost (2008): EUR 7 million
- annual cost: EUR 200 000.

Driving force for implementation
Reduction of NOx emissions.

Example plant(s)
Concerning refinery energy systems, SCR has been applied to FCC off-gases, gas turbines, process boilers, process heaters such as naphtha reformers, steam reformers, crude and vacuum distillation units, thermal cracking and hydroprocessing units. SCR has been also successfully applied to gas streams with high particulate content in high sulphur coal-fired utility industry and FCC units combined with upstream particulate removal. A report on US refineries shows that 20.7 % (or 31 boilers/heaters) of 150 boiler/heater installations at 8 refineries employ SCR as a control technique. The same study shows that three SCR installations have been applied to the four turbines found in the eight refineries analysed.

Reference literature
[181, HP, 1998], [107, Janson, 1999], [45a, Sema and Sofres, 1991], [250, Winter, 2000], [115, CONCAWE, 1999], [348, Ashworth Leininger Group, 2001], [17, Jeavons and Francis 2008], [36, CONCAWE n°4/09 2009 ], [Questionnaire n° 9].

(*) Based on currency conversion rate of 0.73822 at 1/07/2007
Chapter 4

4.10.4.8 DeNO\textsubscript{x} scrubbing

Description
A separate spray tower is usually required prior to the main SO\textsubscript{2} absorption spray tower. An additive applied in this extra tower oxidises the NO to NO\textsubscript{2}, which is then absorbed with the SO\textsubscript{2}. The reaction for the absorption of NO\textsubscript{2} is \(3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}\).

Achieved environmental benefits
Reduction of NO\textsubscript{x} emissions.

Cross-media effects
If using wet gas scrubbing, slurry can be expected as a solid waste from this process. Nitrates generated should be treated in the WWTP. Because the gas effluent from this process generates NO\textsubscript{x}, it may need further reduction of NO\textsubscript{x} emissions.

Economics
Wet deNO\textsubscript{x} scrubbing has advantages including lower capital costs, if installed in conjunction with SO\textsubscript{2} wet gas scrubbing.

Driving force for implementation
Reduction of nitrogen oxides emissions.

Examples
It is normally used in nitric acid production.

Reference literature
[108, USEPA, 1995].

Note to TWG: Proposed to delete as no example has been reported in a refinery energy system.

4.10.4.9 Low temperature oxidation

Description
See Section 4.25.3.1

Achieved environmental benefits
Reduction of NO\textsubscript{x} emission by XX %, with an outlet concentration reduced to 10 ppm.
See Section 4.25.3.1

Cross-media effects
Low temperature oxidation (LoTO\textsubscript{x}) should be necessarily associated with a new or existing scrubbing unit, which generates waste water to be treated properly. An increase in nitrate load to the existing WWTP might have to be considered. Nitric acid is produced and needs to be neutralised with an alkali used in the scrubbing section.

In order to oxidise the NO\textsubscript{x} to soluble higher oxides, ozone is required and should be generated on site using an ozone generator, which consumes oxygen and electrical energy.

Operational data
NO\textsubscript{x} removal performance is directly linked to the ozone injection rate. It can be regulated on a real-time basis in relation to the NO\textsubscript{x} outlet concentration target. The outlet NO\textsubscript{x} can be adjusted by varying the set point on the system controller. In Figure XXX below, Reported values show that the control level the set point was set up in order to respect the permit conditions of 20 ppm.
Applicability
The LoTOx process operates optimally above 150 °C and does not require heat input to maintain operational efficiency, enabling maximum heat recovery from the flue-gas. Applicable to both new and retrofitted applications;

Economics
No data available

Driving force for implementation
Demands for very low-NOx emissions in the case of installations either already equipped with a wet scrubbing system or aimed at being treated with such.

Example plants
There have been examples of applications since 1997 in the US for two small gas-fired boilers (California) and one coal fired 25 MW power plant (Ohio).

Reference literature
[18, Confuorto 2007].

4.10.4.10 Catalytic reduction of CO and NOx

Description
The technology uses a single platinum-based catalyst coated with potassium carbonate (K₂CO₃) that operates in two cycles: oxidation/absorption and regeneration. The catalyst works by simultaneously oxidising CO to CO₂, NO to NO₂, and then absorbing NO₂ onto its surface through the use of a potassium-carbonate absorber coating. The regeneration of the catalyst is accomplished by passing a controlled mixture of regeneration gases across the surface of the catalyst in the absence of oxygen. The regeneration gases are steam, hydrogen and carbon dioxide. Consequently the nitrates are reduced to nitrogen. An additional catalyst layer is required to reduce SO₂ emissions and preserve the CO- and NOx-reducing catalyst when sulphur is present in the fuel.

Because the regeneration cycle should take place in an oxygen-free environment, a section of catalyst undergoing regeneration must be isolated from exhaust gases. This is accomplished using a set of louvers, one upstream of the section being regenerated and one downstream. During the regeneration cycle, these louvres close and a valve opens, allowing regeneration gas into the section.
Achieved environmental benefits

By using this technique, combined cycle gas turbines can be operated with very low-NO\textsubscript{x} emissions levels. At the same time, the system reduces emissions of CO and non-methane volatile organic compounds. It uses no ammonia. In conjunction with a sulphur-removal catalyst technique this system can also be used for reducing sulphur compounds from exhaust gas if required. Achievable levels are the following:

- NO\textsubscript{x} emissions below 2 ppm (4 mg/Nm\textsuperscript{3} as NO\textsubscript{2} at standard conditions 0 °C; 1013 mbar)
- conversion rate of CO into CO\textsubscript{2} is 90 %;
- destruction of non-methane volatile organic compounds (NMVOC) is greater than 90 % at 315 °C;
- destruction of formaldehyde and acetaldehyde has been measured at 97 % and 94 % respectively at 150 °C.

Cross-media effects

The catalyst is very susceptible to fouling by sulphur in the flue-gas and may need an additional specific sulphur absorption catalyst. The system emits CO\textsubscript{2}, H\textsubscript{2}O, N\textsubscript{2} and trace levels of SO\textsubscript{2} to the stack. Due to the masking and poisoning of the catalyst, annual or every 6 months catalyst cleaning is required with de-ionised water and a potassium-carbonate solution (K\textsubscript{2}CO\textsubscript{3}). The spent cleaning fluids can be neutralised and disposed of through the sewerage system and are harmless to the water and soil. Precious metals on the spent catalyst have a residual value and can be reclaimed. There is no waste disposal issue caused by spent catalyst.

Operational data

This system requires electricity for control systems, valves and actuators, natural gas for regeneration gas production and steam both for regeneration gas production and as a dilution carrier. The typical pressure drop is between 8.5 mbar and 15 mbar. The system can operate...
effectively at temperatures ranging from 150 °C to 370 °C. The utility requirements for a 25 MW gas turbine are steam (333 to 389 °C): 1590 kg/h and natural gas: 14 kg/h.

The US EPA has stated its concerns (19 November 1999 letter) over the technical uncertainties of such a technique, especially about applying it to large combined cycle turbines.

Applicability
Applicable to both new and retrofitted applications, the system can operate effectively at temperatures ranging from 150 °C to 370 °C and does not limit gas turbine performance. Such a unit can be installed at the back of the boiler or in the heat recovery steam generator within the same envelope reserved for a conventional SCR system.

Economics
The estimated cost numbers presented refers to a typical 400 MW size combined-cycle gas-fired power plant. The cost estimate numbers below are based on 8000 h/yr of operation and a NO\textsubscript{x} reduction from 25 ppm to 5 ppm (50 to 10 mg/Nm\textsuperscript{3} as NO\textsubscript{2} at standard conditions 0 °C; 1013 mbar), which equals approximately 666 tonnes annually of NO\textsubscript{x} removed. Included in the numbers are investment costs, operational and maintenance costs and indirect annual costs.

<table>
<thead>
<tr>
<th>Cost</th>
<th>EUR million</th>
<th>Including</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment</td>
<td>19.2</td>
<td>Delivery, erection and commissioning/start-up</td>
</tr>
<tr>
<td>Operation and maintenance</td>
<td>1.6</td>
<td>General maintenance; Steam and natural gas consumption in the regeneration cycle; Pressure drop across the unit (approx. 10 mbars) (converted to power consumption); Average cost/yr for catalyst replacement (7 year catalyst life for leading row); Catalyst disposal/refund.</td>
</tr>
</tbody>
</table>

NB: Additional indirect annual costs to the contractor are not included.

A reduction of NO\textsubscript{x} from 25 ppm to 2 ppm (50 to 4 mg/Nm\textsuperscript{3} as NO\textsubscript{2} at standard conditions 0 °C; 1013 mbar) will contribute to an increase in the investment due to the need for additional catalyst. It will also somewhat increase the operation and maintenance costs due to the increased consumption of natural gas and steam and increased pressure drop.

A second example gives an installation cost of EUR 6.2 million for the application of this technique to a gas turbine of 25 MW. The operating costs are estimated to be approximately EUR 0.42 million/yr, including maintenance, steam and natural gas, pressure drop through the system, and the cost of catalyst replacement.

Driving force for implementation
Demands for very Low-NO\textsubscript{x} emissions and limitations of air pollution control equipment utilising ammonia, especially for plants situated in densely populated areas.

Example plants
There are example applications in the US in small gas power plants. For example, a combustion turbine of 32 MW is operating at the Federal Cold Storage Cogeneration facility in California.

Reference literature
[276, Alstom Power, 2000], [268, TWG, 2001] [ 91, JEA 2008 ].

4.10.4.11 Combinations of NO\textsubscript{x} control and abatement techniques

Table 4.62 provides some examples of the use of a combination of NO\textsubscript{x} control and abatement techniques that may be applicable to refineries.
Chapter 4

<table>
<thead>
<tr>
<th>Energy-production technology</th>
<th>Fired-heaters and boilers firing refinery blend gas</th>
<th>Gas turbines firing refinery blend-Gas</th>
<th>Gas turbines firing natural gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>DeNOx technology</td>
<td>Fine gas-recirculation plus low-NOx burners</td>
<td>Low-NOx burners plus SCR</td>
<td>Ultra-low-NOx burner plus SCR</td>
</tr>
<tr>
<td>NOx reduction performance (%)</td>
<td>70</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>Down to approx. 3 % O₂</td>
<td>45</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>Investment costs (EUR millions)</td>
<td>0.9</td>
<td>2.1 - 3.5</td>
<td>8.3</td>
</tr>
<tr>
<td>Operating costs per year (excludes capital charge) (EUR millions)</td>
<td>0.08</td>
<td>0.15 - 0.26</td>
<td>2.1</td>
</tr>
<tr>
<td>Cost-effectiveness EUR/tonne NOx removed (excludes capital charge at 15 %)</td>
<td>2000 - 4000</td>
<td>9100 - 10500</td>
<td>9100 - 10500</td>
</tr>
<tr>
<td>Other impacts</td>
<td>Add energy for fan</td>
<td>Risk of NH₃ emissions; catalyst disposal; regeneration</td>
<td>Energy to produce steam and risk of NH₃ and higher CO₂ emissions; catalyst disposal; regeneration</td>
</tr>
</tbody>
</table>

Table 4.62: Performance of combined NOx-reducing techniques applied to the energy system

Reference literature
[115, CONCAWE, 1999], [268, TWG, 2001]

4.10.5 Particulate abatement techniques

Particulate loads (containing metals) from refinery combustion plants are normally fairly low unless heavy residues are burnt. These particulates may be abated using a number of methods including electrostatic precipitators (ESP), bag filters and wet scrubbing, as described in Section 4.25.4.

4.10.5.1 Switching to low-ash content fuels

Description
Refinery fuel gas and hydrotreated liquid refinery fuels contain less lower particulate loads than heavy liquid refinery fuels. Switching to these fuels has a positive impact on the reduction of particulates emissions. The achieved emission particulate levels as well as cross-media effects, operational data, applicability and economics have already been described in Section 4.10.2. and 4.10.3.1.

4.10.5.2 Steam injection atomisation for liquid fuel

Description
Steam injection together with while burning the liquid refinery fuel leads to atomisation and to lowering the particulate concentration.

Achieved environmental benefits
In the flue-gas of the older furnaces firing liquid refinery fuel of older furnaces, PM content may range from 500 - 1000 mg/Nm³. For new optimal burner design with steam atomisation, this can be well below 200 mg/Nm³ in the range of 20 – 250 mg/Nm³ (see Section 4.10.3.1). For boilers, all these figures are on average lower. The range of 150 - 500 mg/Nm³ represents
the current typical range with liquid fuels employed (ash contents) and burners installed (Low-NOx with steam atomisation).

**Cross-media effects**
Improved fuel oil atomisation reduces droplet size with an increase in the intensity of combustion. This results in higher flame temperatures and can lead to increased NOx emissions.

**Applicability**
Steam injection in fired furnaces/boilers is widely practised with liquid fuel.

**Driving force for implementation**
Reduction of particulate emissions.

**Reference literature**
[118, VROM, 1999].

### 4.10.5.3 Filters
See Section 4.25.4

**Description**

**Achieved environmental benefits**
See Section 4.25.4. PM values of less than 5 mg/Nm$^3$ can be achieved.

**Cross-media effects**
Pressure drop. Filter material life is limited and may add to disposal problems.

**Operational data**
Limited utilities (e.g. compressed air) are needed. For more information, see Section 4.25.4.

**Applicability**
Bag blinding can arise from 'sticky' soot particles from boilers when burning fuel oil. Filters are normally used for cleaning flue gases with flows below 50000 Nm$^3$/h.

**Economics**
Investment cost details depend on the installation. Operating costs are low, but the filters normally need to be changed every 1–2 years.

**Example plants**
There are many power plants in Europe operating with bag filters.

**Reference literature**
[250, Winter, 2000], [118, VROM, 1999]

### 4.10.5.4 Electrostatic precipitator (ESP)

**Description**
For more information, see Section 4.25.4.2.

**Achieved environmental benefits**
They ESPs can achieve dust particulates matter (PM) emissions of $\leq 10 – 50$ mg/Nm$^3$ with up to 95 % reduction. Sootblowing is an operation that is carried out at regular intervals to remove soot that has accumulated on the furnace equipment which has hampered proper functioning. During this operation the PM content of the exhaust gas can reach
values of 2000 mg/Nm$^3$. ESPs and similar dust removal techniques installed for normal operations will be effective in reducing the PM emissions to the accepted level. Thus, ESPs working on process furnaces normally yield higher average concentrations due to sootblowing.

**Cross-media effects**
Electricity consumption, dust disposal and, in some cases, ammonia emissions. For more information see Section 4.25.4

**Operational data**
ESPs consume electricity. More information in Section 4.25.4

**Applicability**
ESPs are widely applied in FCC units, in thermal power plants and incinerators. ESPs may not be applicable for some particulates with high electric resistance. They can be installed both in new and existing plants. They require space for their application.

**Economics**
Typical installed capital costs for ESPs are from EUR 1 million to 3.8 million.

**Driving force for implementation**
Reduce emissions of particulates and metals or other hazardous substances contained on them.

**Examples**
Wet ESPs are the most common type used for the abatement of particulates in heavy fuel oil combustion processes. In refineries, ESPs are both used on FCC units and on heavy oil and residue cracker units. They can be used to treat emissions from heavy liquid or solid fuel combustion.

**Reference literature**
[247, UBA Austria, 1998], [45a, Sema and Sofres, 1991].

### 4.10.6 Sulphur oxides abatement techniques

The release of sulphur dioxide is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Techniques to reduce sulphur oxide emissions are fuel optimisation (described in Section 4.10.1), fuel desulphurisation (hydrotreatments described in Section 4.10.2.3) or flue-gas desulphurisation. The lower the sulphur content of the fuel, the lower the emission of sulphur dioxide. In this section, techniques for the capture of SO$_2$ from the flue-gas after combustion or flue-gas desulphurisation techniques and the use of additives are included. More generic general information on these techniques is given in Section 4.25.5.4.

#### 4.10.6.1 Additives to fuels

**Description**

a. Use of lime or limestone as additive to fuels to capture the sulphur oxides.

b. Use of magnesium-based additives for the inhibition of the SO$_2$ to SO$_3$ oxidation.

   Magnesium combines with the vanadium pentoxide generated during the heavy liquid fuels combustion.

**Achieved environmental benefits**

a: This technique would abate the SO$_2$ release by about 90 %. 100 % limestone in excess of the stoichiometric quantity would be required.

b: The purpose of this technique is not to reduce SO$_x$ emissions, but to reduce the amount of SO$_3$ in the plume for mitigating its visibility.
Cross-media effects
A  Limestone/gypsum mixture has to be disposed of.
b  No noticeable effects to be mentioned.

Operational data
b  The injection rate used has been around one litre for every 5.6 tonne of liquid fuel burnt.

Applicability
a  For conventional refinery boiler and furnaces, the injection of lime or limestone into the furnace for sulphur capture cannot be applied. If the heaters and boilers are fluidised-bed or circulating fluid boilers to burn petroleum coke or heavy bitumens resulting from solvent deasphalting, then lime/limestone injected into the furnace as abatement would be practical.
b  This technique was applied as a trial (2008) in a European refinery to reduce the visible plume from two out of the six boilers. At the time of writing (2010) the technique is out of service, as the site was not able to prove quantitatively the improvements achieved.

Driving force for implementation
To reduce the sulphur oxide emissions.

Reference literature
[45a, Sema and Sofres, 1991] [Questionnaire No 45].

4.10.6.2 Flue-gas desulphurisation processes

Description
The techniques that may be considered for application to the flue-gas desulphurisation are e.g.: Wet limestone scrubber, the Walther process, the Wellman-Lord process, the SD-process, the AI process, the SNO₃ process and seawater scrubbing. More Detailed information about these processes can be found in Section 4.25.5.4.
Note to TWG: Relevant info from former text has been moved to 4.25.5.4
Chapter 4

4.11 Etherification

4.11.1 Catalytic distillation

Description
The catalytic distillation process combines reaction and fractionation into a single unit operation. It requires a two-reactor design where one is a boiling-point fixed-bed reactor followed by final conversion in a catalytic distillation column. Reactors use an acidic ion exchange resin catalyst.

For more information see Section 2.11.

Achieved environmental benefits
Increased conversion process efficiency decreases the energy consumption within the system per tonne of product manufactured.

Cross-media effects
This technique requires an additional reactor. Catalyst handling in elevated places during installation and catalysts change may cause safety risks.

Operational data
The advantages of the process that include where the reaction catalyst is within the distillation column include essentially complete isooolefin conversions. Etherification can be applied for MTBE, ETBE or TAME production. Conversions of 98 % of isobutylene are typical for refinery feedstocks. Conversion is slightly less for ETBE than for MTBE. For TAME, isoamylene conversions of >95 % are achievable.

<table>
<thead>
<tr>
<th>Typical utility requirements, per m³ of product</th>
<th>Range depending on the technology licensor</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>1.3 – 3.1</td>
<td>kWh</td>
</tr>
<tr>
<td>Steam (10.3 barg)</td>
<td>600 – 1 150</td>
<td>kg</td>
</tr>
<tr>
<td>Steam (3.4 barg)</td>
<td>100 – 1 150</td>
<td>kg</td>
</tr>
<tr>
<td>Water cooling (ΔT=17 °C)</td>
<td>1.5 – 4</td>
<td>m³</td>
</tr>
</tbody>
</table>

Economics
Investment costs: EUR 25000 18 850 per m³/d of MTBE product

(Costs calculation based on 1999 rate EUR = 1.1680 USD, for a 1 500 bpsd capacity unit and a cost of 3 500 USD per bpsd of MTBE)

Example plants
This technique is widely applied.

Reference literature
[212, Hydrocarbon processing, 1998] [ 76, Hydrocarbon processing 2011 ].

4.11.2 Prevention of upsets in the waste water biotreater

Description
Water effluents from MTBE and TAME production contain releases of methanol, formic acid and ethers. These compounds or their degradation products can be toxic for the fauna of the biotreater. Therefore, high concentrations of these components need to be prevented from entering. This can be easily controlled by the use of a storage tank or by the planning of production in order to dosify the right flow to the waste water treatment.
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Achieved environmental benefits
The methanol, formic acid and ethers content of the waste water generated in the etherification processes need to be controlled to prevent upsets in the waste water biotreater.

Applicability
Fully applicable.

Economics
The implementation of this technique is not expensive.

Driving force for implementation
To avoid upsets of the biotreater.

Reference literature
[272, Shawcross, 2000].

4.11.3 Prevention of leaking of water-soluble compounds

Description
Ethers produced in the etherification processes are very highly soluble in water. If they leak, they may contaminate the soil, raining water and groundwater. It can be seen as a part of a programme for prevention, detection and control of the soil and groundwater (see Section 4.25.1).

Achieved environmental benefits
Reduction of the risk of contamination of water by ethers and alcohols used in these processes.

Driving force for implementation
To avoid contamination of groundwater and surface water by ethers.

Reference literature
[349, Finnish Environmental Institute, 2001].
4.12 Gas separation processes

The gas plant is a relatively simple process and the temperature levels are not high enough to create the opportunity for steam generation. No great efficiency improvements are to be expected within a gas plant, but heat integration with upstream plants will normally make use of e.g. reboiling heat available from upstream plant streams, saving direct heating capacity in the gas separation plant. More information on energy management is available in Section 4.10.1.

4.12.1 Increase the of heat integration with upstream plants

**Description**

**Achieved environmental benefits**
Reduction in energy consumption in the gas plant and therefore in the refinery as a whole.

**Cross-media effects**
No cross-media effects.

**Driving force for implementation**
To reduced energy consumption within the refinery.

**Example plants**
Technique widely applied.

**Reference literature**
[282, Conoco, 2000].

4.12.2 Improve the condensate knock-out system

**Description**
Resizing/improving condensate knock-out system on gas streams and on site recycling.

**Achieved environmental benefits**
Appreciable waste minimisation.

**Applicability**
Relatively minor modifications are needed.

**Driving force for implementation**
To reduced waste generation.

**Reference literature**
[115, CONCAWE, 1999].

4.12.3 Fugitive emissions reduction

**Description**
Gas plants process light compounds and are consequently more likely to produce fugitive emissions. The use of double dual mechanical seals on pumps, compressors and agitators can reduce VOC emissions. Use of low-leaking valves also can contribute to reducing VOC emissions. This topic is described as an integrated measure within Section 4.25.6.1 because fugitives emissions occur in all refinery processes, but it is mentioned here explicitly because the light compounds used lead to a relatively high level of fugitive emissions.
Achieved environmental benefits
Applying these techniques, fugitive emissions such as VOC, H₂S and other sulphur compounds can be reduced considerably.

Cross-media effects
See Section 4.25.6.1.

Operational data
See Section 4.25.6.1.

Applicability
See Section 4.25.6.1.

Economics
See Section 4.25.6.1.

Driving force for implementation
To reduce reduction product loss.

Example plants
Programmes of minimisation of VOC emissions can be found in many European and non-European refineries.

Reference literature
See Section 4.25.6.1.

4.12.4 Reuse of the fuel gas used in LPG production

Description
Molecular sieve dryers used in LPG production are regenerated using hot fuel gas.

Achieved environmental benefits
The fuel gas can be vented to fuel gas drums to be reused instead of being flared.

Applicability
Easily applicable.

Driving force for implementation
To reduce flaring.

Example plants
Many examples exist.

Reference literature
[18a, Irish EPA, 1992]

4.12.5 Prevention of emissions of LPG odorant

The storage and handling of odorants used in the LPG production is going to be covered in the horizontal BREF on Emissions from Storage BREF [5, EC 2006]. However the dosing of odorant to the LPG product needs to be handled in a proper way to prevent emissions to the environment. This technique is included in the Section 2.21.
4.13 Hydrogen-consuming processes

4.13.1 Hydrotreating

Note to TWG: Hydrotreating is already addressed in Section 4.10.2.3

Description
See Section 2.13 and 4.10.2.3. Another technique that can be used is the use of heat recovery from high-temperature process streams in WHB and power recovery in the high pressure units (letting down liquid) to increase heat integration.

Achieved environmental benefits
Reduction of sulphur, nitrogen, aromatics and particulate emissions. Hydrotreatment, in addition to removing sulphur compounds, will remove nitrogen compounds by about 15-40% (very severe hydrotreating might achieve higher percentage removals).

Cross-media effects
Energy consumption, waste generation, effluent water and air emissions.

Operational data
See Section 2.13.

Applicability
Fully applicable.

Economics
The investment associated with the installation of a hydrotreating unit depends on the feed characteristics and the product specifications. Generally speaking, as the feed gets heavier or the individual product specifications are reduced, the processing requirements are increased. These more severe processing conditions can result in more pieces of equipment, larger equipment, and higher operating pressure, all of which increase the cost of the unit. The required capital investment for a hydrotreating unit can vary from EUR 12 to EUR 48 per tonne per year of capacity.

<table>
<thead>
<tr>
<th>Type of hydrotreater</th>
<th>Capacity (Mt/yr)</th>
<th>Typical capital/installed cost 1997 EUR million</th>
<th>Typical operating cost EUR million per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha hydrotreatment</td>
<td>1.3</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>Catalytic feed hydrotreatment (typical feeds: being atmospheric residue and vacuum gas oil)</td>
<td>1.1</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>113</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td>Vacuum residue</td>
<td>1.1</td>
<td>90</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

Driving force for implementation
To reduce sulphur and aromatic content of the feedstock.

Example plants
Many examples exist in refineries.

Reference literature
[166, Meyers, 1997], [112, Foster Wheeler Energy, 1999], [212, Hydrocarbon processing, 1998].
4.13.2 Hydrodesulphurisation processes

Description
See Section 2.13. Another technique that can be used is the use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting down liquid) to increase the heat integration.

Achieved environmental benefits
The reduction of sulphur content of the different fractions is an environmental benefit of this technique. Modern techniques can reduce the sulphur content of distillates to less than 10 ppm. For example, the application of one-step hydration by means of a Co/Mo catalyst (30 - 40 bar) to middle distillates reduces the sulphur content by more than 90 % (down to some 100 ppm) depending on the product, the S-content of the feed and the reaction conditions. If demand for diesel fuel increases, additional compounds (e.g. LCO from the FCC) have to be used in its production. However these feedstocks contain a variety of aromatic compounds, which have to be hydrated under severe conditions (high temperature, high pressure, highly active catalysts, two-step processes).

New Current diesel specifications can be met in conventional single-stage hydrotreating units by lowering liquid hourly space velocity (LHSV) from 3.7 in conventional units to 0.8 – 1.1 by implementing a reactor in series to the existing ones and applying the latest catalyst generation available for gasoil hydrotreating units. Processing a Russian export blend with 1.3 % w/w S and an intermediate sulphur content ahead of the final desulphurisation unit of 0.12 % S, a final sulphur content of 8 ppm S in the raffinate can be achieved during normal operation.

Cross-media effects
Energy consumption, waste generation, effluent water and air emissions.

Operational data
Gasoil hydrotreating units need the additional measure of a high-pressure amine washer in the hydrogen recycle stream to avoid the recombination of H₂S from to maintain hydrogen purity in the recycle stream with hydrocarbons from fresh feed. The unit will operate at 45 bar, utilising 40 Nm³ hydrogen/t of gasoil feed and anticipating a run length of 30 months.

Applicability
Applicable to distillates from naphtha to heavy residues.

Economics
The estimated erected installation costs for a reduced-crude desulphurisation process (basis based on 132 m³/h unit) is EUR 47 million. Another estimated investment summary for a residue desulphurisation system hydrotreater to prepare residue fluid catalytic cracking feed is shown below.

| Feed rate, Mt/yr | 3.8 |
| Run length, days | 335 |
| Operating factor | 0.92 |
| On-plot investment, in million EUR | 272 |
| Total off-plot cost (30 % of on-plot), in million EUR | 82 |
| Catalyst cost per charge, million EUR | 10 |
| NB Basis: second quarter 1995 US gulf coast |

Driving force for implementation
To reduce the sulphur content of the feedstock to achieve the EU specifications: the current value for sulphur is 10 mg/kg (10 ppm) according to Directive 2009/30/EC. Deep desulphurisation is an important technique applied for compliance with Auto-oil programme II.
Costly two stage hydrotreating units applying a noble metal catalyst in the second stage of hydodesulphurisation are not needed to meet the auto oil programme II or the German diesel specifications. But, depending on the final specification on cetane of diesel issued by the European Parliament, two stage units may become mandatory for refiners being short in cetane index in their diesel pool. Normally these refiners do not operate a hydrocracker unit. Two stage units are also mandatory for refiners who need to lower the aromatics content and/or the CFPP in their gasoil pool.

Example plants
Many desulphurisation processes exist in refineries.

Reference literature
[166, Meyers, 1997].

4.13.3 Catalytic distillation

Description
Catalytic distillation for desulphurisation of gasoline in a two-stage process.

Achieved environmental benefits
Reduction of more than 95% of sulphur content in FCC gasoline containing 1800 ppm of sulphur have been achieved. This type of technique consumes less energy than traditional desulphurisation processes.

Cross-media effects
Energy consumption, waste generation, effluent water and air emissions.

Applicability
Fully applicable. This technique may also be used for the reduction of benzene in the reformate.

Economics
A two-stage process is designed to treat 7950 m³/d of FCC gasoline containing 1800 ppm of sulphur. Its efficiency has been of 95% and its investment costs are approximately EUR 20 million.

Driving force for implementation
Since to reduce the sulphur content of gasoline will be reduced to 50 ppm by law, techniques for the reduction of sulphur content will become more used. The current value for sulphur is 10 mg/kg (or ppm) according to Directive 2009/30/EC.

Example plants
At least one catalytic distillation plant for desulphurisation of 7950 m³/d of FCC gasoline is available in Europe. In 2010, in Russian Federation, a 1.26 Mt/yr FCC unit was designed with a catalytic distillation patented process to meet Euro-5 emissions requirements.

Reference literature
[247, UBA Austria, 1998].

4.13.4 On-stream catalyst replacement technology for processing high-metal feeds

Description
While the main objective of this process is to extend catalyst life in a down-stream fixed-bed reactor by maintaining high hydrodemetallisation performance, the catalyst also achieves high
Chapter 5

Hydrodesulphurisation/hydrodemetallisation and hydrodesulphurisation Conradson carbon removal/hydrodemetallisation activity ratios.

Achieved environmental benefits
On-stream catalyst replacement technology improves the residual desulphurisation in the refinery, thereby decreasing the waste generation.

Operational data
The reactor typically operates at 390 °C and 138 bar (2000 psia).

Applicability
Fully applicable.

Driving force for implementation
To extend the catalyst life of the hydrotreatment processes.

Example plants
Until 1997, there were 15 on-stream catalyst replacement techniques worldwide.

Reference literature
[166, Meyers, 1997].

4.13.5 Hydrogenation of light dienes

Description
The hydrogenation of light dienes serves the purpose of producing a more stable refinery stream reducing upstream gum formation. The process converts dienes into useful olefins. For more information see Section 2.13.

Achieved environmental benefits
The process helps reduce acid losses in downstream processes (e.g. alkylation). Typical product diene levels from the selective hydrogenation process unit may range from 25 to 1 ppm.

Cross-media effects
Low energy consumption.

Operational data
Low temperature, liquid-phase operation means that no utilities are required in most cases if the feed and hydrogen are both available at suitable conditions. Heating or cooling duties are limited to cases with relatively high diene concentrations in the feed. Commercial operation for a period of more than two years without the need to regenerate or replace the catalyst is typical.

Applicability
The design of the unit is simple. Most of the units are designed for diene reduction to less than 5 ppm in the product.

Economics
The design of the units is simple and requires low capital and nominal operating costs. The cost of the catalyst is low compared with the installation cost. The capital investment including the catalyst for the unit is small, usually within the range of EUR 0.6 million – 1.2 million. The investment is based on recent project is some EUR 3 million for a plant of 100000 t/yr capacity.

Driving force for implementation
To reduce gum formation in downstream operations. The flexibility and minimal cost of this technology-technique make the unit a valuable processing tool.
Chapter 4

Reference literature
[166, Meyers, 1997]. [261, Canales, 2000].

Note to TWG: It is proposed to delete the two following sections because no new candidate techniques are described in addition to Section 4.10.1.2 on heat integration.

4.13.6 Hydrocracker

Description
Hydrocracking is an exothermic process and heat integration techniques can be applied. For more information on hydrocrackers see Section 2.13. Some techniques to consider are:

   a. Partially recovered of the heat generated in the reactors in a feed/product heat exchanger. A furnace heats the feed to its required temperature. The reactor temperature is controlled via the injection of cold hydrogen between the catalyst beds.

   b. A significant amount of heat is required in the fractionation section. Heat integration is applied to minimise heat consumption.

   c. The energy efficiency can be further increased of energy efficiency by applying a four-stage separator system. The feed to the fractionation section is in that case rendered significantly hotter, and consequently less heat is required in the fractionation section.

   d. The use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting-down liquid)

Achieved environmental benefits
Reduced hydrocracker energy consumption.

Cross-media effects
No cross-media effects are known.

Operational data
The control system needs to be enhanced.

Applicability
In some cases, the heat integration can be difficult to apply. Replacement of existing hydrocrackers by new and highly heat-integrated hydrocrackers is in many cases not justified environmentally and economically.

Economics
The cost of a hydrocracker with heat integration varies from EUR 36 - 84/($/yr). Annual operating cost varies between 0.6 and 1% of the investment cost. In many cases the economics of the process do not justify the replacement of an existing hydrocracker, because the payback period can be very long.

Driving force for implementation
Reduction of energy consumption.

Reference literature

4.13.7 Residue hydroprocessing

Description
See Section 2.13. Another technique that can be used is the use of heat recovery from high-temperature process streams in WHB and power recovery in the high-pressure units (letting-down liquid) to increase the heat integration.
Achieved environmental benefits
Upgrading of fuel oil in lighter products, and reduction of sulphur, nitrogen and metal contents in the fuel oil and other products.

Cross-media effects
Cross-media effects include increased energy consumption and a consequent increase in CO₂ emissions, due mainly to the hydrogen. As discussed in Section 3.14, the production of hydrogen is very energy-intensive, generating large quantities of CO₂. As discussed in Section 4.13, hydrotreatment processes generate a catalyst for disposal and increase H₂S production with direct consequences (enlarge or new) for the sour water stripper and sulphur recovery units. Other cross-media effects are the increase of waste generation (catalysts) and effluent waste water (containing H₂S).

Operational data
Hydroconversion is an exothermic reaction, the heat generated in the reactor system being partially recovered in the feed product exchanger. Normally a high level of heat integration and heat recovery is applied in the fractionation section. The amount of hydrogen required depends on feed (heavier feeds tend to increase hydrogen consumption) and process objectives (lower sulphur, nitrogen, aromatics content in the products, higher hydrogen consumption). In most cases extra energy is required.

Applicability
Commercial experiences range from low-sulphur atmospheric residues to high-metal, high-sulphur vacuum residues with over 300 ppm metals.

Economics
Investments costs for the various options depend strongly on the feed properties and process objectives of the residue hydroprocessing unit. Investments costs for a typical new single-string 5000 t/day unit will range from USD 200 – 300 million, the higher figure including an integrated hydrocracker.

Driving force for implementation
Residue hydroprocessing is used for the upgrading of fuel oil into lighter products.

Example plant(s)
Many different concepts of residue hydroconversion processes are licensed. The selection of the type of process depends on feedstock quality (metal content and Concarbon number) and the required conversion and product quality.

Reference literature
[115, CONCAWE, 1999], [212, Hydrocarbon processing, 1998].
4.14 Hydrogen production

For SO₂ emissions reduction, hydrogen gains more and more importance as a key reacting agent for the supply of hydrotreating units that are now crucial to the desulphurisation and upgrading of intermediate feedstocks and final products.

Hydrogen production using a hydrocarbon-rich feedstock requires, as a first step, the conversion of the feedstock into a carbon oxide and hydrogen rich synthesis gas. The synthesis gas generation can be conducted by different techniques such as steam reforming (see Section 4.14.1), gas heated reforming (GHR)(see Section 4.14.2) and partial oxidation (see 4.14.3). An additional purification step is then needed (see Section 4.14.4). Figure 4.29 shows H₂/CO ratio for various hydrogen production techniques available.

As mentioned in Section 2.14, the production of hydrogen is not exclusive to the refinery sector. Therefore the sector-specific information contained in this chapter can be completed as necessary by the information available in the other BREF documents, e.g. LVIC-AAF [92, EC 2007] covering industrial sectors where hydrogen is typically produced and used, in particular the BREF on Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers. Some information from this chapter should also be seen as applied to other industrial sectors where hydrogen production is necessary (e.g. ammonia production, chemical industry, etc).

![Figure 4.29: H₂/CO ratio for hydrogen production processes available in a refinery](source: EIGA)

**4.14.1 Gas Heated Steam Reformer Technology Steam methane reforming**

**Description**
- Gas Heated Steam reforming replaces the reformer furnace: the reforming heatload is provided by cooling the exit gas from a secondary reformer which uses oxygen. The feed consists of natural gas or light naphtha.

Facing SO₂ emission challenge for oil refining, hydrogen gains more and more importance as a key reacting agent for the supply of hydrotreating units that are now crucial to the desulphurisation and upgrading of intermediate feedstocks and final products. As described in
Section 2.14, the production of necessary hydrogen in a refinery context is available through the following main processes:

- Hydrogen recovery from the refinery fuel gas or eventual petrochemical offgases available at the site, by pressure-swing absorption (PSA), membrane or cryogenics
- Steam reforming of external methane or internal light hydrocarbon feedstocks
- Gasification/partial oxidation of heavier products

Description of this most commonly used process is made in Section 2.14. Either exclusively or primarily as a hydrogen production process, steam methane reforming is intrinsically advantageous from both a product yield and an energy consumption point of view. Figure 4.29 shows the product yield ranges typically obtained for each process in terms of the ratio of hydrogen to carbon monoxide.

The steam reformer has to supply a large amount of heat at high temperature for the steam reforming reaction by burning fuel, with the result that a large amount of heat is potentially lost in the flue-gas. As a result, many refineries recover heat as part of their heat integration. In order to minimise the amount of heat lost in the stack, a large well-sized appropriate heat recovery system is should be used. Unless using the Gas Heated Steam Reforming add-on technique described in Section 4.14.2, a large proportion of the recovered heat is can be recovered by raising and superheating steam. Some heat integration is possible around the solvent absorber and the methanator.

However, the values displayed in Figure 4.29 do not take into consideration, as a more general approach, the potential reduction of air emissions that can be obtained from co-production synergies. All of the processes in Figure 4.29 can be used within a refinery to export steam as a valuable product, thereby eliminating the need for dedicated steam production elsewhere and translating directly into energy and CO₂ emissions savings. Furthermore, if there are other chemical facilities nearby, there may be demand for carbon monoxide which can be productively used instead of being emitted as CO₂. Steam methane reforming reduces the potential for CO₂ emissions with its requirement for lighter feed stocks.

Achieved environmental benefits

- Gas heated steam reforming reduces the energy consumption of the reforming process.
- Recovery of heat from flue gas can be used elsewhere in the refinery, reducing consumption elsewhere.
- Either exclusively or primarily as a hydrogen production process, steam methane reforming is intrinsically advantageous from both a product yield and an energy consumption point of view (see Figure 4.29 showing product yield ranges, as hydrogen to carbon monoxide ratio, for different process).
- Steam methane reforming of natural gas typically has a small the smallest carbon footprint of all hydrogen production processes. When available, maximising the use of external methane imported to the refinery for hydrogen production instead of thermal power generation could be seen as a preferable option when hydrogen production needs to be increased.
- Steam methane reforming typically requires 10 – 15 % excess air with the minimum value being limited by safety considerations. This relatively small quantity is an intrinsic primary measure for the reduction of NOₓ emissions.
- As it is a close loop process, the obligation to thoroughly monitor the excess O₂ and/or CO content in the SMR flue-gas also provides the opportunity for the enhanced control and the reduction of CO and unburned hydrocarbon emissions.
- The steam methane reforming process requires a very deep desulphurisation of the feed so as to prevent catalyst poisoning. As a result, the tail gas from the PSA is virtually free of sulphur. As it forms up to 90 % of the fuel, SOₓ emissions are correspondingly reduced and will only depend on the sulphur content of the supplementary fuel.
Cross-media effects
The environmental regulations with the most impact on plant design are typically NO\textsubscript{x} limitations.

The choice of heat recovery system can have a major effect on NO\textsubscript{x} production, since both the amount of fuel fired and the flame temperature will be affected. Preheating combustion air will reduce firing, but since NO\textsubscript{x} formation is strongly influenced by flame temperature, there will be an overall increase in NO\textsubscript{x} formation concentration limiting the overall NO\textsubscript{x} mass flow reduction. Other methods of reducing firing, such as pre-reforming or heat-exchange, will reduce the amount of fuel fired and therefore NO\textsubscript{x} production. The production of CO\textsubscript{2} is also important. For every tonne of H\textsubscript{2} produced, some 12 tonnes of CO\textsubscript{2} are also produced (7.5 tonnes if related to the steam generation), including the amount related to steam production. Such value may vary widely depending upon the strategy for conducting the steam production. Other impacts, such as SO\textsubscript{x} or water emissions, are minimal, because low-sulphur fuel is typically used and there are lower emissions other than flue-gas.

Operational data
The combination of high temperature and pressure imposes severe demands on the steam reformer tubes, which must have thick walls to withstand the stresses and must be fabricated from expensive alloys. The furnace box must be large to obtain the high rates of heat transfer from the flue-gas to the tubes. These combined factors make the steam reformer the largest and single most expensive piece of equipment in a hydrogen plant. The large size of the unit means that it takes a long time to heat up and cool down, and this makes it the most time-consuming part of the start-up and shutdown procedure. The large thermal inertia makes it liable to damage during plant upsets.

Applicability
Fully applicable.

Economics
Relative hydrogen production costs of the two processes are primarily a function of feedstock cost. A new hydrogen plant for a 7950 m\textsuperscript{3}/day FCC unit feed hydrotreater or hydrocracker would typically cost in range of EUR 60 million - 75 million (1997).

Driving force for implementation
Production process. The need for additional sources of hydrogen is more and more often a crucial requirement for maximising the hydrotreatment capacity available in the refinery and meeting NO\textsubscript{x} challenges and sulphur content enforced in final product quality standards.

Example plants
A new alternative, already proved commercially for ammonia and methanol production, is the Gas Heated Steam Reformer Technology. There are many examples of steam methane reforming plants in operation associated with European oil refineries.

Reference literature
[112, Foster Wheeler Energy, 1999] [56, EIGA 2009] [76, Hydrocarbon processing 2011].
4.14.2 Gas Heated Steam Reforming (GHR)

Description

Hydrogen production using a hydrocarbon rich feedstock requires, in a first step, the conversion of the feedstock into a carbon oxide and hydrogen rich raw synthesis gas. The synthesis gas generation can be conducted by different technologies such as steam reforming (see Section 4.14.1) and partial oxidation processes. The gas heated steam reforming (GHR) technique generally uses compact unit heated by presents an add on to the above mentioned conventional synthesis gas generation processes when using light hydrocarbons like natural gas and naphtha. The GHR recovers high temperature waste heat from the raw synthesis gas, often by means of a heat exchanger-type reactor downstream of the conventional synthesis gas generator. In other examples, the GHR can also be fully integrated into the synthesis gas generator.

The recovered heat is used in the GHR to drive the endothermic reforming reactions instead of solely using this heat for steam generation in a steam boiler. Consequently, a hydrogen production plant with a GHR unit produces less excess steam than a conventional synthesis gas production plant based on a steam reformer or partial oxidation reactor.

Achieved environmental benefits

Gas heated steam reforming reduces the energy consumption of the reforming synthesis gas production process itself. It is especially appropriate for refineries where high pressure steam is not strictly needed for operating other production units.

Cross-media effects

When GHR is applied, little or even no steam is produced from the hydrogen plant. Depending on the specific configuration of the site energy system, the steam production in other units may need to be increased. The benefits from the application of GHR must then be balanced with the associated steam reduction demanded by the industrial steam network and/or the additional energy consumption and air emissions that would accompany the increase of steam production outside the hydrogen production plant.

Operational data

GHR recovers sensible heat from the process gas to drive the endothermic reforming reaction in an additional reactor. Many different possibilities to design a GHR exist, and many only use a small additional feed (i.e. 10 – 20 %) as a fraction of the total feed. The resulting economics can vary widely. One exemplary embodiment of the GHR application is essentially a special heat exchanger filled with highly active catalyst.

The severe operating conditions (high temperature) require very careful design. Because of the higher wall temperatures of the heat exchange surface compared to conventional steam boilers and the reducing gas atmosphere, there is a high likelihood of severe and instantaneous corrosion of particularly high-alloyed materials by the metal dusting corrosion phenomena are highly likely. Besides the risk on operation by failure of the heat exchange equipment, the resulting metal and carbon particles accumulate in the process condensate and can have an impact to the plant operation. Therefore, specific HSE and reliability/availability requirements will have to be taken into account for application of the GHR technology.

The integration of the GHR technology into a synthesis gas plant requires special procedures for start-up, operation and shutdown and consequently requires operational effort to maintain the catalyst lifetime.

Applicability

Fully applicable. However, the application of GHR as a steam reduction process technology must be evaluated against other design options which may include using the excess steam for power generation or mechanical power in rotating equipment. Gas heated steam reforming may
represent an attractive alternative process technology if high pressure steam can not be consumed by other units outside the synthesis gas generation unit.

**Economics**
Economics depend strongly on specific site configuration. Because of the severe conditions of gas heated steam reforming (high temperature, corrosive atmosphere), the typical embodiment as described above - a special heat exchanger filled with highly active catalyst - represents a significant capital expenditure.

Note for TWG (notably EIGA): could you please provide some examples of cost investments:
- for new plants (part of cost related to the GHT equipment subset)
- GHR retrofitting on existing hydrogen plants? No data made available

**Driving force for implementation**
Hydrogen is needed more and more for hydrotreatments performed in the refinery.

**Example plants**
GHR is a new alternative, already proved commercially for few applications, e.g. in ammonia and methanol production. As far as refining is concerned, GHR is typically applied to de-bottleneck existing conventional SMR-based hydrogen plants.

**Reference literature**
[56, EIGA 2009].

### 4.14.3 Partial oxidation - Coke and heavy oils gasification

**Description**
The IGCC plant can also function as a hydrogen supplier, in which case hydrogen is removed from the syngas (after the sulphur removal) where the feed reacts at high temperatures with oxygen. For more information see Sections 2.14, 2.10 and 4.10.3.5.

**Achieved environmental benefits**

**Coke gasification**
A fixed-bed desulphurisation system using regenerable zinc ferrite as the sorbent has been tested as a continuation of the gasification exhaust gases treatment. Sulphur levels of 10 - 20 ppm in the treated gas were achieved in this system. The product gas also contains traces of ammonia (less than 5 %) and hydrogen cyanide (HCN), derivatives of the nitrogen in the feed. Using limestone in the gasifier tends to reduce the level of these components. Ammonia is not removed by zinc ferrite in the external desulphurisation process. If there is any alkali in the feed, some of it may vapourise in the gasifier and may have to be removed by an alkali sorbent or by cooling the gas going to the filter. The particulates in product gas are removed in the barrier filter to a level of less than 5 ppm.

**Heavy oil gasification**
Another environmental benefit of gasification is that it reduces heavy oils which, when used in another way, may pollute the environment much more. See also Section 4.10.3.5.

**Cross-media effects**
Partial oxidation requires an oxygen plant (95 - 99 % purity), which increases costs.
Operational data

Normally, an IGCC plant includes a water purification section with the following units:

- soot recovery either by washing with naphtha and recycling of the naphtha/soot mixture to the gasification section and/or by filtration;
- water pretreatment to remove solids (carbon, metals, salts) by filtration before final treatment in biological plant e.g. a grey water treatment (GTW).

The Grey water treatment (GWT) is designed to treat water blowdown from a carbon extraction unit with syngas condensate and possibly the amine regeneration overhead system; water from grey water treatment is finally sent to biological treatment. The GWT may employ physical and chemical treatment for cyanide destruction and the removal of heavy metals followed by a sour water stripper, which removes sulphides, ammonia, and carbon dioxide from the water.

The gaseous streams are totally washed to remove any contaminant and the process normally includes the following ancillary units for gas purification:

- washing with water and sometimes oil to remove soot and particulate;
- reactor for COS or cyanides by hydrolysis;
- sour gas absorbing with amine or equivalent system and the production of elemental sulphur from H₂S in the Claus unit.

Applicability

Relative hydrogen production costs are primarily a function of feedstock cost. The main problem with investment in a gasification plant is its capital and operating cost. To be attractive commercially it usually needs to be undertaken on a large scale. Typical requirements for chemicals production are the generation of more than 200 MWₑ of electrical power through IGCC or the use of hydrogen, carbon monoxide and steam on a large scale.

Economics

Generally accepted investment costs for an oil gasification-based combined cycle plant in the 200+ MWₑ range are EUR 1300 – 1700 per kW installed, with a thermal efficiency of around 40 % and close to 99 % sulphur emission abatement. As On average, electrical demand in a refinery is usually less than 80 MWₑ, the investment in IGCC often depends on the opportunity to export the surplus of electrical power generated. However, high pressure steam can also be a valuable gasification product and there are examples of much smaller gasification units that fit in well with a refinery.

Relative hydrogen production costs of the process are primarily a function of feedstock cost. Steam reforming of methane usually produces hydrogen at lower costs than the partial oxidation of fuel oil. if the cost of methane is less than about 65 % of fuel oil cost on an energy basis.

Driving force for implementation

The production of hydrogen costs, the reduction of the production of heavy oils produced, power export and production of the synthesis gas produced as feed for petrochemistry are the driving forces for the implementation of gas-heated steam reforming.

Example plants

At least five gasification processes are currently running in European refineries.

Reference literature

[166, Meyers, 1997], [297, Italy, 2000].
4.14.4 Purification of hydrogen

Description
Information about the processes of purification can be found in Section 2.14. Some techniques that may be applied to the hydrogen purification units to achieve better environmental performance are given below.

- Use of several adsorber beds are used and the gas flow is periodically switched: switching the gas flow from one vessel to another to allow regeneration of the adsorbent by pressure reduction and purging, thus releasing the adsorbed components. The desorbed gas is normally accumulated in a vessel and used as fuel at a convenient location.
- One technique to reduce air emissions is to Use of PSA systems only for purification of hydrogen to reduce air emissions.
- Use the PSA purge gas as refinery fuel gas in the reforming furnace instead of higher C/H ratio fuels.
- Use of membranes technique which can achieve purification ratios of 80 % v.

Achieved environmental benefits
Reuse of waste fuel gas as a fuel within the process.

Cross-media effects
Because of loss of hydrogen to the PSA tail gas, the reformer and front end of a PSA plant are larger than in a wet scrubbing plant. However, a PSA plant uses less process steam and does not require heat for the reboiler. PSA is a high energy consumer due to the high vacuum/pressure systems that it uses.

Operational data
The PSA system is completely automatic and offers a higher purity product. The PSA unit is simpler to operate than a wet scrubbing system, since it has no rotating equipment or circulating solutions. The conventional process produces a hydrogen product of maximum 97 - 98 % v/v purity, while the pressure swing adsorption process produces a very pure hydrogen product between 99.9 % v/v and 99.999 % v/v. The residual constituents of the product gas are mainly methane and less than 10 ppm CO. Some data on the utility consumption of the PSA system are: 3700 Nm³/h with a H₂ content of at least 85 % and a pressure between 37 and 47 bar. Product-stream: 2400 Nm³/h purified H₂ with a concentration of at least 99.5 %, temperature: 45 °C, pressure: 35 bar; waste gas: 1300 Nm³/h, P: 3 bar, T: 30°C, contains 60 % H₂, 1.4 % H₂S and 40 % C₁-C₆ compounds with higher boiling points.

Driving force for implementation
Production process To purify the hydrogen. The choice between the PSA system and the scrubbing system depends on the product purity required, reliability and process economics. The extra investment for the PSA system for large plant capacities can normally be offset by the lower operating cost. Also a PSA system will yield a higher H₂ purity.

Example plants
Many examples exist as PSA is commonly used.

Reference literature
[166, Meyers, 1997], [297, Italy, 2000], [211, Ecker, 1999].
Chapter 5

4.15 Integrated refinery management

This section is structured in the same way as Chapter 2 and 3 and contains these integrated refinery management activities that are not included in other sections. The first techniques to consider are environmental management activities and other utility management techniques.
Note to TWG: The following text is based on new standard text for EMS

4.15.1 Environmental management tools

4.15.1.1 Environmental management system

Description
A formal system to demonstrate compliance with environmental objectives.

Technical description
The Directive defines ‘techniques’ (under the definition of ‘best available techniques’) as ‘both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned’.

In this respect, an environmental management system (EMS) is a technique allowing operators of installations to address environmental issues in a systematic and demonstrable way. EMSs are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

An EMS focuses the attention of the operator on the environmental performance of the installation; in particular through the application of clear operating procedures for both normal and other than normal operating conditions, and by setting out the associated lines of responsibility.

All effective EMSs incorporate the concept of continuous improvement, meaning that environmental management is an ongoing process, not a project which eventually comes to an end. There are various process designs, but most EMSs are based on the plan-do-check-act cycle (which is widely used in other company management contexts). The cycle is an iterative dynamic model, where the completion of one cycle flows into the beginning of the next (see Figure 4.30).

Figure 4.30: Continuous improvement in an EMS model
An EMS can contain the following components:

1. commitment of management, including senior management;
2. definition of an environmental policy that includes the continuous improvement of the installation by the management;
3. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
4. implementation of procedures paying particular attention to:
   (a) structure and responsibility
   (b) training, awareness and competence
   (c) communication
   (d) employee involvement
   (e) documentation
   (f) efficient process control
   (g) maintenance programmes
   (h) emergency preparedness and response
   (i) safeguarding compliance with environmental legislation;
5. checking performance and taking corrective action paying particular attention to:
   (a) monitoring and measurement - see also the document on the General Principles of Monitoring [46, EC 2003].
   (b) corrective and preventive action
   (c) maintenance of records
   (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
6. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
7. preparation of a regular environmental statement;
8. validation by a certification body or an external EMS verifier;
9. following the development of cleaner technologies;
10. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
11. application of sectoral benchmarking on a regular basis.

Achieved environmental benefits

An EMS promotes and supports the continuous improvement of the environmental performance of the installation. If the installation already has a good overall environmental performance, an EMS helps the operator to maintain the high performance level.

Environmental performance and operational data

Cross-media effects

None reported. The systematic analysis of the initial environmental impacts and scope for improvements in the context of the EMS sets the basis for assessing the best solutions for all environmental media.

Technical considerations relevant to applicability

The components described above can typically be applied to all installations within the scope of this document. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.
Economics
It is difficult to determine accurately the costs and economic benefits of introducing and maintaining a good EMS. There are also economic benefits that are the result of using an EMS and these vary widely from sector to sector.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum [Author: the website is already lodged in BATIS with ID number 10152; please associate it with the BREF and then insert the reference here].

Driving forces for implementation
The driving forces for the implementation of an EMS include:

- improved environmental performance
- improved insight into the environmental aspects of the company which can be used to fulfil the environmental requirements of customers, regulatory authorities, banks, insurance companies or other stakeholders (e.g. people living or working in the vicinity of the installation)
- improved basis for decision-making
- improved motivation of personnel (e.g. managers can have confidence that environmental impacts are controlled and employees can feel that they are working for an environmentally responsible company)
- additional opportunities for operational cost reduction and product quality improvement
- improved company image
- reduced liability, insurance and non-compliance costs.

[Author: please insert any available information on customer demand for an EMS in the whole sector or an identifiable sub-sector]

Example plants
EMSs are applied in a number of installations throughout the EU.

Reference literature
DG Environment EMAS website [93. DG Environment 2010 ]
ISO 14000 technical committee. [94. ISO 2010 ]

Reference literature
[118, VROM, 1999], [285, Demuynck, 1999] [66, EC 2008 ] [67, EC 2006 ]

4.15.1.2 Energy conservation techniques
Note for TWG: Text moved from 4.10.1.1.2
A concerted and well-managed effort based on an integrated approach to reduce energy use, improve operations, maintain good housekeeping, and management and selective investments are the best practices worth highlighting here. There follows a list of techniques that are considered for the determination of BAT in the refinery sector. As can be seen, some of them are related to each others, others in some way.
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Achieved environmental benefits
All measures to reduce energy consumption will result in a reduction of all emissions to air including CO₂. Any energy conservation action has an impact on pollution due to the marginal fuel consumption.

Applicability
Especially applicable to these refineries with very high specific energy consumption (see Section 3.10.1). The wide range of specific energy consumption in refineries (by a factor of 4, see Section 0) means that in certain refineries, a considerable reduction in energy consumption can be realised.

Reference literature
[297, Italy, 2000], [118, VROM, 1999].

4.15.2 The bubble concept

Note for the TWG:

Conclusions of the kick-off meeting
KOM conclusion 7.2: TWG strongly invited to indicate which bubble concepts (and associated emission levels) they consider useful for the BREF, notably regarding:

- **parameters** to cover: NOₓ, SOₓ, and others, accompanied with the appropriate reference conditions (e.g. oxygen content), and the volume of exhaust gases;
- **scope**: which units should be precisely considered inside the bubble;
- **averaging periods**: annual (representative of stable operating conditions) and eventually others (i.e. daily, weekly, monthly);
- **site complexity/flexibility**: relationship between the contribution of units and their individual BAT-AELs;
- **site capacity**: concentration, load, specific load;
- **local conditions**.

The main task of the EIPPCB will be to:
- review TWG proposals and requests
- check consistency with data to be made available along the data collection process, and adapt if necessary.

Information identified or promised to be delivered by the TWG:
Chapter 5

- DE will submit proposals (done: BREF Reference n°28 available in BATIS)
- UK will provide information (done)
- CONCAWE will contribute to this item (done: preliminary and definitive contributions in BATIS)
- FR could propose wording for improving bubble definitions, reconciling site-level bubble BAT-AELs with unit-level individual BAT/BAT-AELs (done: available in BATIS)

Achievements of the Subgroup meeting (10-11 May 2010):
- Additional contributions from CONCAWE, EEB, FR, IT, NL (available in BATIS)
- Orientations given to the TWG in the Summary Report (10 June 2010)

Achievements of the Subgroup meeting (23-24 May 2011):
- the ‘bubble’ presentation has been kept as a air emission site level management technique in Chapter 4
- a ‘bubble’ methodology has been introduced in a dedicated Annex according to the orientations given by the Subgroup
- The Annex will describe the scope, the calculation and the monitoring associated to the ‘bubble’

4.15.3 Good housekeeping

It is proposed to delete this section

Description

This section includes good practices applied to maintenance, cleaning and other horizontal issues within refineries. What was considered ‘good housekeeping’ in the past may nowadays seem self-evident, as it is embedded in day to day refinery practice. New measures, based on experience gained, are however included over time. ‘Good housekeeping’ is often used in the broader context of good management and conduct of the business. Quite a number of business performance parameters, such as safety, maintenance, efficiency (of energy and manpower), product quality, information, unit/equipment reliability, human resources and finance require approaches that start with a concept of ‘good housekeeping’. For refineries, safety provides numerous examples of this approach, often grouped under the heading of safety management. Similarly, product quality management stands for should be well-developed approach to assure customer satisfaction and maintenance management for improved unit reliability/on-stream time and maintenance effectiveness. There are also systems for the other business parameters. All these systems are in place to assure that the correct practices are adopted, and that the ‘lessons learned’ are reflected in these systems (e.g. ISO 9000 series).

The more traditional aspects of good housekeeping are included in this section. These systems can also be regarded as the tools to ensure that the right procedures are adhered to in order to safeguard the proper functioning of the refinery hardware. The following techniques are considered to be good environmental practices within the industrial sectors.

- Planning and carrying out of maintenance by:
  - All plant and equipment should be subject to regular preventive maintenance programmes for all plant and equipment, in line with operational requirements, to ensure continued optimum performance;
  - prompt clean up of minor spillages with absorbents;
  - Regular cleaning of equipment and refinery premises. Cleaning, by its nature, generates waste. By choosing the right procedure and technique this waste may be minimised or its nature altered so as to make it more easily disposable. Examples of cleaning techniques include:
    - draining equipment to the maximum;
    - recycling ‘spent’ rinse water;
    - using high-pressure water cleaning rather than detergents or chemicals;
using on site pretreatment whenever possible, e.g. wash/steam filter material (e.g. filter clays) prior to dumping, recycling, regeneration or appropriate waste disposal;
minimising tank sludge prior to cleaning (solvent and mixers);
during cleaning, directing vents and vessel steaming to be directed to flare. This technique may raise serious safety issues if oxygen is present. In addition when Hg is present particularly when steaming overhead coolers mercury emissions may occur;
in many refineries, using high pressure water to clean heat exchanger bundles generates and releases water and entrained solids to the refinery waste water treatment system. Exchanger solids may then attract oil as they move through the sewer system and may produce finer solids and stabilised emulsions that are more difficult to remove. Solids can be removed at the heat exchanger cleaning pad by installing concrete overflow weirs around the surface drains or by covering drains with a screen. Other ways to reduce solids generation are by using anti fouling on the heat exchanger bundles to prevent scaling and by cleaning with re-usable cleaning chemicals that also allow for the easy removal of oil;
cleaning at designated places in order to have control over run off material and contaminated water;
prompt clean up of minor spillages with adsorbents;
installing weirs at cleaning places, in order to hold back solids, which otherwise might attract oil in CPI separators;
minimising and re-using cleaning chemicals.

Using techniques in common industrial equipment (pumps, compressors, etc.) that can reduce the environmental impact, for example:
implementation of operational improvements in new designs;
equipment reliability improvement;
use of lubrication techniques based on the lubrication by an oil mist. The technique consists of a vortex generator, which generates, with the help of dry pressurised air, a mixture of air and lubricant oil. This mixture is called oil mist, and lubricates the dynamic equipment. Once lubricated, the air is recirculated to the vortex.

Some techniques that may be considered as good housekeeping techniques are already included in other sections. These include for example:
application of advanced process control (see Section 4.15.5) that can include the on line continuous (equipment and process) performance measurement, the measurement of performance and comparison with targets;
prevention of soil contamination (see Section 4.27.1);
leak detection and repair (LDAR) (see Section 4.25.6.1);
minimisation and prevention of spillage of hydrocarbons (see Section 4.25.6.1);
minimisation of waste generation (included in each of the process sections).

Achieved environmental benefits
The lubricant technique can reduce the use and subsequent waste of lubricant oil by up to 75% and reduce the electrical consumption within the electrical motors.

Operational data
These systems are dynamic; they are kept alive by the incorporation of continuous improvement opportunities.

Applicability
The lubricant technique can be applied to lubrication of dynamic equipment with lubricated bearings, e.g. centrifuge pumps, electrical engines, gear assemblies, intermediate supports.

Economics
Less than two years pay off is claimed by the technique provider in the lubricant technique.
Example plants
The lubricant technique has been already used by the main petrochemical companies.

Reference literature
[118, VROM, 1999], [285, Demuynek, 1999], [19a, Irish EPA, 1993], [316, TWG, 2000], [324, Sicelub, 2001].

4.15.4 Training
Note to TWG: Part covered by section on EMS

Staff training plays an important role in the prevention of contamination within the refinery. Some important aspects are:

- including environmental concerns and environmental issues in the training of the refinery staff;
- training staff to reduce solids in sewers. A facility training programme which emphasises the importance of keeping solids out of the sewerage systems will help reduce that portion of waste water treatment plant sludge arising from the everyday activities of refinery staff;
- training staff to prevent soil contamination. Contaminated soil can be reduced by educating staff on how to avoid leaks and spills.

Reference literature
[118, VROM, 1999], [256, Lameranta, 2000].

4.15.5 Production planning and control
KOM conclusion 5.7: TWG to provide relevant information on specific organisation and practises/approaches for:

- ensuring the full use (in terms of availability and capacity) of key abatement techniques (e.g. by avoiding unnecessary bypass);
- limiting the deterioration of air quality under adverse conditions, e.g. adverse meteorological conditions. 
  info expected from FR and NL

No specific information provided

Description
Some techniques to consider in this respect are regarding production planning and control are

To ensure the full use of key abatement techniques (for both availability and capacity) some procedures can be defined for specific conditions wherer the operating parameters of a waste gas or waste treatment system may have a significant effect on the overall achieved removal efficiency (e.g. quantity of alkaline reagent, working temperature, waste gas flow, by-pass operations, etc.).

Special procedures can be defined for specific operating conditions, in particular:

- start-up or shutdown operations
- other special operations which could affect the proper functioning of the system (e.g. regular and extraordinary maintenance work and cleaning operations of the furnace and/or of the waste gas treatment system, or severe production change)
- insufficient waste gas flow or temperature which prevents the use of the system at full capacity.
pollution control equipment should, in general, be kept running during start-up and shutdown, for as long as it is necessary to ensure compliance of authorisations, provided no other safety or operating considerations prevent it;

- reduce the start-ups and shutdowns to a minimum. Proper production planning can reduce the frequency and duration of process-shutdown;
- implementation of advanced process control for the planning and control of production;
- advanced process control to optimise energy use within the refinery (related to Section 4.10.1.1.2);

Reference literature
[118, VROM, 1999]. IEF 22-5 Standard text

4.15.6 Safety management

Safety management in refinery is mainly addressed through the requirements of Seveso II directive (96/82/CE). An important cross-effect of environmental measures. Any direct relation of influence exists. Measures may affect safety in:

- A positive way. Closed loop sampling minimizes accidental releases of material.
- A no way. The process water recycle to desalters has no relevant impact on safety.
- A negative way. Gas recovery systems often have to deal with explosive atmospheres, where the untreated off-gases are outside the explosibility limits. Negative impacts on plant safety can reach such an extent that the additional dangers exceed what a plant is willing to handle. Even by for other reasons, promising techniques may lose applicability by that criterion at least, until significant improvements of the safety properties of such techniques are developed.

Some techniques to consider are the following:

- prepare a safety report and practice risk management;
- use results obtained from risk analyses;
  - identified risks are assessed with reference to the acceptance criteria for risk in the activities in order to identify the dimension of accidental events.
  - Dimensioning accidental events form the basis for a systematic selection of the technical, operational and/or organisational risk-reducing measures to be implemented. Risk-reducing measures consist of probability-reducing and consequence-reducing measures, including contingency measures.
  - The effect of the risk-reducing measures to be implemented is documented, assessed both individually and in a wider perspective.
  - Implementation of the risk-reducing measures and of the basic assumptions made in the risk analysis is systematically followed up in order to ensure that safety in the activities is maintained within the defined acceptance criteria for risk.
  - Results from of risk analyses are communicated to the employees and shall be used actively in preventive safety efforts.

Reference literature
[118, VROM, 1999], [285, Demuyck, 1999], [302, UBA Germany, 2000], [260, Sandgrind, 2000].

4.15.7 Water management

Note for TWG: For consistency and to avoid repetitions, section 4.26 on waste water treatment will cross reference to the present section when needed.
4.15.7.1 Water stream integration (WSI)

The previous text has been partly redistributed and reduced to fit in with the standard structure.

**Description**

Studies for the optimisation of water, effluent and drainage are often relevant. Similar to the identification of energy-saving opportunities, water pinch studies can be carried out to identify process water integration options and water reduction and reuse opportunities. In most refineries, some internal water streams are already commonly used as desalter wash water, such as condensate water and steam-stripped sour water. There is scope for increased water reduction and reuse in refineries, which will lead to reduced size and costs of both water make-up and end-of-pipe treatment facilities.

**Technical description**

**Purpose and principle**

The purpose of water stream integration (WSI) is the reduction of process water produced for final treatment prior to discharge, in order to save operational costs. It saves high-quality potable and demineralised water, which can be expensive at some locations; it reduces the size, investment and running costs of the water supply and effluent treatment facilities. Moreover, it reduces the size and the environmental impact of effluent discharges.

The principle of WSI is maximising to use prevention, reduction, recycling and reuse of process water, rainwater, cooling water and sometimes contaminated groundwater with the aim of minimising reducing the amount of process water for end-of-pipe treatment. WSI needs to be carried out as part of a water master plan for the refinery. This plan aims at the optimisation of the use and reuse of all water streams in the refinery. For greenfield refineries and in existing refineries, when new treatment installations are installed, a win-win situation is created when the amount of imported water, the size of effluent treatment facilities and the discharge are all minimised. Ideally it may become feasible to use treated effluent as a source for the make-up of process water, cooling water and/or boiler feed water. Every refinery has its specific optimum WSI scheme.

The process water used for the process generated in a refinery is of the magnitude of 0.1 to 0.8 m$^3$ per tonne of crude oil input feed. Some techniques to consider for the minimisation reduction of freshwater consumption, can be, but are not limited to, the following:

- by substitution of wet cooling processes by dry processes
- recirculation of cooling water
- use of treated process water as cooling water
- use of condensates as process water
- use of rainwater as process water.

**Concept description**

The concept or methodology to design an effluent/water integration system for a refinery is to inventories take an inventory of water demand and effluent production for each refinery unit operation and to assess the water losses. This inventory provides the water balance across the refinery. It is recommended to visualise the water balance by a block scheme as presented as an example in Figure 4.31. The next step is to identify all possibilities to reduce the amount of water required and to reuse as much as possible by matching (quantity and quality) effluents by means of a water optimisation scheme. This ‘water-pinch’ methodology includes giving consideration to the reuse of treated effluent. The WSI concept aims at ‘closing the water loop’.
WSI is mainly dependent on the refinery configuration, location, availability and type of raw water, the crude quality and the level of desalting required, the cost of potable water, the type of cooling water system and the availability of rainwater. Within a refinery, a number of standard process-integrated effluent/water treatment provisions are available as well as a number of standard possibilities for water reduction and reuse.

![Diagram of process water integration scheme for a cat cracker refinery configuration (10 Mt/yr)](image)

**Figure 4.31:** Example of a process water integration scheme for a cat cracker refinery configuration (10 Mt/yr)

In most refineries, a number of these options have already been implemented to some extent, either in the original design or by retrofit:

1. Condensed steam that has not been in contact with product. These condensate streams are suitable for direct reuse as boiler feed water (BFW), leading to cost savings;
2. Sour water is produced if wash water and/or steam comes into contact with hydrocarbon products that contain H₂S and NH₃. In the SWS, the H₂S and NH₃ are largely eliminated. This renders a treated effluent into a suitable quality wash water for the desalter;
3. The reuse of stripped sour water as wash water for crude desalting is a first step in any WSI. A crude desalter uses 5-10% water on crude, dependent on the crude quality and the level of desalting required;
4. The standard provisions for process water treatment are the sour water stripper (SWS), to treating streams the sour water produced in from various process units) and the desalter, which is a major water-consuming unit, whereas the water quality requirement in the desalter does not constrain the use of SWS effluents. Sour water is produced if wash water and/or steam comes into contact with hydrocarbon products which contain H₂S and NH₃. In the SWS, the H₂S and NH₃ are largely eliminated. This renders a treated effluent into a suitable quality wash water for the desalter;
5. Process units that produce significant quantities of waste water are the crude distillation unit (CDU) and the fluid catalytic cracker (FCC) has already been defined. In the CDU...
overhead, 2–3% waste water on crude intake is produced as steam condensate. This water does not require SWS treatment but can be directly routed as wash water in the desalter. An FCC unit, if present in the refinery, also produces significant quantities of waste water in the range of 5–10% on feed. This amount can be reduced to 2–4% if recirculating of wash water is accomplished. Stripped sour water can in principle be used as wash water and, on the other hand, the FCC wash water can either be recycled to the SWS or used as desalter wash water. Depending on the quantities of effluent-generated, optimisation of water integration is possible;

5. boiler blowdowns, cooling water blow-downs, and treated rainwater run-off are water streams that may be suitable for desalter wash water as well, dependent on the salt concentration;
6. a site-specific water masterplan can be designed, applying the concept of WSI. It will be dependent on-and will take account of the location and site-specific elements such as climate/rainfall, river/sea, existing segregation, availability of two desalters/SWS, specific refinery units, fresh water costs, groundwater situation, etc;
7. use of phenolic spent caustic for stripped water neutralisation and subsequent desalter wash to allow phenol resorption into the crude;
8. if the stream generated in the boiler feed water production is not recycled to the desalter, biotreatment is required because of anti-foaming agents and corrosion inhibitors;
9. refinery waste water need to be properly segregated to ensure the most effective treatment or reuse. A typical segregation scheme for a petroleum refinery would provide a ‘clean’ water sewer, an oily water sewer, and a highly contaminated water sewer;
10. water pinch or water optimisation studies;
11. water coolers/condensers may be replaced by air coolers (closed cooling water systems) (reference to cooling section);
12. air cooling, reduced cooling water blowdown, using hydrocracking and hydrotreating processes that produce less waste water than older processes; and using improved drying, sweetening and finishing procedures to minimize the generation of spent caustics and acids, water washes and filter solids; recycling and reusing waste water elsewhere in the refinery;
13. treated waste water that can be reused in makeup to process and pump cooling systems, washdown water and water from fire control systems;
14. use of vacuum liquid ring compression instead of steam ejectors to minimize water consumption; use waste-water-free vacuum technique (recirculation of water) if otherwise harmful substances are transferred to the environment.

Energy and process materials utilisation
The steam boilers and steam system require corrosion inhibitors and oxygen scavengers and the de-aerator uses LP steam. The DAF unit and the sludge work-up require polyelectrolytes. The biotreater requires nutrients (phosphor) if no sanitary waste water or cooling water blowdown (which could contain phosphates as corrosion inhibitor) is co-treated. A comprehensive WSI will result in minimization of these expensive chemicals and in minimum pollution and discharge levels.

Achieved environmental benefits Environmental aspects
Water stream integration mainly aims at reducing the consumption of fresh water. The environmental implications of the conceptual approach of a process water integration scheme are favourable. Enclosed systems and closed-water loops limit the hydrocarbon emissions to air and discharges to surface water, and also lead to the reduced generation of waste in the form of sludges. The quantification of the reductions of the water used (and products lost) vary from location to location but can be substantial (>50%).

Environmental performance and operational data
Minimising Reducing the volume of water discharged reduces the size of the effluent treatment plant required, the amount of energy and chemicals used, and the quantity of pollutants discharged to the environment. Data on actual fresh water usage are included in Section 3.1.1.2. Table 3.3 and Section 3.15. Based on the TWG data collection, specific consumption mainly
ranges between 0.2 and 25 m$^3$/t of feedstock, the largest part still being used for cooling. As a general guide, approximately 0.1–5 m$^3$/t of waste water (process waste water, cooling water and sanitary waste water) per tonne of crude is generated when cooling water is recycled.

Cross-media effects
Reducing the water volume can lead to increased pollutants concentrations entering the waste water treatment plant but the process, if properly designed, can generally deal with this issue.

Technical considerations relevant to applicability
Generally applicable to existing plants but when included in the initial design it can lead to higher efficiency.

Economics
Data available on costs?

Driving force for implementation
The reduction of fresh water use is a goal for most refineries for two main reasons. Firstly, fresh water, particularly high quality water, is a valuable resource which in many parts of Europe is becoming increasingly scarce. Where water of lower quality is used, treatment to acceptable standards also requires the use of energy and chemicals. Secondly, water used has to be discharged.

Example plants
A newly built refinery in Thailand generates only 40 t/h process water at a crude throughput of 8 Mt/yr due to such an approach. Values of 0.5 m$^3$ per tonne of crude oil have been also achieved within Europe.

Reference literature
[118, VROM, 1999], [113, Noyes, 1993], [268, TWG, 2001], [117, VDI, 2000], [77, REF TWG 2010]

4.15.7.2 Water and drainage system

Purpose and principle
The ideal for a flexibility is needed in water and drainage systems to create the flexibility to cope with changing circumstances such as sudden rainfall, firefighting, process upsets, process changes, additional plants, capacity extensions and new regulatory demands. A basis for integrated water management is also needed, including spill prevention and potential reuse of water streams without or after treatment. The principle is based on a thorough qualitative and quantitative analysis of the various water and effluent streams, the assessment for reuse potential with maximum reliability and environmental protection. A flexible water and drainage design allows for water integration and allows for short-term and long-term changes at optimised cost. An enclosed sewerage system for the transfer of contaminated water from tanks and processes to separation facilities is also a technique to consider.

System description
A modern and optimised water and drainage system of an industrial site is the result of a conceptual design of many unit operations lined up in such a way that water management can be optimised. The basis of the concept is segregation of the different water streams into oil-free water streams, accidentally oil-contaminated (AOC) streams and continuously oil-contaminated (COC) streams. The latter may be subdivided into low and high BOD streams with the possibility for biotreatment, effluent polishing and reuse (see Figure 4.32).

The application of a segregation concept takes a certain level of housekeeping and operational discipline into account. The decision to choose a different route for a certain type of effluent would be based on the monitoring of water qualities, both internal streams and the collective
discharge. The environmental performance and the effluent management of the refinery requires a constant level of alertness and dedication, sufficient training and motivating instructions and an extensive monitoring (sampling and analysis) scheme. The concern is mainly with the first flush for which principle it entails the collection, separation and treatment of the first charge of rainwater from the potentially contaminated refinery surface. After the first flush the rest of the rainwater is collected, analysed and discharged without treatment, if acceptable.

**Achieved environmental benefits**
Prevention of pollution due to discharge without appropriate treatment of water coming from the whole refinery drainage system.

**Environmental performance and operational data**
XXX

**Energy and process materials utilisation - Cross-media effects**
Energy requirements are mainly for pumping the waste waters and are system and site-dependent.

**Application - Technical considerations relevant to applicability**
A number of elements of the current design philosophy for a new water and drainage system can be considered for implementation in existing refineries, and more particularly in cases where the old effluent and drainage system has become obsolete.

**Economics**
Note to TWG: Any recent data available?

**Environmental aspects - Driving force for implementation**
A new problem in most refineries is the management of contaminated groundwater. Possibilities exist to manage and reuse this stream either inside the refinery (after iron removal) or to accommodate and route this stream directly to the WWTP facilities. Source reduction and spill prevention by good housekeeping are also essential elements for VOC and odour emission reduction at CPI, API, DAF units and biotreaters. Some refineries employ an H$_2$S oxidation tank to prevent toxic and odorous emissions from process water prior to DAF and biotreatment.
Status Example plants
Not many refineries have segregated process water and rainwater run-off. If they do, these streams are routed to separate and dedicated treatment systems. The extent of segregation varies from refinery to refinery (by design or retrofit). Most refineries use stripped sour water and/or some condensate streams as desalter wash water (see Section 4.9). Other effluent streams are also candidates for desalter wash water such as cooling water and boiler blowdowns. Reuse of treated effluent (biotreatment, sand filtration followed by reversed osmosis) as a source for boiler feed water is technically feasible. Reuse of treated effluent as cooling water make-up is done at several locations. First flush principles treatment is applied are followed in several refineries. Figure 4.32 shows a block diagram of an example of an optimised water/effluent routing for a refinery.

Reference literature
[308, Bakker and Bloemkol, 1994], [118, VROM, 1999], [19a, Irish EPA, 1993].

4.15.7.3 Rainwater

Some techniques that may be applied to rainwater are given below:

- Surface water run-off or rainwater can be segregated into oil-free, accidentally oil-contaminated and continuously oil-contaminated effluents. These effluents may require treatment. Rainwater on contaminated surfaces may lead to effluent to be treated in a CPI/API.
- In specific situations rainwater may be a useful source of raw water for the preparation of process water make-up, boiler feed water and cooling water.
- Some refineries have segregated effluent and drainage systems. In modern refineries the water and drainage system includes a segregation of process water, condensate blowdowns, rainwater and cooling water in order to minimise reduce the environmental
impact of effluent discharges at minimum cost. Moreover, adequate process water integration and water management measures will include a review of all options to recycle water streams with the aim of achieving a significant reduction of end-of-pipe treatment. Segregation of the process water discharges, surface water run-off, cooling water and boiler feed water blowdowns and other effluents may be considered. Separation of storm water and other effluents of different origins in order to permit appropriate treatment options may be considered. In some cases, retrofitting costs can be very high.

Reference literature
[118, VROM, 1999], [113, Noyes, 1993].

Proposed to delete

4.15.7.4 Use of sanitary waste water

Sanitary waste water effluent is collected in a septic tank. As this stream is small compared to the total waste water of a refinery and contains sufficient nutrients (micronutrients and phosphorus) required for an industrial biotreater, this effluent can be usefully combined with the process water to a dissolved air flotation unit preceding a the biotreater. However, local regulations may prohibit to combine sanitary waste water with process waste water.

4.15.7.5 Ballast water

Ballast water is typically discharged at a very high rate provoking the generation of high-volume waste water peaks. That waste water contains high salt concentrations (seawater), and are heavily polluted with oil. It can easily lead to an upset of existing effluent treatment systems. Therefore the use of ballast water tanks is an important equalisation tool for feeding the water in a controlled way to either the process water system or the COC system, if the COD is lower than 100 ppm. Because of this, (and because jetties are often remote from the rest of the refinery) ballast water is often treated in a separate dedicated plant dedicated to that. As more and more crude tankers are equipped with double hulls, the ballast water problem is slowly phasing out.

4.15.7.6 Firefighting water

Some techniques to consider are:

- The firefighting water system can sometimes be a water reuse sink within the refinery.
- Provision should be made to reduce the potential for pollution as a result of firefighting activities (e.g. to collect firefighting water in a lagoon basin). Serious pollution has been caused by the release of firefighting water in an emergency. Design of Containment Systems for the Prevention of Water Pollution from Industrial Accidents can be found in the Construction Industry Research and Information Association Report 164 1996.

Proposed to delete

4.15.7.7 Blowdown systems

The blowdown liquid system is typically composed of mixtures of water and hydrocarbons containing sulphides, ammonia, and other contaminants, which are sent to the waste water treatment plant.

4.15.8 Groundwater monitoring

Text moved to Section 3.28 and annex 9.8
For consistency with the way this topic is addressed in the various BREF, the previous text has been partly moved to an annex as an illustrative example. Main description and principles are kept and moved to Section 3.28 on Monitoring.

Section proposed to delete

4.15.9 Emissions integrated management

Some of the air emissions issues are by its nature refer to many processes or activities then they should be considered as a refinery as a whole issue. Under these issues, we can include in particular sulphur emissions and VOC emissions. The application achievement of a good environmental performance should take involve the refinery as a whole as well as and address, in the case of the sulphur, the amount of sulphur contained in the products. A good environmental planning for the reduction of these emissions should consider these aspects. In order to clarify these aspects, Table 4.63 shows where in this document topics that may have integrated related issues are tackled.

<table>
<thead>
<tr>
<th>Integrated environmental issue</th>
<th>Sections in Chapter 4 where it is analysed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur emissions from refineries</td>
<td>4.15.9.1 and 4.25.5</td>
</tr>
<tr>
<td>VOC and fugitive emissions</td>
<td>4.25.6.1</td>
</tr>
<tr>
<td>Priority substances</td>
<td>4.15.9.2</td>
</tr>
<tr>
<td>Protection of from contamination of soil and groundwater</td>
<td>4.15.8</td>
</tr>
<tr>
<td>Waste generation</td>
<td>4.27</td>
</tr>
<tr>
<td>Energy</td>
<td>4.10</td>
</tr>
<tr>
<td>Steam</td>
<td>4.10.1-2.2.4</td>
</tr>
<tr>
<td>Noise</td>
<td>4.23.9 and 10</td>
</tr>
<tr>
<td>Odour</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.63: BREF sections where to find complementary information on emission integrated management

Section proposed to delete

4.15.9.1 Sulphur balance management

KOM conclusion 2.2: TWG to provide info on relevant strategies and techniques for improving the sulphur management in existing refineries (site level).

→ UK: info have been promised on the work done over the last years.
No additional information received – Topic partially addressed through ‘bubble’ approach.

4.15.9.2 Priority substance-driven management

KOM conclusion 2.3: EIPPCB to consider the ‘tracking’ of priority substances in EMS

Specific information on concrete examples from FR contribution.

Description

Within the framework of European legislation (specifically Directive 2000/60/EC, the water Framework Directive) this technique is a strategy to identify and reduce the water releases of substances classified as ‘priority substances’.

An appropriate strategy could be implemented and include the following steps:

- establishing a list of substances that may be released by the refinery sites;
- setting sampling prescriptions for monitoring normal operating conditions (temporary or permanent plan);
- determining the most relevant period for a temporary monitoring plan, e.g. a 6 month period, and carrying it out;
analysing the results and establishing a concrete action plan for reducing emissions of the corresponding substances to be included in the EMS. This could result, e.g. in adding substances to the regulatory monitoring plan.

**Achieved environmental benefits**
Reduction of hazardous substances discharge from refineries.

**Operational data**
Based on the results from the French monitoring campaign the following table may be used to determine the substances to be monitored monthly during a six month transitory plan. In the last step, a relevant list of substances to monitor for each plant will be defined. When appropriate, specific actions will have to be carried out by operators in order to achieve reduction.

<table>
<thead>
<tr>
<th>Substances</th>
<th>CAS(1) number</th>
<th>WFD(2) number</th>
<th>Limit of quantification (µg/l)</th>
<th>Transitory monitoring(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>71 – 43 – 2</td>
<td>4</td>
<td>1</td>
<td>Systematic for benzene production sites only</td>
</tr>
<tr>
<td>Xylenes (o,m,p)</td>
<td>1330 – 20 – 7</td>
<td></td>
<td>2</td>
<td>Systematic</td>
</tr>
<tr>
<td>Anthracene</td>
<td>120 – 12 – 7</td>
<td>2</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>206 – 44 – 0</td>
<td>15</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>91 – 20 – 3</td>
<td>22</td>
<td>0.05</td>
<td>Systematic</td>
</tr>
<tr>
<td>Benzo (a) pyrene</td>
<td>50 – 32 – 8</td>
<td>28</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Benzo (b) fluoranthene</td>
<td>205 – 99 – 2</td>
<td>28</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Benzo (g,h,i) perylene</td>
<td>191 – 24 – 2</td>
<td>28</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Benzo (k) fluoranthene</td>
<td>207 – 08 – 9</td>
<td>28</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Indeno (1,2,3-cd) pyrene</td>
<td>193 – 39 – 5</td>
<td>28</td>
<td>0.01</td>
<td>Systematic</td>
</tr>
<tr>
<td>Cadmium and compounds</td>
<td>7440 – 43 – 9</td>
<td>6</td>
<td>2</td>
<td>Systematic</td>
</tr>
<tr>
<td>Lead and compounds</td>
<td>7439 – 92 – 1</td>
<td>20</td>
<td>5</td>
<td>Systematic</td>
</tr>
<tr>
<td>Mercury and compounds</td>
<td>7439 – 97 – 8</td>
<td>21</td>
<td>0.5</td>
<td>Systematic</td>
</tr>
<tr>
<td>Nickel and compounds</td>
<td>7440 – 02 – 0</td>
<td>23</td>
<td>10</td>
<td>Systematic</td>
</tr>
<tr>
<td>Arsenic and compounds</td>
<td>7440 – 38 – 2</td>
<td>5</td>
<td></td>
<td>Systematic</td>
</tr>
<tr>
<td>Zinc and compounds</td>
<td>7440 – 66 – 6</td>
<td>10</td>
<td></td>
<td>Systematic</td>
</tr>
<tr>
<td>Copper and compounds</td>
<td>7440 – 50 – 8</td>
<td>5</td>
<td></td>
<td>Systematic</td>
</tr>
<tr>
<td>Chromium and compounds</td>
<td>7440 – 47 – 3</td>
<td>5</td>
<td></td>
<td>Systematic</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>92 – 52 – 4</td>
<td></td>
<td>0.05</td>
<td>Additional</td>
</tr>
<tr>
<td>Tributyl phosphate</td>
<td>126 – 73 – 8</td>
<td></td>
<td>0.1</td>
<td>Additional</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>118 – 74 – 1</td>
<td>16</td>
<td>0.01</td>
<td>Additional</td>
</tr>
<tr>
<td>Chloroform</td>
<td>67 – 66 – 3</td>
<td>32</td>
<td>1</td>
<td>Additional</td>
</tr>
<tr>
<td>Perchloroethylene</td>
<td>127 – 18 – 4</td>
<td></td>
<td>0.5</td>
<td>Additional</td>
</tr>
</tbody>
</table>

(1) CAS Chemical Abstract Service.
(2) WFD: Water Framework Directive.
(3) Additional means case-by-case approach.

*Source: TWG 2010-FR French Strategy to reduce discharges of dangerous substances.*
Applicability
Applicable to existing installations.

Economics
Costs may vary greatly depending on the total number of substances monitored and on the duration of the transitory monitoring programme put in place which are very site specific. It may be necessary in some cases to also measure these substances in the raw water uptaken by the refinery, eventually increasing the number of samples and analyses. The cost for an analysis of a dozen substances is estimated (2010) between EUR 1 500 and 3 000.

Driving force for implementation
Community legislations.

Example plants
In France, 13 refineries were concerned.

4.15.9.3 Site-level optimisation management of air emissions

Note for TWG: According to subgroup meeting (23 – 24 May 2011) conclusions, ‘bubble approach’ is proposed to be mainly addressed in this section as one tool for site level management and taking into account the proposals made during the aforementioned meeting.

Description
Refineries meet some or all of their energy needs with a variety of gaseous and liquid fuels that are by-products of the various processes. In this respect, refineries differ from other industries that generally buy all their specified fuels from outside. Another particularity of the refining sector is the recognised complexity of refineries. Aspects of this complexity include, in a modern refinery, numerous emission points interrelationships between feedstock, types of processes and variations in different operating conditions in relation to product slate and product quality requirements. Furthermore, a refinery operates using, at different plants and at different times, the various fuels it produces in-house.

One of the most used techniques for site level management of air emissions is known as the ‘bubble approach’ and can be described as follows.
The ‘bubble approach’ is a generic tool for expressing and comparing the level of emissions achieved or expected at refinery site level, from a clearly identified set of combustion and process units, and for a given substance or parameter. As represented in Figure 4.33, this approach consists of considering all concerned emissions together, as emitted through a single ‘virtual single stack’.
This approach is considered especially suitable to oil refining, where some flexibility is needed for expressing or evaluating the environmental performance at the site level. This flexibility is notably justified by the following factors:

- the recognised complexity of refining sites, with multiplicity of combustion and process units, often interlinked for their feedstock and energy supply;
- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received;
- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements;
- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls have been duly justified as not being possible and have to be compensated elsewhere.

Based on the exchange of information within the TWG, a proposal for a harmonised methodology for the bubble calculation is provided in Annex 9.9. This example enables to set a site level air emission value based on BAT. It provides a method for calculations of \( \text{SO}_2 \) and \( \text{NO}_x \) equivalent concentration (\( \text{mg/Nm}^3 \)) and can also be used for setting global loads (e.g. tonnes per year).

This ensemble of techniques consists of setting, in the refinery management system appropriate targets, dedicated procedures and specific monitoring instruments in order to allow the operator:

- to set clear emission targets at the site level
- to monitor permanently the site environmental performance against the set targets
- to optimise together possible site energy requirements with their related air emissions
- to identify the most cost-effective places for the application of new primary or end-of-pipe techniques for further reduced emissions
- to better prepare and anticipate retrofitting difficulties
- to maximise the availability and stability of abatement processes and equipment.
### Technical description

Focusing on the most used technique for site level management the ‘bubble approach’, as described in Annex 9.9 is based on the main items given below.

**Bubble perimeter**

The exact bubble perimeter to be considered for a given site will depend on the purpose the bubble tool is used for. For the purpose of applying BAT, the proposal methodology provided in Annex 9.9 is designed to cover, as necessary, all sources of permanent emissions of a refinery; i.e. combustion plants, cat crackers, sulphur recovery units, coke calciners and other processes where appropriate.

**Bubble substances or parameters**

Some competent authorities have considered covering simultaneously all usual main parameters (CO, PM, NOx, SO2 and eventually VOC) in a bubble approach, with the aim to address site energy consumption and air emissions in a consistent way, and to introduce the same site-level flexibility for all these parameters which are very often interdependent.

In the context of the work undertaken for the revision of this document, SO2 and NOx have been recognised as the two parameters which deserve priority in a BREF common methodology for a site-level bubble-expressed AEL calculation, and for which enough supporting information and data have been provided. Therefore, the methodology developed in Annex 9.9 focuses on SO2 and NOx and is based on the available data provided. Nevertheless, extensions to other pollutants (e.g. PM, CO) are not excluded.

**Bubble averaging period**

The averaging period to be considered will depend on the purpose the bubble tool is used for. In the particular context of this document, the methodology proposed has been based primarily on a yearly average, since a long term period has been considered as the most appropriate for reflecting best performances achievable in normal operating conditions, and giving enough time and flexibility to integrate necessary feedstock, process and fuel adjustments.

However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter term bubble can be derived from the long term bubble using monitoring results.

**Bubble calculation**

The site-level bubble is a sum of two terms:

- A first term related to the energy system, including at least all furnaces, standalone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable AEL concentration ranges expected on each category of installations.
- A second term related to the process units including at least an FCC UNIT if any, and an SRU. This term should be driven by suitable AEL concentrations or specific emission ranges expected on each of them when BAT is applied.

In the context of this document, and for the purpose of expressing meaningful AELs at the site or partial site level, the bubble determination should always be based on concentration and specific emission ranges expected on all concerned installations when BAT is applied, and should involve the following steps:

- Step 1: exhaustive identification and geographical mapping of all included sources
- Step 2: determination of the offgas volumetric contributions expected from all included sources
- Step 3: determination of the mass contributions expected from all included sources
- Step 4: determination of the bubble-associated monitoring regime
The actual details of the calculation and necessary information on each of these steps are given in Annex 9.9.

**Achieved environmental benefits**

By allowing flexibility in how to reduce refinery emissions, the bubble approach puts the focus on environmental benefit (decreasing overall emissions) rather than on individual source compliance.

Examples of how to achieve environmental targets by various reduction means are made available under the following heading..

**Environmental performance and operational data**

Note to TWG: The following examples are taken from real sites data provided by TWG (especially CONCAWE) to illustrate the achieved environmental benefits.

Example 1 is a refinery with a small FCC unit which currently uses 32% of liquid fuel firing and has a SRU unit that operates at a recovery efficiency of 98%. The options considered potentially viable to reduce sulphur emissions are:

- to replace a fraction of the liquid fuel firing with natural gas
- to use sulphur reducing additives (SRA) in the FCC unit
- to install a wet gas scrubber on the FCC unit
- to upgrade the sulphur recovery tail gas treatment unit which could be to two levels corresponding to the process chosen.

The current total site bubble is 1 165 mg/Nm$^3$ (at 3% O$_2$) with contributions of 795 mg/Nm$^3$ from the combustion system, 2 500 mg/Nm$^3$ from the FCC and 19 000 mg/Nm$^3$ from the SRU. The combustion system contributes 88% of the flue-gas, the FCC 11% and the SRU 1%. By mass emission the combustion system contributes 60%, the FCC 24% and the SRU 16% of total SO$_2$.

Table 4.65 shows the effect of applying different control options. In this refinery the base capacity of the SRU is limited and this imposes a maximum use of SRA in the FCC which has to be regenerated. Two degrees of substitution of the liquid fuel are considered to reflect the fact that this is not a commercial fuel and conversion would have to be considered.

Option 1 considers measures on all three sources (Combustion, FCC and SRU) substituting part of the liquid firing, introducing SRA to 30% removal and upgrading the SRU tail gas unit to a sub-dew point system. The reason for this choice is that the existing unit is a 2 bed Claus unit which does not offer an economic advantage to the installation of a SuperClaus unit. This achieves a 31% reduction in mass emissions. Option 2 focuses on eliminating liquid firing only. It achieves a 42% reduction in emissions. Option 3 focuses on upgrading the SRU tail gas unit to a SCOT plant but achieves only a 16% reduction in emissions. Option 4 focuses on scrubbing emissions from the FCC unit and achieves a 21% reduction in emissions.

Options 5, 6, 7 and 8 consider combined actions based on a full fuel switch to natural gas firing supplemented by actions on the FCC (5), SRU (6,7) and both FCC, SRU (8). The incremental improvements in mass reduction range from 7% (5) to 15% (7) over the fuel switch alone.
Table 4.65: Example of options for SO₂ emissions reduction with site level management

<table>
<thead>
<tr>
<th>% Flue-gas volume</th>
<th>100 %</th>
<th>88 %</th>
<th>11 %</th>
<th>1 %</th>
<th>Combination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total bubble mg/Nm³</td>
<td>Combustion mg/Nm³</td>
<td>FCC mg/Nm³</td>
<td>SRU mg/Nm³</td>
<td></td>
</tr>
<tr>
<td>Current situation</td>
<td>1 165</td>
<td>795</td>
<td>2 500</td>
<td>19 000</td>
<td>FCC: 32 % liquid fuel firing -SRU 98 %</td>
</tr>
<tr>
<td>Option 1</td>
<td>802</td>
<td>583</td>
<td>1 750</td>
<td>9 700</td>
<td>Partial fuel switch + FCC SRA 30 % + SRU 99 %</td>
</tr>
<tr>
<td>Option 2</td>
<td>675</td>
<td>239</td>
<td>2 500</td>
<td>19 000</td>
<td>Full fuel switch</td>
</tr>
<tr>
<td>Option 3</td>
<td>984</td>
<td>795</td>
<td>2 500</td>
<td>990</td>
<td>SRU 99.9 %</td>
</tr>
<tr>
<td>Option 4</td>
<td>917</td>
<td>795</td>
<td>250</td>
<td>19 000</td>
<td>FCC Scrubber 90 % SO₂ Removal</td>
</tr>
<tr>
<td>Option 5</td>
<td>593</td>
<td>239</td>
<td>1 750</td>
<td>19 000</td>
<td>Fuel switch and FCC SRA 30 %</td>
</tr>
<tr>
<td>Option 6</td>
<td>582</td>
<td>239</td>
<td>2 500</td>
<td>9 700</td>
<td>Fuel switch and SRU 99 %</td>
</tr>
<tr>
<td>Option 7</td>
<td>495</td>
<td>239</td>
<td>2 500</td>
<td>990</td>
<td>Fuel switch and SRU 99.9 %</td>
</tr>
<tr>
<td>Option 8</td>
<td>500</td>
<td>239</td>
<td>1 750</td>
<td>9 700</td>
<td>SRU 99 % and FCC SRA 30 % and fuel switch</td>
</tr>
</tbody>
</table>

NB: Example 1: 32 % oil firing, small size FCC, SRU 98 %
Source: CONCAWE 2011

Example 2 shows how NOₓ control options might be considered. The refinery combustion system comprises many small units ducted to common stacks. The fluegas temperature at the stacks is too low for SCR to be technically applicable to the combustion system. There are negligible NOₓ emissions from the SRU. In this case, controls on the combustion system comprising a complete switch to gas-firing and upgrading the burner system (Option 1) would reduce NOₓ emissions by 58 %. Measures on both NOₓ sources (Option 3) comprising a partial fuel switch and application of SNCR to the FCC unit would achieve a reduction of 35 %. Measures on the FCC alone (Option 2) are ineffective resulting in a reduction of 11 %

Table 4.66: Example of options for NOₓ emissions reduction with site level management

<table>
<thead>
<tr>
<th></th>
<th>Total bubble mg/Nm³</th>
<th>Combustion mg/Nm³</th>
<th>FCC mg/Nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current situation</td>
<td>501</td>
<td>492</td>
<td>600</td>
</tr>
<tr>
<td>Option 1</td>
<td>210</td>
<td>161</td>
<td>600</td>
</tr>
<tr>
<td>Option 2</td>
<td>446</td>
<td>492</td>
<td>100</td>
</tr>
<tr>
<td>Option 3</td>
<td>327</td>
<td>332</td>
<td>300</td>
</tr>
</tbody>
</table>

NB: Example 2: 32 % oil firing, small size FCC.
Source: CONCAWE 2011.

These TWO examples show that the several ways to reduce overall emissions from a refinery can differ in their effectiveness.

**Cross-media effects**

On the operational aspect, in cases when the optimisation process is only challenged and evaluated through equivalent concentrations or specific loads set up at the site level rather than...
at the unit level, it can theoretically lead to possible concern linked to the risk of higher emissions at the lower stacks (e.g. SRU). Nevertheless, although all sources are inside the bubble there may be additional constraints on specific source emissions, e.g. from low stacks, to be limited for local air quality requirements.

This can easily be redressed by requiring that the flue gases of the cleaner fuels be discharged at the lower stacks and the high stacks be used to avoid high concentrations of pollutants at ground level, affecting workers and the neighbourhood.

Technical considerations relevant to applicability

**Applicability**

This technique is fully applicable, provided that emitting units and processes are equipped with appropriate necessary continuous monitoring systems including emissions measurements or process parameters monitoring (see Annex 9.9).

Table 4.67 displays, for a selection of main air emission pollutants and parameters, specific emission ranges which are considered achievable by refineries where are implemented a suitable combination of the techniques described in 4.15. These values are based on the whole data gathered by the TWG in charge of the revision of the present document through the 61 site-levels questionnaires (see in particular Table 3.4, Table 3.6). Error! Reference source not found.

<table>
<thead>
<tr>
<th>Substance or parameter</th>
<th>Specific load (g/t)</th>
<th>Air emission range (g/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5^th – 95^th Percentile</td>
<td>50^th Percentile</td>
</tr>
<tr>
<td>SO₂</td>
<td>58 – 1548</td>
<td>500 – 750</td>
</tr>
<tr>
<td>NO₂</td>
<td>78 – 515</td>
<td>240 – 750</td>
</tr>
<tr>
<td>VOCs&lt;sup&gt;(3)&lt;/sup&gt;</td>
<td>60 – 301</td>
<td>24 – 150</td>
</tr>
<tr>
<td>PM₁₀</td>
<td>0.1 – 45</td>
<td>1 – 15</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>0.01 – 13</td>
<td>0.01 – 1</td>
</tr>
<tr>
<td>Carbon-monoxide</td>
<td>40 – 445</td>
<td>40 – 50</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.1 – 22</td>
<td>0.1 – 1</td>
</tr>
<tr>
<td>Hydrogen-sulphide</td>
<td>0.15 – 4.2</td>
<td>0.15 – 0.1</td>
</tr>
<tr>
<td>Hydrofluoric-acid&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.01 – 0.1</td>
<td>0.01 – 0.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.18 – 2</td>
<td>0.18 – 0.1</td>
</tr>
<tr>
<td>BTEX</td>
<td>1.74 – 10</td>
<td>1 – 15</td>
</tr>
<tr>
<td>PAH-16</td>
<td>0.001 – 0.4</td>
<td>0.001 – 0.005</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>&lt;10&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>&lt;10&lt;sup&gt;(2)&lt;/sup&gt;</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.001 – 0.014</td>
<td>&lt;0.001 – 0.002</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.001 – 0.002</td>
<td>&lt;0.001 – 0.002</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.001 – 0.025</td>
<td>&lt;0.001 – 0.007</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.001 – 0.002</td>
<td>&lt;0.001 – 0.008</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.001 – 0.002</td>
<td>&lt;0.001 – 0.006</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;(1)&lt;/sup&gt;</td>
<td>0.0002 – 0.0005</td>
<td>0.0002 – 0.0004</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0001 – 0.001</td>
<td>0.0001 – 0.001</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0001 – 0.0001</td>
<td>0.0001 – 0.0001</td>
</tr>
<tr>
<td>Se&lt;sup&gt;(4)&lt;/sup&gt;</td>
<td>0.0001 – 0.1</td>
<td>0.0001 – 0.1</td>
</tr>
<tr>
<td>X</td>
<td>0.0001 – 0.1</td>
<td>0.0001 – 0.001</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0001 – 0.02</td>
<td>0.0001 – 0.004</td>
</tr>
<tr>
<td>Heavy-metals&lt;sup&gt;(3)&lt;/sup&gt;</td>
<td>&lt;0.01 – 1.5</td>
<td>&lt;0.01 – 0.40</td>
</tr>
</tbody>
</table>

<sup>(1)</sup> For these parameters, only min, max and average are provided given the limited number of available values.

<sup>(2)</sup> Sum of individual percentile data for the following metals: Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, Zn.

<sup>(3)</sup> Total VOC including all diffuse (and fugitive) emissions.

Table 4.67: Achievable ranges of specific emissions into the air for well managed oil refineries.

---

References:

Table 3.13 and Table 3.16
Economics
Monitoring for emissions to a site-specific bubble limit is no different to monitoring for individual sources. It serves two purposes:

- to ensure better protection for the environment as a whole by being continuously aware of total emissions and enabling to control them
- to provide measurement/calculation data to evidence compliance with individual limit values where set.

Monitoring for a bubble requires that all the information needed to assess site wide emissions is brought together in an automated way so that an accurate picture is held. This involves combining different types of information obtained in different ways, e.g. analytical samples, continuous sensor output, discrete measurements with interpolating calculations.

This requires that the site data collection system can assemble this information and generate appropriate management reports at timely intervals, enabling dynamic management. This is very much the same sort of system that should be in place for individual source permitting.

Therefore the extra costs of monitoring for a bubble should be small and related to the generation of formal informational data that can be used for site reporting alongside the real time picture of site emissions.

Driving force for implementation
Management and reduction of air emissions and related cost effectiveness.

Example plants
A number of European refineries have already implemented a full scale management and monitoring system for the site-level optimisation management of their SO₂ emissions of SO₂, NOₓ, PM, CO. Examples of air emission site management of two Belgium refineries are described in EIPPCB report dated 17/05/2011. The UK approach to define SO₂ air emissions values based on short term requirement for air quality is illustrated through EIPPCB report dated 16/11/2011.

Reference literature
[ 65, EC 2003 ] [ 77, REF TWG 2010 ] [ 97, CONCAWE 2011 ] [ 90, EIPPCB 2011 ] [ 98, EC EIPPCB 2010 ] [ 126, CONCAWE 2011 ] [ 127, France 2010 ].

4.15.9.4 Anticipation and adaptation to unfavourable meteorological conditions

Description
Directive 2008/50/EC on ambient air quality and cleaner air for Europe defines and establishes objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole and also ensures that such information on ambient air quality is made available to the public. In certain unfavourable meteorological conditions, pollutant concentration peaks may be detected in the surroundings of refineries even when they are normally operated, using properly all expected primary and abatement techniques according to their permit. In such conditions, specific measures and tools can turn out to be necessary to anticipate, and further manage and reduce emissions as necessary in order to guarantee that concentration limit values in the ambient air around the site are being respected.
Chapter 5

Two examples of such tools are described in more detail in the Operational Data section. They only concern the management of SO₂ emissions.

- The first example is applied by the Total refinery in Donges (France). It is based on a daily prediction of the concentrations likely to be reached at most exposed urban areas. A specific dispersion model fitted to the local conditions has been developed for this purpose.
- The second example relates to the specific organisation set out for the anticipation of pollution peaks in the surrounding of the ExxonMobil refinery in Notre Dame-de-Gravenchon (France). This organisation is based on the evolution of real time ambient concentration measured in several locations distributed according to most exposing wind directions.

In each case, when the tool predicts the likely occurrence of excessive ambient concentrations, appropriate actions are taken at the site level. As a first step, a progressive switch to low sulphur fuels is required on key energy consuming units. If needed, a further step consists of a progressive production slow down or shutdown.

**Technical description**

**No data submitted**

**Achieved environmental benefits**

A meteorological model-based system has been implemented for the Donges refinery since the end of 2006. Between 2007 and 2008, five meteorological episodes with SO₂ ambient air concentrations over the limit values have been reported, compared to 28 episodes recorded between 2002 and 2005.

**Environmental performance and operational data**

**In the case of Donges**

The system is predictive and follows the steps illustrated in Local weather forecast is handled a minima on a daily basis, using a dedicated software that actually adjusts and refines by physical calculation the spot meteorological conditions in particular areas of interest based on generic meteorological data provided by the national agency locally. The model has been initially configured with local historical and physical data. Concentrations are predicted by dispersion modelling based on these calculated meteorological conditions, where all main emission contributing sources are physically described and separately addressed. The results are used by the Scheduling Department of the refinery for daily adjustment of the operational planning.
Figure 4.34: Flow chart of an emission management system for anticipating unfavourable meteorological conditions - Example of Total refinery in Donges

In the case of Rouen

The system is reactive and based on an existing network of 15 permanent multi-parameter automatic measuring devices settled all over the Rouen urban and industrial harbour area, that is handled and maintain by a local air-monitoring non-profit organisation. Two of these measuring devices have been selected due to their geographical location, the results of them being processed according to the two following procedures as displayed in Figure 4.35.

Figure 4.35: Flow chart of an emission management system for anticipating unfavourable meteorological conditions - Esso refinery in Notre Dame de Gravenchon

Cross-media effects
No data submitted.
Chapter 5

Technical considerations relevant to applicability
Systems based on local modelling require the existence of public or private meteorological services which are able to provide the necessary forecast data on a continuous basis. The applicability of systems based on a continuous measuring of ambient air concentrations in urban target areas is significantly facilitated when they can rely upon an existing air quality monitoring organisation which already operates and maintains a network of appropriate sensors.

Economics
In the case of Donges, the initial investment for the system development and basic configuration is around EUR 0.45 million (2006). The annual operating costs are evaluated at EUR 0.1 million/year, covering software and hardware maintenance as well as the acquisition of daily meteorological forecasts at the appropriate frequencies and geographical scales for providing, as necessary, calculation starting conditions to the system. As such, the measures actually taken for the SO$_2$ reduction by itself during concerned meteorological episodes are highly variable by year. They were in the range 1 – 6 million EUR/year in 2006, 2007 and 2009.

Driving force for implementation
Prevention or limitation of potential exposure to ambient air concentrations over limit values, by anticipation or early detection of unfavourable meteorological episodes, in order to prevent and reduce health and environmental impacts.

Example plants
A number of both kinds of systems are implemented by French refineries in France (see above). In Italy, similar systems have existed for more than 15 years in the province of Siracusa (East Sicily) a densely populated area with 4 refineries, and several chemical and power plants. The system works with a permanent monitoring network of 24 fixed stations (SO$_x$, NO$_x$, PM, VOC, Benzene, …). It includes a permanent meteorological station equipped to predict the thermal inversion conditions and worsening of the air quality. In south of Spain, the Cepsa La Rabida Refinery uses a model taking into account real time and meteorological data.

Reference literature
[ 39, French contribution to TWG (item 4) 2009. ]
4.16 Isomerisation

4.16.1 Active chloride promoted catalyst isomerisation process

Description
More information can be found in Section 2.16.

Achieved environmental benefits
Higher process efficiencies compared with the zeolitic catalysts and lower reaction temperatures (less energy consumed).

Cross-media effects
The chloride promoted, chlorinated alumina catalyst (containing platinum) requires the addition of very small amounts of organic chlorides to maintain high catalyst activities. This is converted to hydrogen chloride in the reactor. The chloride-promoted catalyst cannot be regenerated.

Operational data
The highly active chloride promoted-catalyst, and the chlorinated-alumina catalyst (containing platinum), operates at a relatively low temperature (150 – 175 °C and 20 barg) and gives the highest octane improvement. In such a reactor, the feed must be free of oxygen and sulphur sources, including water to avoid deactivation and corrosion problems. The oxygen deactivation is not reversible, nevertheless the sulphur can be desorbed from the catalyst surface. This desorption process of sulphur species from the catalyst consumes utilities and energy.

Applicability
This catalyst is very sensitive to sulphur, so deep desulphurisation of the feed to 0.5 ppm is required.

Economics
Investment estimated (basis ISBL, US Gulf Coast 1998) EUR 4150 - 10400 per m³/d. Investment erected cost for installation (basis: based on: 2Q98 US Gulf Coast) were evaluated for 1590 m³/d of fresh feed capacity of EUR 8.8 million (±50 %).

Driving force for implementation
Production process.

Reference literature
[212, Hydrocarbon processing, 1998], [316, TWG, 2000].

4.16.2 Zeolitic isomerisation process

Description
More information is given in Section 2.16. Some refiners need more octane from the light straight run naphtha fraction than is possible from the O-T zeolitic isomerisation process. Adsorption technology can then be used to remove the unconverted normal paraffins. The utilities needs for that process are quite low.

Achieved environmental benefits
No chloride compounds are used in these types of processes. The zeolite and sulphated zirconia catalyst can be regenerated several times before sending the catalyst to a reclaimer to recover the platinum.

Cross-media effects
Higher temperature of the process, requiring more heating.
Chapter 5

Operational data
The zeolite catalyst operates at significantly higher temperatures (250 - 275°C and 28 barg) and is much more tolerant to contaminants, though the resulting octane improvement is lower.

Applicability
The zeolite catalyst is mainly used for non-hydrotreated feedstreams. Lower reaction temperatures are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures.

Refiners with idle hydproprocessing equipment, such as old catalytic reformers or hydrodesulphurisation units, can consider converting this equipment to the once-through zeolitic isomerisation process. With isomerisation, a 10 to 12 octane-number increase for the C\textsubscript{5} - 71 °C light naphtha can be achieved.

Economics
Estimated cost of the reaction process is EUR 4654 per m\textsuperscript{3}/d. For the absorption process, the investment is EUR 18 900 – 25 160 per m\textsuperscript{3}/d. The catalyst and adsorbent cost is around EUR 1700 per m\textsuperscript{3}/d.

Driving force for implementation
Production process. Selection of a once-through or recycle scheme depends on factors such as quantity of light naphtha to be blended in the gasoline pool, the required octane number of the gasoline pool and the availability of other high-octane gasoline blend components. If the isomerate product has an octane number exceeding 87, a recycle scheme is the only option. Selection of a fractionation-based scheme or an absorption-based scheme is dependent on feed composition and to a certain extent on the product requirements. In general it can be said that the fractionation-based scheme is lower in investment but significantly higher in operating costs as a result of high energy requirements.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [316, TWG, 2000].

Proposed to deletion: product characteristic option

4.16.3 **Increase of the cyclic hexanes in the isomerisation feedstream**

**Description**
As the benzene content in the gasoline pool is being reduced by new specifications, the practice will be to fully dehexanise the reformer feed, leaving in the cyclic hexanes to pass to the isomerisation unit (preventing their conversion to benzene in the reformer).

**Achieved environmental benefits**
Reduced benzene content in the gasoline out of from the reformer.

**Reference literature**
[247, UBA Austria, 1998].
4.17 Natural gas plants

As mentioned in the Scope sections and in Section 2.17, the processes treated in this section are these used in the refining of natural gas. As with mineral oil refineries, the processes used on production platforms are not included in this BREF.

4.17.1 Amine sweetening of natural gas

Description

Many reactions may take place. The reaction occurring in the process where H₂S is absorbed into an aqueous blended amine solution, mainly by proton transfer is as given below.

\[ \text{RNH}_2 + \text{H}_2\text{S} \rightarrow \text{RNH}_3^+ + \text{HS}^- \]
\[ \text{R'R'NH} + \text{H}_2\text{S} \rightarrow \text{R'R'NH}_2^+ + \text{HS}^- \]

Where

\[ \text{R} = \text{C(CH}_3\text{)}_2\text{CH}_2\text{OH} \]
\[ \text{R'} = \text{CH}_2\text{CH}_2\text{OH} \]

Technical description

The process is illustrated in Figure 4.42 of Section 4.25.5.1. If the recovered H₂S gas stream is not to be used as a feedstock for commercial applications, the gas is usually passed to a tail gas incinerator in which the H₂S is oxidised to SO₂ and is then released to the atmosphere via a stack. More information can be found in Section 4.25.5.1.

Achieved environmental benefits

Reduction of H₂S concentration in natural gas.

Environmental performance and operational data

See Section 3.17

Cross-media effects

See Section 4.25.5.1.

Operational data

The recovered hydrogen sulphide gas stream may be:

1. vented (2)
2. flared in waste gas flares or modern smokeless flares,
3. incinerated or
4. used for the production of elemental sulphur or sulphuric acid.

Technical considerations relevant to applicability

Fully applicable.

Economics

Section 4.25.5.1.

Driving force for implementation

To comply with sulphur specifications of natural gas.

Example plants

At present, the amine process (also known as the Girdler process) is the most widely used method for H₂S removal.

Reference literature

[136, MRI, 1997] [144, HMIP UK, 1997] [99, Mandal et al. 2005].
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4.17.2 Sulphur recovery unit

Extensive information can be found in Section 4.25.5.2.

Proposed to deletion

4.17.3 Reuse of carbon dioxide

Description

Acid gas streams containing which contain carbon dioxide free from sulphur and hydrocarbon compounds may be vented directly to air, although this may require heating of the stream to air dispersion. However, carbon dioxide can be used for other purposes. If the CO₂ stream has a significant hydrocarbon content, it can be used within combustion processes, e.g. mixed into site fuel gas or used in a utility designed to burn gas of low flame stability.

Reference literature

[144, HMIP UK, 1997].

4.17.4 Techniques to reduce VOC emissions

During the routine operation of natural gas terminals and other processes, it is necessary to prevent releases to air of natural gas. Techniques to consider to reduce these emissions are given below:

- Minimise the frequency of sphere pigs use by operating sealines at a high velocity, i.e. use 'mist flow' conditions.
- Minimise the recovery of spheres by use of receivers holding several devices
- Vent receivers of high-pressure gas to a low-pressure part of the process for gas recovery by recompression, before opening for access to sphere pigs.
- The occasional shutdown and venting of process plant is necessary, e.g. for maintenance, upset and changeover purposes. This need to be minimised by appropriate plant selection and design.
- Avoiding the use of refrigerants for gas dew point control that are of significant environmental concern (CFCs).
- Overheads and any gas vented from storage and glycol and methanol regeneration units should be condensed and incinerated.
- Leak detection and repair programme. More information can be found in Section 4.25.6.1.
- VOC emissions, including fugitives, can be maintained within a range of 200 to 250 kg/h (300 - 350 kg/MNm³).

Reference literature

[144, HMIP UK, 1997], [268, TWG, 2001].

4.17.5 Techniques to reduce NOx emissions

NOx emissions come from the combustion processes applied in the natural gas plant. The techniques that can be applied for control and abatement of NOx are the same as these applied to refinery fuel gas. See Sections 4.10.4 and 4.25.3 for a detailed explanation.
4.17.6 Techniques to reduce water emissions

Description
Prevention techniques that may be applied to reduce the releases to water can be:

- Minimising and controlling, if possible, the quantity and contamination level of waste water to be treated on-shore need to be minimised and controlled ‘at source’, i.e. waste water coming from off-shore activities;
- Use of a three-phase separator can be used on the liquids from the slugcatcher to control and minimise the hydrocarbon content of the aqueous phase;
- Treatment of sour water can be treated in a sour water stripper unit. See Section 0;
- Keeping of process effluent from glycol or methanol regeneration plants and any other high BOD/COD effluents should be kept separate from other streams, e.g. surface water, and treated before discharge to the site effluent system;
- Water management techniques (See Section 4.15.7).

The techniques that may be used in the waste water treatment are the ones described in Section 4.26.

Achieved environmental benefits
The achievable emission levels that may be achieved with for a well-performing waste water treatment within a natural gas plant are shown in Table 4.68.

Table 4.68 Typical WWTP performance in natural gas plants

<table>
<thead>
<tr>
<th>Water parameter/compound</th>
<th>Concentration (ppm)</th>
<th>Load (kg/MNm³ feedstock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water</td>
<td>160 m³/MNm³</td>
<td></td>
</tr>
<tr>
<td>Total oil content</td>
<td>0.1 – 5</td>
<td>0.4 – 0.6</td>
</tr>
<tr>
<td>TOC</td>
<td>60 – 100</td>
<td>3.5 – 12</td>
</tr>
<tr>
<td>COD</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>Suspended solids</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>0.1 – 0.5</td>
<td></td>
</tr>
</tbody>
</table>

NB: Values in this table are daily average.

Reference literature
[144, HMIP UK, 1997], [268, TWG, 2001] [77, REF TWG 2010].

4.17.7 Techniques to reduce waste generation

Description
Techniques that may be applied to reduce waste generation are:

- Returning catalysts, absorbents, adsorbents, etc. can be returned to the manufacturers for recycling.
- Desalination of glycol purge stream which is practised this will give rise to solids for disposal and any residual glycol in these should first be reduced to a low-level.
- Some of the gas fields contain mercury vapour in very low concentrations. This mercury is removed from the gas in a ‘cold trap’ (e.g. by gas expansion) and recovered as a mercury-containing sludge. A specialised company processes this sludge by treatment in a vacuum distillation unit.

Reference literature
[144, HMIP UK, 1997], [268, TWG, 2001].
4.18 Polymerisation

4.18.1 Reduction of emission and use of catalyst within the process

Description
More information is given in Section 2.18.

Achieved environmental benefits
Reduction of the process emissions and reduction of acid consumption and consequently waste. Good polymerisation units can reduce the phosphoric acid consumption to levels of 0.1 - 0.2 gr/t of polymer produced. Another source relates that the typical catalyst consumption (H₃PO₄ + support) and is around 1.18 kg catalyst per tonne of polymer produced.

Cross-media effects
No cross-media effects.

Operational data
Available data is provided in Table 4.69.

Table 4.69: Typical utility consumption of a polymerisation plant

<table>
<thead>
<tr>
<th>Utilities</th>
<th>20 – 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric power (kW/tonne of C₅+ product)</td>
<td></td>
</tr>
<tr>
<td>Steam (t/tonne of C₅+ product)</td>
<td>0.7 – 1.1</td>
</tr>
<tr>
<td>Cooling (m³/tonne of C₅+ product)</td>
<td>4.4 – 6.0</td>
</tr>
</tbody>
</table>

Applicability
Production process.

Economics
The catalytic condensation process is relatively simple to operate and requires a minimum of labour. Its simplicity is reflected in the operating requirements summarised in Table 4.70.

Table 4.70: Typical operating costs of a catalytic condensation process

<table>
<thead>
<tr>
<th>Costs</th>
<th>5.00 – 8.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst and chemical cost (EUR/tonne of C₅+ product)</td>
<td></td>
</tr>
<tr>
<td>Labour and operating cost (workforce)</td>
<td>1 operator-helper</td>
</tr>
<tr>
<td>Typical operating cost (EUR/t C₅+ product)</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Investment (EUR1995/(t/yr) of C₅+ product)</td>
<td>50 – 95</td>
</tr>
</tbody>
</table>

Only one operator is required. Overall, the cost of operating a catalytic condensation unit ranges from EUR 16 – EUR 22.6 per m³ of C₅+ polymer gasoline. This cost includes utilities, labour, catalyst, chemicals, and an allowance for process royalty, but does not include any direct or indirect capital-related costs.

Driving force for implementation
Production process.

Example plants
Some polymerisation processes are running in European refineries. Nowadays alkylation units are more predominant than polymerisation units, even though polymerisation units are cheaper.

Reference literature
[166, Meyers, 1997], [212, Hydrocarbon processing, 1998], [268, TWG, 2001].
4.18.2 Management and reuse of the catalyst

Description

Two techniques can be applied to minimise the impact of catalyst disposal.

- the catalyst to be disposed of from the process is potentially pyrophoric and requires special treatment. However, removal by steam/water avoids prevents any risk of fire. The catalyst solidifies in situ, and removal is achieved manually under nitrogen purge, or more recently by ‘explosive’ steam decompression with steam suppression to a catchment system. The catalyst may then be sent for either off-site disposal as special waste or on-site treatment. On-site treatment involves neutralisation and fixing with cement. The material may then not be classified as special waste;
- the spent catalyst can be reused as fertiliser or as phosphorous feed to the biotreater.

Achieved environmental benefits

Reduction of risk of fire due to the pyrophoric characteristics of the catalysts and reduction of waste generation.

Cross-media effects

No cross-media effects.

Operational data

Disposal frequencies of up to 12 times per year may be expected.

Applicability

Fully applicable.

Driving force for implementation

Treatment of catalyst and reuse of phosphorous compounds within the refinery.

Example plants

?

Reference literature

[34a, Italy, 1999].
4.19 Primary distillation units

As mentioned in Section 3.19, the atmospheric and vacuum distillation units are large consumers of heat. The techniques to consider for application to the crude oil furnaces are these described in the section dealing with the energy system (Section 4.10).

4.19.1 Progressive distillation unit

Description
A progressive distillation unit with integrated CDU/HVU, which saves up to 30% on total energy consumption for these units. The technique includes atmospheric distillation (topping), vacuum distillation, gasoline fractionation, a naphtha stabiliser if required and a gas plant.

Achieved environmental benefits
The heater process duty (MWh/100 tonnes of crude) of a distillation capacity of 10 million tonnes per year is around 17.3 for an Arabian light crude. Using progressive crude distillation it is reduced to 10.1. The specific energy consumption (overall energy consumption in tonnes of fuel equivalent per 100 tonnes of crude) for a distillation capacity of 10 million tonnes per year is 1.7-2.0 for an Arabian light crude, whereas using the progressive distillation unit only consumes 1.15. The energy savings for a 9 700 000 tonnes/year refinery is in the range of 50 000 tonnes heavy fuel compared to conventional techniques.

Total primary energy consumption
For Arabian light or Russian export blend: 1.25 tonnes of fuel per 100 tonnes of crude
For Arabian heavy: 1.15 tonnes of fuel per 100 tonnes of crude.

Progressive distillation is the extreme of heat integration between atmospheric and vacuum distillation. It also prevents the avoidance superheating of light cuts to temperatures higher than
strictly necessary for their separation and it prevents degrading the thermal levels associated with the drawing-off of heavy cuts.

**Cross-media effects**
No cross-media effects identified.

**Environmental performance and operational data**

### Table 4.71: Energy consumption of the progressive crude distillation when the same plant is used to process two types of crude oil

<table>
<thead>
<tr>
<th></th>
<th>Heavy Arabian (887 kg/m³) 6.5 Mt/yr</th>
<th>Ekofisk (810 kg/m³) 5 Mt/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Consumption</td>
<td>TOE/h</td>
</tr>
<tr>
<td>Fuel (MWh/h)</td>
<td>67.5</td>
<td>5.81</td>
</tr>
<tr>
<td>Steam (tonnes/h)</td>
<td>15.95</td>
<td>0.8</td>
</tr>
<tr>
<td>Electricity (MWh/h)</td>
<td>6.4</td>
<td>1.41</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>8.02</td>
<td>1.04</td>
</tr>
</tbody>
</table>

**NB:** The energy consumption is defined according to the following hypothesis:
- TOE (tonne of oil equivalent) = 11.6 MWh.
- kg of low-pressure steam = 0.581 kWh.
- Yield of the electrical power plant = 39%.
- Products are sent to storage (cold temperature).

### Table 4.72 Utility requirements typical per tonne of crude feed in the US

<table>
<thead>
<tr>
<th>Utility requirements typical per tonne of crude feed</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel fired [fuel fired] 1100 – 1400</td>
<td>kWh</td>
</tr>
<tr>
<td>Power [power] 6.6 - 8.8</td>
<td>kWh</td>
</tr>
<tr>
<td>Steam, 4.5 barg [steam] 0 - 17</td>
<td>kg</td>
</tr>
<tr>
<td>Water cooling (ΔT = 15 ºC) [water cooling] 1.4 – 2.8</td>
<td>m³</td>
</tr>
</tbody>
</table>

**NB:** Data converted using average value of 1 tonne for 7.3 barrel of crude oil.

**Technical considerations relevant to applicability**
The process is applicable to all or part of these units when being constructed and can also be used in revamps for debottlenecking. It includes, for example, adding a preflash column to reduce the fuel consumption.

**Economics**
Reduced fuel consumption can be achieved and thus reduced operating costs of the distillation units.

**Investment** (based on 11.45 Mt/yr including atmospheric and vacuum distillation, gas plant and rectification tower): EUR 41 000 – 55 000 per t/yr (US Gulf Coast 1998).

**Driving force for implementation**
To reduce fuel consumption in refineries.

**Example plant(s)**
Some European refineries employ a progressive distillation unit with an integrated CDU/HVU.

**Reference literature**
[195, The world refining association, 1999], [212, Hydrocarbon processing, 1998], [247, UBA Austria, 1998].
Chapter 5

4.19.2 Heat integration of crude distillation units

Description
As stated in Section 4.10.1, there is a tendency towards improved heat integration with crude and other units. The high energy consumption of the CDU makes heat integration very relevant. To optimise heat recovery from the atmospheric distillation column, two or three reflux streams are normally kept in continuous circulation at several points per top and middle pumparound. In modern designs, integration with the high vacuum unit and sometimes the thermal cracker is achieved. Some techniques applied are given below:

- Optimise the heat recovery, studying and implementing the optimal energy integration. In this context, major progress has been made in recent years in understanding the design of efficient heat recovery networks. Pinch analysis has emerged as a tool for the evaluation of total systems designs, helping to balance investments against energy savings. See also Section 4.10.1.
- Apply pinch analysis to the crude preheat train heat integration. Increase crude preheat temperature and minimise heat losses to air and cooling water.
- Increase crude distillation column pumparound rates from two to four. Reboil sidestrippers with a heat transfer oil rather than by steam stripping.
- Heat transfer in the crude preheating can be improved using specific antifoulant antifouling treatments in crude heat exchanger train. Antifoulants are available from many chemical companies and, in many applications, are efficient in increasing the run cycle length of the exchangers; an antifoulant can help prevent the plugging of tube exchangers, improving heat recovery and preventing hydraulic losses, depending on the nature of the fouling. Service factors of the various units/trains, as well as heat recovery (energy efficiency) increase at the same time.
- The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits
Reduced the fuel consumption in distillation columns.

Cross-media effects
Control of plants is impaired because disturbances are transferred between them, influencing plant safety. In the case of highly heat integrated units the refinery complex as a whole becomes more susceptible to unstable conditions arising in an individual unit.

Applicability
Integration in retrofitting applications may will normally depend on the plot space available and the possibility to execute these modifications in the available shutdown time. Except in a very few cases this technique is commonly applicable.

Driving force for implementation
Reduce energy consumption and the associated CO₂ emission within the refinery.

Example plants
Heat integration procedures are extensively applied in crude units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature
[147, HMIP UK, 1995], [79, API, 1993], [297, Italy, 2000].
4.19.3 Heat integration of the vacuum distillation units

Description
The number of side-streams in a high vacuum unit is chosen to maximise heat integration of producing streams at different temperatures, rather than to match the number of products required, with the exception of the lub oil vacuum distillation units. Heat integration with the crude units can be achieved. The atmospheric residue is then taken directly from the crude distillation unit to the vacuum furnace, and the product streams and circulating refluxes of the high-vacuum unit are cooled against the crude oil.

The main feed stream to the high-vacuum unit is the bottom stream of the crude oil distillation unit, referred to as atmospheric or long residue, which is either supplied directly hot or (relatively) cold from storage tanks. The latter option requires higher energy consumption.

The application of advanced process control to optimise the energy utilisation within the crude unit.

Achieved environmental benefits
Reduction of fuel consumption in the refinery.

Cross-media effects
Control of plants is impaired because disturbances are transferred between them, influencing plant safety. In the case of highly heat integrated units, the refinery complex as a whole becomes more susceptible to unstable conditions arising in an individual unit.

Applicability
Integration in retrofitting application will normally depend on the space available and the possibility to execute these modifications in the available shutdown time. Except in a very few cases this technique is commonly applicable.

Driving force for implementation
To reduce fuel consumption and the associated CO₂ emission within the refinery.

Example plants
Heat integration procedures are extensively applied in vacuum units. Progressive distillation is the stream of heat integration between atmospheric and vacuum distillation.

Reference literature
[147, HMIP UK, 1995], [79, API, 1993], [297, Italy, 2000].

4.19.4 Use of vacuum pumps and surface condensers
KOM conclusion 3.6: TWG to comment and provide clear references/actual examples of retrofitting from steam ejection to vacuum pumping on existing vacuum distillation units → Info expected from industry, UK and SK No information made available.

Description
This technique consists of the use of vacuum liquid ring compressors instead of steam ejectors.

Achieved environmental benefits
Vacuum pumps and surface condensers have largely replaced barometric condensers in many refineries to eliminate this oily waste water stream. Replacing the steam ejectors by vacuum pumps will reduce the sour water flow from 10 to 2 m³/h. The vacuum may be generated by a combination of vacuum pumps and ejectors to optimise energy efficiency. Other benefits are cross linked with cross-media effects.
Chapter 5

Cross-media effects
Replacement of the steam ejectors by vacuum pumps will increase the electricity consumption for vacuum generation, but will reduce the heat consumption, the cooling water consumption, the electricity consumed for cooling pumps and the consumption of agents used for the conditioning of cooling water. Within the refinery there are many processes where surplus steam can be recovered and be used for the production of vacuum. However, an energy management analysis will help to decide whether the use of surplus steam for steam ejection instead of applying vacuum pumps is more efficient than using surplus steam for other purposes. The reliability of both systems are also to be taken into account, as usually steam ejectors are more reliable than vacuum pumps.

Operational data
The use of vacuum pumps consumes electricity.

Applicability
Fully applicable.

Driving force for implementation
To reduce the environmental production of waste water.

Example plants
At present, vacuum pumps are used more often than ejector sets.

Reference literature
[79, API, 1993], [268, TWG, 2001].

4.19.5 Reduction of the vacuum pressure in the vacuum distillation unit

Description
Lowering the vacuum pressure, e.g. down to 20 - 25 mm Hg, will allow a reduction in the furnace outlet temperature, while maintaining the same target cut-point of the vacuum residue.

Achieved environmental benefits
This technique would provide some benefits, both in terms of energy conservation and of pollution reduction. The environmental benefits are:

- a lowered potential for cracking or coking at furnace tubes
- a reduced cracking of feed to lighter products
- a lowered furnace fired duty and hence lowered fuel consumption.

Cross-media effects
Energy (electricity or steam) is necessary to generate the suction from the vacuum.

Applicability
Applicability is usually limited by the tower capacity, the condensing fluid temperature or other material restrictions.

Driving force for implementation
Reduce the heat duty of the vacuum distillation process.

Reference literature
[297, Italy, 2000], [79, API, 1993].
4.19.6 Treatment of non-condensables from vacuum ejector set condenser

**Description**

Techniques for controlling releases from vacuum units include processes such as amine scrubbing (see Section 4.25.5.1), compression into refinery fuel gas and burning in adjacent process furnaces, or combinations thereof. The gases from some units may contain significant amounts of air and such gases are normally best combusted best locally. Amine scrubbing techniques may need to be applied carefully as hydrocarbon contamination may cause foaming problems in amine regeneration units.

Non-condensables from overhead condensers can be passed to light ends treatment or recovery systems or refinery fuel gas systems; sour incondensable gases vented from sealed barometric pumps of vacuum distillation units should be extracted and dealt with in a manner appropriate to the nature of the sour gas.

This is a control technique applicable to the non-condensable emissions vented from the vacuum ejectors or pumps consisting of venting into blowdown systems or refinery fuel gas systems, and incineration in furnaces or waste heat boilers.

**Achieved environmental benefits**

Vacuum distillation column condensers may emit 0.14 kg/m³ of vacuum feed and can be reduced to negligible levels if they are vented to the heater or incinerator. Pollution reduction is achieved if vacuum gaseous streams (vent gas) are routed to an appropriate amine scrubbing unit instead of being directly burned in the process heater. Vacuum vent gas routing to scrubbing requires significant investment due to compressor costs.

The efficiency of incineration control techniques is generally greater than 99% as regards NMVOC emissions.

**Cross-media effects**

In the incineration technique, the combustion products have to be accounted for. Reuse of waste water generated by the overhead reflux drum might have an effect on desalter pH and the desalted yield of some components.

**Applicability**

Fully applicable.

**Driving force for implementation**

To reduce the emissions of pollutants.

**Example plants**

Applied in some European refineries.

**Reference literature**

[136, MRI, 1997], [127, UN/ECE, 1998].

4.19.7 Waste water treatment and reuse

Consider redrafting with cross reference to other sections.

**Description**

This topic is also treated in Section 4.15.7. Two techniques are considered in this section:
Chapter 5

- Reuse of waste water generated by the overhead reflux drum generates some waste water. That water can be reused as a desalter wash water.
- Passing sour water from atmospheric and vacuum unit condensates should pass to a sour water stripper in enclosed systems.
- Optimising water reuse by application of side-stream softening to blowdown streams.

Achieved environmental benefits
Reduction of water consumption and reabsorption pollutants.

Applicability
Fully applicable.

Driving force for implementation
Reduce the water consumption.

Reference literature
[79, API, 1993].

4.19.8 Other techniques to consider in the atmospheric units

Description
Some other techniques to consider are given below.

1. Where applied, ammonia injection should be handled in enclosed systems. Alternative neutralising techniques are available and can reduce the ammonia/ammonium load on sour water and sulphur recovery systems.
2. De-coking vents need to be provided with suitable knock-out and dust suppression facilities; suitable methods for preventing emissions during clean-out procedures need to be used.
3. Many oily sludges can be sent to crude distillation (or an alternative to the coking unit. See Section 4.7.5) where they become part of the refinery products. This technique typically implies sending the light slops to floating roof tanks (double sealed), and the heavy slops typically to fixed roof tanks. Typically the heavy slop after settling is blend with liquid fuel. The blended light slops after enough settling may also be blended with liquid fuel or sent to the crude distillation at a mixing rate to avoid fouling.
4. Pressure relief valves on column overheads; relief from overhead accumulator should be piped to flare as well as the vent points.
5. Use of spent caustic instead of fresh caustic for corrosion control on distillation unit. (for more information see Section 4.20.2).
6. New additives (amines) can substitute caustic for corrosion control.
7. Special additivation scheme (thiophosphates) can be used in case of treating napthenic scrudes.
8. Online cleaning (wet or dry) of heater convection sections.
9. Floating pressure control: operating the column at the minimum possible pressure minimises the energy cost of separation and improves tray efficiencies and latent heating from vaporisation. The disadvantage is that the operating temperature is no longer an indication of composition.

Operational data
The process of oily sludges in the crude distillation may generate problems in the desalter or may foul up the heat exchangers of the distillation column.

Reference literature
[79, API, 1993], [268, TWG, 2001].
4.20 Product treatments

A brief explanation on which kind of processes are included within this section is given in Section 2.20 and within the Scope.

4.20.1 Cascading of caustic solutions

Description
An overall reduction in the caustic consumption of wet treating units can be obtained if semi-spent caustic from one treating unit can be reused in another one. A typical example of this procedure is the use of the bleed of regenerated caustic (e.g. in mercaptan treaters for catcracked gasoline or for the removal of H₂S or thiophenols) in a pre-wash step of the non-catalysed cat cracked gasoline sweetening processes. An example of a caustic integration scheme is given in Figure 2.32.

Achieved environmental benefits
Reduce Reduction of the use of caustic solutions.

Operational data
Systems handling spent caustic require particular care regarding sulphur compounds.

Economics

Table 4.73 Data on costs associated with various gasoline and distillate sweetening processes

<table>
<thead>
<tr>
<th>Product</th>
<th>Types of gasoline sweetening processes</th>
<th>Estimate capital cost EUR million</th>
<th>Est. operating cost, EUR/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPG</td>
<td>Extraction (1)</td>
<td>2.2</td>
<td>0.05</td>
</tr>
<tr>
<td>Light naphtha</td>
<td>Minalk</td>
<td>1.1</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Caustic-free</td>
<td>1.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Heavy naphtha and kerosene</td>
<td>Conventional fixed-bed</td>
<td>2.6</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Caustic free</td>
<td>2.6</td>
<td>0.40</td>
</tr>
</tbody>
</table>

(1) Include pretreating and post-treating facilities.
Sample economies of the MEROX process on the basis of 1590 m³ per stream day capacity for various applications. The capital costs are for modular design, fabrication and erection of MEROX plants. The estimated modular cost is inside battery limits, US Gulf coast, FOB point of manufacturer. The estimated operating costs include catalysts, chemicals, utilities and labour.

Sweetening treatment is much cheaper than hydrotreating, both in terms of capital investment and in operational costs. The caustic is normally almost fully regenerated and only a small bleed results.

Reference literature
[115, CONCAWE, 1999], [166, Meyers, 1997], [83, CONCAWE, 1990].

4.20.2 Management of the spent caustic

Description
Caustics are used to absorb and remove hydrogen sulphide, mercaptans and phenol contaminants from intermediate and final product streams cannot often be recycled. Spent caustic solutions from some sweetening units are odorous and need to be handled in enclosed systems and treated as necessary before release at a controlled rate to the effluent system. Several techniques exist to maximise the reuse of caustics within a refinery. They include
recycling within the refinery or outside the refinery or destruction within incinerators. Techniques considered are:

- **Treatment of caustic may include** Neutralisation and stripping.
- **Incineration** can be an appropriate alternative to treat water treatment because of the very high concentration of cresylics, naphthenes, mercaptans and other organic compounds in spent caustic solutions (COD >>> 50 g/l).
- **Spent catalyst/caustic need to be handled and disposed** Handling and disposing of dry spent caustic in a manner that avoids prevents dust generation. It should not be disposed of to the land.
- **Some techniques are available** to Reuse of spent caustic within the refinery.
- **Corrosion control** on crude distillation units using spent caustic rather than fresh caustic. **Unstable** Unstable chloridic (magnesium) salts that are not extracted from the crude oil in the desalter will decompose upon heating to the crude distiller and cause chloridic corrosion. To prevent corrosion of the exposed equipment, small quantities of caustic (sodium) are injected in the crude oil feed by which the chloridic components are neutralised due to the formation of stable sodium chloride. For the purpose of the neutralisation of chloridic decomposition products, often spent caustic can be used, which is recommended as well to minimise waste generation.
- **Recycling to downstream of the crude desalter or sour water strippers.**
- **Addition to biotreaters for pH control.**
- **Caustics containing phenols** can also be recycled on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation. The caustic can then be treated in the refinery waste water system.
- **Reuse spent caustic (generally classified into: sulphidic, cresylic and naphthenic)** outside the refinery:
  - In paper mills (sulphidic caustic only)
  - As raw material for Na₂SO₃, cresylic and Na₂CO₃ (may require segregation of sulphidic, cresylic and naphthenic various caustics).
  - **Spent caustics may be saleable** to In chemical recovery companies if concentrations of phenol or hydrogen sulphide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make recovery of the contaminants economical.
- **Measures to regenerate or oxidise spent caustic are:**
  - treatment with hydrogen peroxide.
  - fixed-bed catalyst.
  - pressurised air: 120 – 320°C; 1.4 - 20.4 MPa.
  - biological system.

**Achieved environmental benefits**
Reduction of odour emissions and caustic use.

**Cross-media effects**
The cross-media effects found in the different techniques mentioned above are given below.

1. The addition of caustic **within the desalter** or within the crude unit may enhance the coke formation within later downstream units.
2. The increase of phenols and BTX loads to waste water treatment. As a consequence, the degradation efficiency of the biotreater can be adversely affected or the emissions from the waste water treatment plant for these components can increase. Mercaptans, creosyls, and naphthenes can have an adverse impact on the biotreatment system.
Chapter 4

Operational data
Systems handling spent caustic require particular care regarding sulphur compounds.

Driving force for implementation
To reduce caustic use.

Example plants
Most A number of refineries are able to regenerate their spent caustic, but sometimes they others have to dispose of some excess quantities, mainly from caustic pre-wash activities. Usually these quantities are small and can be managed within their effluent treatment system or, if this is not the case, they are disposed of via contractors for use as a bleaching agent in the paper and pulp industry. Some refineries sell their concentrated phenolic caustic for the recovery of cresylic acids. Some refineries work up the phenolic caustics themselves. From the extraction process, the disulphide recovered can be sold as product, or be recycled to a hydrometer or incinerator.

Reference literature
[115, CONCAWE, 1999], [259, Dekkers, 2000], [268, TWG, 2001].

4.20.3 Incineration of foul air vented from sweetening

Description
Foul air vented from sweetening processes contains sulphur compounds that typically have a strong odour. The range of quantity of sulphur in the foul air vented from the sweetening processes is around 0.7 – 7 kg/day (disulphide concentration can be as high as 400 ppm) for a 10 000 t/d crude unit and the percentage contribution it makes to the stack gases where it is incinerated has been estimated at 0.16 – 2.48 %. For this reason, the abatement prior to incineration is not justified and the foul air vented from sweetening processes is incinerated in local furnaces.

Reference literature
[268, TWG, 2001].

4.20.4 Replace clay filtration with hydrotreating

Description
Where a need to remove colour bodies and olefins exists, hydrotreating is replacing clay filtration as the method of choice. Hydrotreating does a better job of improving colour and increasing stability against oxidation, and has no yield loss (the oil measured in the spent filter clay represents a loss of some of the most valuable products produced in a refinery). It also eliminates the problem of spent clay disposal.

Achieved environmental benefits
Reduction of waste generation.

Cross-media effects
Need for hydrogen and energy consumption. See Section 4.13.1.

Operational data
See Section 4.13.1.

Economics
See Section 4.13.1.
Chapter 5

Driving force for implementation
Product requirements.

Reference literature
[113, Noyes, 1993].

4.20.5 Treating
Description
This section deals with the treatment of gas, LPGs, butanes, gasolines, kerosenes and diesels with caustic, amines, water and acid to remove amines, caustic contaminants, H₂S, COS and mercaptans. Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide may also be used to reach specification (LPG) and prevent odour problems. (See also Section 4.25.9).

Reference literature
[212, Hydrocarbon processing, 1998].

4.20.6 Catalytic dewaxing
Description
The removal of wax is necessary to produce lubricating oil which meets desired low temperature properties. Many processes require solvent, chilling and filtration stages for separation.

Catalytic dewaxing processes, based on selective molecular sieve-based catalyst, typically produces a lower-pour product than solvent dewaxing. This system produces fuel components instead of waxes. A short description of the technique can be found in Section 2.20.

Achieved environmental benefits
Aromatics—The foul odours and the sulphur content of the products produced with this technique are lower than with solvent dewaxing. The products generated by the cracking of the wax remain as part of the product.

Cross-media effects
Hydrogen consumption, typically 20 – 62 m³/tonne feed (100 – 300 scf/bbl).

Applicability
Fully applicable for new units. Catalytic dewaxing is unlikely to be retrofitted on another type of dewaxing process because it is a completely different process. Catalytic dewaxing has a pour point advantage, but has a viscosity index disadvantage compared to solvent dewaxing.

Economics
The following Table 4.74 compares the relative cost of debottlenecking a 300 kt/yr solvent extraction complex to 500 kt/yr with the cost involved in the construction of a new 200 kt/yr solvent extraction complex and hybrid debottlenecking with a catalytic dewaxing.
Table 4.74: Cost data for a 200 kt solvent extraction dewaxing unit

<table>
<thead>
<tr>
<th>Cost parameters</th>
<th>New solvent extraction (200 kt/yr) (% of the total cost)</th>
<th>Hybrid desbottlenecking (from 300 to 500 kt/yr) (% of the solvent extraction cost)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital change</td>
<td>36</td>
<td>24 – 36</td>
</tr>
<tr>
<td>Fixed costs</td>
<td>20</td>
<td>7 – 9</td>
</tr>
<tr>
<td>Variable costs</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Hydrocarbon cost</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>50 – 64</td>
</tr>
</tbody>
</table>


**Driving force for implementation**
To produce distillate with a low wax content.

**Example plants**
It has been identified that uses this process to produce distillates with a low wax content.

**Reference literature**
4.21 Storage and handling of materials

As has been mentioned before, more information on techniques to consider regarding the storage and handling of materials can be found in the EFS BREF [264, EIPPCB, 2001]. Among them, the following techniques are these used in the refinery industry.

4.21.1 Underground caverns

Description
More information on all types of caverns can be found in Section 2.21 and in the EFS BREF.

Achieved environmental benefits

- VOC emissions from underground storage caverns are very low or are non-existent. The main reasons are: the temperature of the cavern is low and stable, the product is under pressure and the breathing gases from the cavern are not led to atmosphere but to an other cavern.
- The land above caverns is free for other purposes.
- Improves safety.

Cross-media effects
Groundwater leaking into the cavern must be removed and treated with other oily waters.

Applicability
The geology of the site should be adequate to install a cavern: non-porous rock.

Economics
The construction costs of storage caverns are markedly lower than for above-ground tank farms. In Finland, profitability begins at 50000 m³ under favourable conditions (depends highly on the rock type and the hydrocarbon product to be stored). Maintenance costs have been calculated to be one-sixth these of above-ground tanks.

Driving force for implementation
Avoidance: Prevention of visual intrusion, the reduction of energy consumption, saving of land surface and economic forces for large storage systems. This technique is one of the safest way of storing large amount of hydrocarbon products.

Example plants
Used in some European countries.

Reference literature

4.21.2 Internal floating roof tanks

Description
Internal floating roof tank (IFRTs). Emissions primarily occur during standing storage, with an additional contribution from withdrawal emissions. In addition to the rim seal area and roof-fitting penetrations, sources of standing loss from internal floating roof tanks (IFRTs) include bolted seams in the floating roof.

As described in the EFS BREF, an internal floating roof tank (IFRT) has both a permanent fixed roof and a floating roof (or deck) inside. The deck in an IFRT rises and falls with the liquid level and either floats directly on the liquid surface (contact deck) or rests on pontoons several centimetres above the liquid surface (non-contact deck). Contact floating roofs can be:
aluminium sandwich panels that are bolted together, with a honeycomb aluminium core;
pan steel decks with or without pontoons;
resin-coated, fibreglass reinforced polyester (FRP), buoyant panels.

The majority of direct contact floating roofs currently in service are aluminium sandwich panel type or pan steel type.

More information can be found in Section 2.21 and in the EFS BREF.

Replacement of primary/secondary seals with tighter seals which can reduce VOC emissions; Some techniques that might be also applied to IFRTs. are:
- the replacement of primary/secondary seals with tighter seals, which can also reduce VOC emissions;
- drain design on floating roof tanks to avoid hydrocarbon contamination of rainwater.

Achieved environmental benefits
Reduction of VOC emissions. Conversion of fixed roof tanks to internal floating roof and seals to minimise evaporation of the product being stored. The control efficiency of this method ranges from 60 to 99 % depending on the type of roof and seals installed and the true vapour pressure of the liquid stored. The EFS BREF reports that emission reductions potential for installing an IFRT with a primary seal ranged from 62.9 to 97.4 % (estimated using the EPA AP-42 method).

Cross-media effects
The net storage capacity of a fixed roof tank is reduced by approximately 10 %. There is a need to consider flammable atmosphere problems as part of the design.

Operational data
Performance data on emissions and other useful information about IFRT are available in [100, API 2002].

Applicability
IFRTs are widely used in the petroleum industry, however, they are only applicable to vertical fixed roof tanks. An IFRT is less effective in tanks with a small diameter because of the poor effectiveness of the rim seal in small tanks. There are possible compatibility issues between stored products and the IFRT construction materials, e.g. aluminium sheets/pontoons and gasket/sealing materials. Where caustic treatment is included downstream of the process, corrosion on the IFRT might give rise to problems of applicability. Floating suctions in existing tanks, high filling rate regimes, mixers and other protuberances all present difficulties in retrofits.

An acceptable alternative to an IFRT is to retrofit a fixed roof tank with an internal floating cover (IFRT).

Economics
The costs of retrofits are given in Table 4.75 below. Costs are dependent on the tank diameter.
## Table 4.75: VOC controls in storage

<table>
<thead>
<tr>
<th>Emission source</th>
<th>Refinery storage</th>
<th>Other roof fitting emission controls (roof legs, still wells) and options (tank paint)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control technology</td>
<td>Internal floating roofs in fixed roof tanks</td>
<td>Secondary/double seals on floating roof tanks</td>
</tr>
<tr>
<td>Efficiency</td>
<td>90 – 95 %</td>
<td>95 %</td>
</tr>
<tr>
<td>Investment costs (EUR million)</td>
<td>0.20 –&gt;0.40 for 20 - 60 metres diameter tanks(1)</td>
<td>0.05 – 0.10 for 20 - 50 metres diameter tanks(2)</td>
</tr>
<tr>
<td>Operating costs</td>
<td>Minor</td>
<td>Replacement every 10 years</td>
</tr>
<tr>
<td>Other impacts comments</td>
<td>Requires tank to be taken out of commission reduces the net storage by 5 – 10 %</td>
<td>Can reduce maximum storage capacity of tank</td>
</tr>
</tbody>
</table>

References: (Installed and retrofitted)
(1) UN-ECE/IFARE, and Industry Propriety Information.
(2) UN-ECE/IFARE and Industry Propriety Information (UN-ECE EC AIR/WG6/1998/5).

### Driving force for implementation

European Directive 94/63/EC (Stage 1) prescribes either fixed roof gasoline storage tanks are fitted with internal floating roofs (with a primary seal in existing tanks and with secondary seals in new tanks) or are connected to a vapour recovery unit. Vapour destruction is also a technically viable option which may be applied, provided energy recovery is included.

### Reference literature

### 4.21.3 Fixed-roof tanks

#### Description

The fixed-roof tank (FRT) can give rise to emissions in the following ways described below.

- **Filling losses:** during tank filling the existing tank vapour space, which is more or less saturated with vapour, is expelled to the atmosphere, while when a tank is emptied the incoming air is slowly saturated with vapours, which are then expelled by subsequent filling and/or breathing. Generally these emissions are greater than standing emissions. A technique to reduce VOC from these tanks is to increase the storage pressure by blanketing.
- **Breathing losses:** during storage of the liquid there will be vapour emissions from tank breathing caused by the difference in night and day temperatures and by changes in atmospheric pressure. To a certain extent, pressure controllers and insulation can prevent breathing losses.
- **Vapours released during water draining.**

The technique that is considered to reduce emissions from fixed roof tanks is:

- a technique to reduce VOC from these tanks is to blanket them with an internal floating roof.

It is to be noted that blanketing tanks by introducing inert gas is a safety measure to avoid explosive atmosphere but do not prevent the product from evaporating.

### Achieved environmental benefits

The installation of an internal floating roof in fixed-roof tanks can reduce VOC emissions up to 90 – 95 % (see Table 4.75)
Chapter 4

Cross-media effects
The installation of an internal floating roof in a fixed roof tank requires the tank to be taken out of commission and reduces the net storage by 5 - 10 %.

Operational data
Performance data on emissions and other useful information about FRT are available in [323, API, 1997], [100, API 2002].

Applicability
Fixed roof tanks are typically used for low-or non-volatile products material with true vapour pressure (TVP) at less than 14 kPa, e.g. kerosene, heating oil. These tanks can be retrofitted to internal floating roof tanks, but are not suitable for all products, e.g. bitumen tank with an internal floating roof will not work due to bitumen solidifying in the flaw between the wall and the internal floating roof.

Economics
The investment cost of installing internal floating roofs in fixed roof tanks can be EUR 0.2 - 0.4 million for tanks 20 - 60 metres in diameter.

Driving force for implementation
Reduction of VOC emissions.

Reference literature
[107, Janson, 1999], [115, CONCAWE, 1999], [323, API, 1997], [268, TWG, 2001], [100, API 2002].

4.21.4 External floating roofs

Description
External floating roof tanks (EFRT) are used to store crudes, light products and intermediate stocks having a vapour pressure of more than 14 kPa but less than 86 kPa at normal storage temperature. More information can be found in Section 2.21 and in the EFS BREF.

With external floating roof tanks (EFRT), filling and breathing losses with external floating roof tanks are greatly diminished in comparison with fixed roof tanks. However, the following vapour losses described below are inherent to this type of tank and should be minimised:

- Standing storage emissions from floating roof tanks include rim seal and roof-fitting emissions, which result from stock vapour pressure changes due to temperature, and pressure variations but more importantly wind effects as well as openings in the roof. The influence of wind effects is not a factor on internal floating roof tanks. Standing emissions on external floating roof tanks are generally much more significant than withdrawal emissions.
- Wetting losses by evaporation of liquid from the wet wall, when the level of the liquid is lowered by discharge.
- Vapours released during water draining.
- In many cases, for an external floating roof tank, the emissions through fittings can exceed the rim seal losses especially on tanks with secondary seals. In terms of fitting losses, the major source is from the slotted stillwell (sample well or dipping well).
Techniques to minimise emissions of external floating roof tanks include but are not limited to the following:

- installing improved primary seals at the floating deck, e.g. from a vapour mounted to a liquid mounted seal;
- installing sleeves around the pipe, incorporating still well wipers;
- installing floats with wipers inside the slotted pipe;
- land the floating roof tanks as infrequently as possible to avoid unnecessary vapour releases;
- sealing of all floating roof openings (e.g. gauging poles, support legs) with appropriate wrappings, sleeves or compensators;
- installation of improved secondary or tertiary seals between tank walls and roof (see 4.21.6);
- drain design on floating roof tanks to avoid hydrocarbon contamination of rainwater.

![Figure 4.37 Example of a floating roof tank](image)

**Achieved environmental benefits**

For the same substance, e.g. gasoline, EFRTs have the advantage over fixed roof tanks of significantly lower emissions to the atmosphere of as VOCs. An EFRT can avoid 95% of the losses from a fixed roof. Product savings give operating benefits.
Cross-media effects
They have potentially more emissions to water than fixed roof tanks, since it is possible for rainwater to enter the tank past the roof seal. Any such water needs to be drained before dispatch of the product to a customer since the quality of the product can be seriously jeopardised.

Operational data
Performance data on emissions and other useful information about EFRT are available in [100, API 2002]. Examples of emissions reduction efficiency (compared to fixed roof tank) when retrofitting external floating roofs are given in the following tables [77, REF TWG 2010].

Table 4.76: Tank construction working hypothesis

<table>
<thead>
<tr>
<th>Product</th>
<th>Diameter (m)</th>
<th>Height (m)</th>
<th>Calculated annual emissions (kg/yr)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha, heavy</td>
<td>23</td>
<td>14.5</td>
<td>3 942</td>
</tr>
<tr>
<td>Naphtha, light</td>
<td>30</td>
<td>17</td>
<td>2 492</td>
</tr>
<tr>
<td>Crude oil</td>
<td>57</td>
<td>16.5</td>
<td>5 519</td>
</tr>
</tbody>
</table>

(* ) Based on rim seal area, dipping wells/still wells, roof fitting penetrations, without wetting losses

Source: TWG 2010 DE

Table 4.77: Option of sealing and correspondant expected efficiency

<table>
<thead>
<tr>
<th>Seal construction</th>
<th>Efficiency (%)</th>
<th>Naphtha, heavy</th>
<th>Naphtha, light</th>
<th>Crude oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>Double rim seal (fitted secondary seals) dipping wells/still wells not sealed, roof legs not sealed</td>
<td>51.8</td>
<td>50</td>
<td>95.7</td>
</tr>
<tr>
<td>Case 2</td>
<td>Double rim seal (fitted secondary seals) dipping wells/still wells sealed, roof legs sealed</td>
<td>92.5</td>
<td>92</td>
<td>98.3</td>
</tr>
<tr>
<td>Case 3</td>
<td>Double rim seal (fitted secondary seals) dipping wells/still wells sealed, inkl. helicoat roof legs sealed</td>
<td>93.3</td>
<td>93</td>
<td>98.8</td>
</tr>
<tr>
<td>Case 4</td>
<td>Double rim seal (secondary seal with access to ponton) dipping wells/still wells sealed, roof legs sealed</td>
<td>95.6</td>
<td>96.1</td>
<td>98.9</td>
</tr>
<tr>
<td>Case 5</td>
<td>Triple rim seal dipping wells/still wells sealed, roof legs sealed</td>
<td>97.1</td>
<td>97.5</td>
<td>99.1</td>
</tr>
<tr>
<td>Case 6</td>
<td>Triple rim seal dipping wells/still wells sealed, helicoat roof legs sealed</td>
<td>97.9</td>
<td>98.1</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Source: TWG 2010 DE

Applicability
In retrofit situations where a change in the service of the tank is desired, an acceptable alternative to an EFRT is to retrofit a fixed roof tank with an internal floating cover.

Economics
Investment costs for the retrofitting of a fixed roof tank to a EFRT is EUR 0.26 million per tank of diameter 20 m. An operator is necessary for tank draining, giving rise to some operating cost.
Driving force for implementation
The Directive 94/63/EC (Annex 1) defines an appropriate floating roof tank as one having at least a VOC release efficiency of 95% as compared with a fixed roof one with no vapour-containment controls (that is a fixed-roof tank with only a vacuum/pressure relief valve).

Reference literature
[45a, Sema and Sofres, 1991], [252, CONCAWE, 2000], [258, Manduzio, 2000], [100, API 2002], [268, TWG, 2001] [5, EC 2006], [77, REF TWG 2010].

4.21.5 Pressurised vessels
Pressurised vessels such as bullets and spheres are often fitted with pressure relief valves, which vent to atmosphere or flare. VOC emissions can occur if these valves or bypass block valves have internal leaks. See EFS BREF.

4.21.6 Double and secondary seals increase Floating roof seals tightness

Description
Two or three seals at the floating roof rim provide a double multiple barrier to control VOC emissions from storage tanks. Fitting secondary and tertiary roof rim seals is an accepted efficient technologies techniques for emission reduction. Tertiary seals can generally be retrofitted to existing rim seals. When retrofitting rim seals to floating roof tanks for non-waxy products, the second or third seal can be equipped with a contact element for draining the inner tank wall (additional weather seal function). Rim-mounted seals (as opposed to shoe-mounted seals) are favoured, since the former offer emission control if the primary seal fails.

![Diagram of multiple seal for floating roof tank](image)

Figure 4.38: Example of multiple seal for floating roof tank used in a German refinery
Achieved environmental benefits
VOC emissions can be significantly reduced by installing secondary and tertiary seals on storage tanks. The Amoco/US EPA joint study estimated that VOC losses from storage tanks could be reduced by 75 to 95 % compared to emissions generated by a fixed-roof tank of the same capacity without any floating roof. Tertiary seals can achieve up to a 99 % reduction (see Section 4.21.2). When they are applied to EFRT, secondary seals also reduce the likelihood of rainwater ingress into the tank. Secondary seals for gasoline storage can reduce VOC emissions by up to 95 %.

Cross-media effects
Retrofitting seals usually results in a loss of operating capacity of by about 5 %.

Operational data
Performance data on emissions and other useful information about rim seals are available in [100, API 2002].

Applicability
Multiple seals can be readily installed in new units (named double or triple seals) and can also be generally retrofitted (as secondary and tertiary seals). It is reported to be generally difficult to retrofit tertiary seals.

Economics
Equipping an average tank with a secondary seal system was estimated to cost about USD 20 000 (1991). Investment costs: EUR 0.05 - 0.10 million for tanks with a 20 - 50 metre diameter. Operating costs: replacement likely every 10 years.

Driving force for implementation
European Directive 94/63/EC (Stage 1) prescribes secondary seals for external floating roof tanks and for new internal floating roof tanks for gasoline storage in refineries and terminals.

Example plants
Secondary seals are of in common use worldwide. Tertiary seals are used in several refineries and depots in Germany.

Reference literature
[45a, Sema and Sofres, 1991], [252, CONCAWE, 2000], [100, API 2002], [268, TWG, 2001], [28, Tebert et al. 2009].

4.21.7 Storage strategy

Description
The need for certain tanks can often be eliminated through improved production planning and more continuous operations. This technique is closely related to Section 4.15.5. An example is the implementation of an in-line blending system (see Section 4.21.14).

Achieved environmental benefits
Since storage tanks are one of the largest sources of VOC emissions, a reduction in their number contributes to a reduction of VOC emissions. By minimising the number of storage tanks, tank bottom solids and decanted waste water may also be reduced.

Applicability
The reduction of in the number of tanks typically requires a full change in the management of product and intermediates. As a consequence, this technique is more easily to be applied applied to new units.
Driving force for implementation
Space usage can be improved by reducing the number of storage tanks in operation.

Reference literature
[268, TWG, 2001].

4.21.8 Prevention of leakage through tank bottoms
It follows techniques to consider in the determination of BAT for the prevention of leakage through tank bottoms. This topic is well documented in EEMUA publication 183 ‘Guide for the Prevention of Bottom Leakage from Vertical, Cylindrical, Steel Storage Tanks’.

4.21.8.1 Double tank bottoms

Description
Double bottoms can either be retrofitted into existing tanks or incorporated into the design of new tanks. If retrofitted, the existing tank bottom is normally used as the secondary flooring, and sand, gravel or concrete can be installed between the new primary and the secondary floors. In this case, it is general practice to keep the interstitial space to a minimum and therefore the secondary bottom should slope in the same way as the primary bottom. The slopes to the base of tanks can be either straight, cone-up (sloping from the centre down to the tank perimeter) or cone-down (sloping downward from the tank perimeter). Nearly all tank floors are made of carbon steel. If a double bottom is to be installed (either retrofit or new build), there are choices in material selection for the new floor. A second carbon steel floor can be utilised or a more corrosion-resistant stainless steel floor can be installed. A third choice is to use a glass fibre-reinforced epoxy coating over the steel.

The use of double bottom tanks allows a vacuum system to be installed, and in this case the space between the lower and upper floor is not filled, but retained as an air space using steel spacers (which can typically be made of steel reinforcement mesh). In this more recent system, the space between the floors is kept under a vacuum that is continuously monitored. Any leak in the primary or secondary floor will dissipate the vacuum and trigger an alarm. A further test of the extracted air will indicate an upper floor failure if product or vapours are present, or a lower floor failure if neither product nor vapours are present (subject to any previous underfloor contamination).

Achieved environmental benefits
Installing a second impervious bottom to a tank provides a measure of protection against non-catastrophic releases due to corrosion, faulty weld joints, or flaws in the bottom material or the construction details. In addition to containment, the secondary bottom provides a means of allowing detection of a bottom leak which is not obviously visible to an operator, as a similar shell defect would be.

Cross-media effects
In the case of retrofitting, the application of this technique may prolong the outage time of tanks during the installation of the double tank bottom. Its application can reduce the capacity of the tank.

Operational data
By installing double tank bottoms, the time between inside inspections and the number of annual tank cleaning procedures are decreased.

Applicability
Applicable to either retrofitted or newly built tanks.
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Economics

Typical retrofitting costs for double tank bottoms, as quoted from German or Swiss suppliers, are as follows and include the provision of a vacuum leak detection system:

- carbon steel: EUR 110/m²
- stainless steel: EUR 190/m²
- glass fibre-reinforced epoxy: EUR 175/m²

A UK refinery reported that the actual cost of installing a double bottom on a 10,340 m³ tank was EUR 600,000.

Driving force for implementation

Prevention of leaks from storage tanks.

Reference literature

[253, MWV, 2000], [112, Foster Wheeler Energy, 1999].

4.21.8.2 Impervious membrane liners

Description

The impervious membrane liner is a continuous leak barrier under the entire bottom surface of the tanks. It can be an alternative to a double tank bottom or it can be added as an extra measure of safety below the double tank bottom. Like the double tank bottom, it is primarily intended to arrest the small but persistent leak rather than address a catastrophic failure of the entire tank. The key to an effective liner is that the seams need to be liquid-tight against either the steel shell of the tank or the concrete wall that supports and surrounds the tank. The minimum thickness of the flexible membrane is 1 mm, although 1.5 to 2 mm thick sheets are commonly used. The membrane needs to be chemically resistant to the product stored in the tank.

Achieved environmental benefits

Prevention of leaks from storage tanks.

Cross-media effects

Prolonged tank outage if the liner has to be retrofitted to an existing tank.

Applicability

They Impervious membrane liners can be installed either in a new-build design or as a retrofitted design, especially during the overhaul of a tank, and they generally include a leak detection system.

Economics

The cost of retrofitting a liner is slightly higher than installing a double bottom as it involves jacking up the existing tank to install the membrane and leak detection system. An indicative cost is of the order of EUR 200/m². For a new build. As new build construction, an impervious liner may be cheaper than a double bottom, but it may have a higher life cycle cost. This is because any future failures of the liner would require re-lifting the tank or reverting to a new double bottom solution.

The following are costs per unit for placing the following materials on the ground:

- concrete: EUR 30/m²
- asphalt: EUR 24/m²
- HD polyethylene: EUR 23/m²
- bentonite: EUR 18/m²
- clay: EUR 11 – 17/m²
These costs exclude the cost of lifting the tank for installation. However, costs of placing such materials in the floors of bunds would be of in this order. An additional cost arises from moving any pipework in the bunds.

For comparison of the installed costs of such a liner, one refinery reported that since 1994, it had installed a clay bottom liner under each lifted tank during maintenance. A leak detection system was installed at the same time. The cost of this was about EUR 20000 to 30000 per tank with the cost of the clay liner being 11 to 17 EUR/m². The total cost for 14 tanks amounted to EUR 350000. A similar cost (EUR 35000) was quoted in another installation of an impervious liner (plus leak detection) for a 12000 m³ concrete tank.

Recently updated costs data (2011) from UK operators (Source: UKPIA) are shown in the following table.

### Table 4.78: Estimated costs for retrofitting impervious membrane liners to different tanks

<table>
<thead>
<tr>
<th></th>
<th>Small tanks</th>
<th>Medium tanks</th>
<th>Large tank</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 small tanks (22 m) (dia), 20 m (h), sharing a bund</td>
<td>3 medium tanks (48.5 m) (dia), 20 m (h), sharing a bund</td>
<td>1 large tank (81m) (dia), 20 m (h), dedicated bund</td>
</tr>
<tr>
<td>Tank volume m³ (single tank)</td>
<td>7 603</td>
<td>36 949</td>
<td>103 060</td>
</tr>
<tr>
<td>Tank footprint m² (single tank)</td>
<td>380</td>
<td>1 847</td>
<td>5 153</td>
</tr>
<tr>
<td>Required bund area (all tanks, 2m wall height)(*)</td>
<td>4 942</td>
<td>24 017</td>
<td>56 683</td>
</tr>
<tr>
<td>Cost for installing membrane under tank floor</td>
<td>EUR(*)</td>
<td>EUR(*)</td>
<td>EUR(*)</td>
</tr>
<tr>
<td>Lining of bund floor</td>
<td>317 755</td>
<td>1 672 754</td>
<td>4 787 890</td>
</tr>
<tr>
<td>Lining bund walls</td>
<td>282 575</td>
<td>621 892</td>
<td>1 038 379</td>
</tr>
<tr>
<td>Lining under tanks</td>
<td>110 079</td>
<td>535 644</td>
<td>498 195</td>
</tr>
<tr>
<td>Jacking</td>
<td>680 904</td>
<td>1 021 356</td>
<td>907 872</td>
</tr>
<tr>
<td>Total per bund</td>
<td>1 391 314</td>
<td>3 851 647</td>
<td>7 232 335</td>
</tr>
<tr>
<td>Total per tank</td>
<td>464 150</td>
<td>1 284 639</td>
<td>7 232 335</td>
</tr>
<tr>
<td>Cost for replacing tank floor, installing new tank foundation</td>
<td>EUR(*)</td>
<td>EUR(*)</td>
<td>EUR(*)</td>
</tr>
<tr>
<td>Lining of bund floor</td>
<td>317 755</td>
<td>1 672 754</td>
<td>4 787 890</td>
</tr>
<tr>
<td>Lining bund walls</td>
<td>282 575</td>
<td>621 892</td>
<td>1 038 379</td>
</tr>
<tr>
<td>Installing new foundation and replacing tank floor</td>
<td>1 429 898</td>
<td>2 859 797</td>
<td>1 815 744</td>
</tr>
<tr>
<td>Total per bund</td>
<td>2 030 229</td>
<td>5 154 443</td>
<td>7 642 013</td>
</tr>
</tbody>
</table>

Source: CONCAWE/UKPIA 2011

(*) EUR Costs based on currency conversion from GBP of 1.13484 on 25/07/2011.

NB:
- Required bund area is based on 110 % of the tank rated capacity for the largest tank in the bund
- Costs related to project management and design, tank emptying and cleaning are excluded, but expected to be 10-15 % of total cost per tank.
- For large tanks >48.5m in diameter, tank jacking is not an option, therefore costs are based on an estimate for removing and replacing tank floor.
- Costs related to the need to hire tank space during extended outage to complete works (likely to be 9 months per tank) are also excluded.
- The lining of bund walls includes fixing at the top of the bund wall, and sealing it to existing bund flooring (where applicable).
- Installing a new tank foundation after removing the existing tank floor may be a more effective solution where the ground is too permeable, or where there is concern that the liner may not remain intact following replacement of the tank.
- No account has been taken of the increase in business rates following secondary and tertiary containment upgrades.
- Bund wall lengths are likely to increase depending upon the shape of the bund, also bund height of 2m does not take into account the slope of the bund wall, which will increase the area.

Source: CONCAWE/UKPIA 2011
Driving force for implementation
Avoid To prevent soil contamination.

Example plant(s)
Impervious membrane liners are used in lieu of double bottoms in a number of non-European countries.

Reference literature
[45a, Sema and Sofres, 1991], [268, TWG, 2001].

4.21.8.3 Leak detection

Description
As with sewers, one way to protect against soil and groundwater contamination is by detecting leaks at an early stage. Leaks through a tank bottom can be detected by a leak detection system. Conventional systems include inspection ports, inventory control and inspection wells. More advanced systems include electronic sensing probes or energy pulse cables whereby product that comes into contact with the probe or cable will alter its impedance and trip an alarm. In addition, it is common practice to use a variety of inspection procedures on tanks at intervals to prove their integrity. See also Section 4.25.6.1 LDAR programme. Some techniques to consider are:

- Equipping storage tanks with overflow alarms and, if appropriate, automatic pump shut-offs.
- Installing double bottoms with integrated leak detection systems on tanks where practicable.

Relief valves on pressurised storage should undergo periodic checks for internal leaks. This can be carried out using portable acoustic monitors or, if venting to atmosphere with an accessible open end, tested with a hydrocarbon analyser as part of an LDAR programme.

Achieved environmental benefits
Avoid Prevention of soil and groundwater contamination.

Applicability
Probes and cables have to be packed pretty densely if the leak to be detected is small. Consequently, inspection, where possible, may in some cases be more reliable than probes.

Economics
One refinery reported that the installation of a leak detection system on a group of four 12 m diameter tanks cost a total of EUR 55 000 with an operating cost of EUR 4000 per year. The routine inspection of tanks at another refinery was quoted as EUR 2000/tank per year.

Driving force for implementation
Avoid To prevent soil and groundwater contamination.

Reference literature
[253, MWV, 2000].
4.21.8.4 Cathodic protection

Description
Avoid To prevent corrosion on the underside of the tank bottom, tanks can be equipped with cathodic corrosion protection.

Achieved environmental benefits
Avoidance of soil and groundwater contamination and air emissions due to the prevention of corrosion.

Cross-media effects
Electricity is needed when impressed current cathodic protection (ICCP) requires a DC power source.

Driving force for implementation
Avoid To prevent the corrosion of tanks and pipes, and to reduce the maintenance costs.

Reference literature
[253, MWV, 2000] [101, INERIS 2008].

4.21.9 Tank farm bund containment

Description
Whereas double tank bottoms or impervious liners protect against the small but incessant leak, an impermeable tank farm bund is designed to contain large spills (for safety as well as for environmental reasons), such as caused by a shell rupture or a large spill from overfilling. The bund consists of a wall or dike around the outside of the tank to contain all or part of the tank contents in the event of a spill, and (in some cases) an impermeable ground barrier between the tank and the dike to prevent infiltration of the product into the ground. The dike is typically constructed of well-compacted earth or reinforced concrete. The height is normally sized to accommodate the maximum contents of the largest tank within the volume enclosed by the dike. However this principle of total capture is flawed if the ground between the tank and dike is permeable. Oil can permeate downward and under the dike in these situations. Asphalt, concrete surface or high density polyethylene (HDPE) liner are some of the possibilities.

Achieved environmental benefits
Containment of large spills from liquid storage tanks.

Cross-media effects
This technique might call for the soil to be compacted, which may be seen as a negative impact. A study in the United States has concluded that the effectiveness of liners in protecting the environment is limited because of their unreliability and the difficulty in inspecting or testing their integrity. Also, there are few releases that would be contained by such liners, and moreover, they are expensive to install. Because of this, it was concluded that other preventative measures are more effective in protecting the environment and are more cost-effective in the long run.

Applicability
In some cases, retrofitting may not be possible.

Economics
Some refineries have quoted the total cost for installing concrete paving under 6 big large tanks at EUR 1.3 million (0.22 million per tank), the cost of sealing the bund dike walls with asphalt (around 10 tanks) at EUR 0.8 million, and the cost of concrete paving bunds at EUR
70 - 140/m². One refinery quoted the cost of installing 200 m of impermeable HDPE barrier along the site boundary at 150 000 EUR (EUR 750/m).

**Driving force for implementation**

Containment of large spills that may occur from liquid storage tanks is normally regulated by national laws. In Italy, current legislation foresees for some liquids a volume of the bund less than 100 % of the tank volume. French regulation requires any liquid storage to be associated with a containment volume superior to the highest value from:

- 100 % biggest tank volume;
- 50 % total capacity of associated tanks.

**Reference literature**

[147, HMIP UK, 1995].

**4.21.10 Reduce Reduction of the generation of tank bottoms**

**Description**

Minimisation of tank bottoms can be carried out through careful separation of the oil and water remaining in the tank bottom. Filters and centrifuges can also be used to recover the oil for recycling. Other techniques to consider are the installation of side entry or jet mixers on tanks or the use of chemicals. This means that basic sediment and water is passed on to the receiving refineries.

**Achieved environmental benefits**

Tank bottoms from crude oil storage tanks constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem due to the presence of heavy metals. Tank bottoms are comprised of heavy hydrocarbons, solids, water, rust and scale.

**Cross-media effects**

Passing the sediments and water from the crude oil tanks to the refinery means that they will most probably show up in the desalter.

**Reference literature**

[147, HMIP UK, 1995].

**4.21.11 Tank cleaning procedures**

**Description**

For routine internal tank inspections and for the purpose of repair, crude oil and product tanks have to be emptied, cleaned and rendered gas-free. A technique to clean tank bottoms includes dissolving the majority of the tank bottom content (>90 %) with hot diesel fraction at temperatures of around 50 ºC where it disolves most of the tank bottom contents and they can be blended after filtration to the crude tanks. Oil tank cleaning is traditionally performed by workers entering the tank and removing sludge manually, exposed to potentially explosive and toxic atmospheres. Fully automated techniques of tank cleaning are also available typically using the following procedures.

- Installation of the process equipment: low pressure/high impact nozzles are installed either in the tank roof or through the existing wall manholes and operated over the liquid surface.
- Tank blanketing: an inert gas is injected and monitored to maintain an oxygen level below 8 %, securing non-igniting conditions.
- Desludging and cleaning: the sludge is sucked out and recirculated via the cleaning nozzles, using the oil in the tank as a cleaning agent. If needed, crude oil or gas oil is added and/or the recirculated media is heated to lower the viscosity.
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- Oil separation and recovery: part of the sludge is mechanically separated (decanter) without the addition of chemicals.
- Water wash: final wash with hot water is performed and finally the inert gas is vented.

Achieved environmental benefits
Emissions during the cleaning of tanks arise during natural or mechanical ventilation. A variety of cleaning methods has been developed for the cleaning of crude oil tanks. Knowledge of the technology technique for cleaning crude oil tanks has improved, so that with primary measures emissions of VOC of less than 0.5 kg/m² tank bottom area can be achieved. With secondary specific measures, e.g. installation of mobile flares, which are currently under development for cleaning crude oil and product tanks, further emission reductions of VOC of up to 90% can be expected. Automated tank cleaning techniques working in closed-loop systems, where the atmosphere from the oil tank is degassed, reduce the venting of VOC to the ambient air.

Cross-media effects
When natural or forced ventilation is used, VOC emissions may be significantly higher during tank cleaning when compared to VOC emission from normal operation of an oil tank. Due to the recirculation of water, automated cleaning achieves savings of fresh water and reuse of the oil in as a cleaning agent. Electricity consumption for the cleaning process and generation of inert gas is higher than for manual cleaning. Solid and liquid waste is reduced by using automated cleaning. Closed loop system under inert conditions leads to safer conditions as risk of explosion and human exposure to hazardous substances are reduced.

If the refinery operates its own sludge incineration plant, cleaning residues can be supplied to it.

Operational data
The emissions arising during the cleaning of crude oil tanks and the reduction of these emissions are exhaustively described in [302, UBA Germany, 2000]. The use of hot diesel to clean up the tank bottoms requires heating. The corresponding consumption is strongly dependant on the type and size of tank and the type of residues processing. According to information from a supplier of automated tank cleaning (Add ref to ORECO), the following operational data are reported.

<table>
<thead>
<tr>
<th>Table 4.79: Typical crude oil tank cleaning utility requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automated cleaning</td>
</tr>
<tr>
<td>Hydrocarbon emissions</td>
</tr>
<tr>
<td>Fuel consumption</td>
</tr>
<tr>
<td>Waste for incineration</td>
</tr>
<tr>
<td>Waste water</td>
</tr>
<tr>
<td>NB: Crude oil tank: diameter 50 to 80 m - floating roof - 2 000 m³ oil sludge</td>
</tr>
</tbody>
</table>

Applicability
Tank cleaning procedure is fully applicable.

Economics
According to the operational costs given in Table 4.80 are typical for crude oil tank cleaning [102, ORECO 2011].
Table 4.80: Typical crude oil tank cleaning estimated costs

<table>
<thead>
<tr>
<th></th>
<th>Automated cleaning</th>
<th>Manual cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct cleaning cost</td>
<td>300 000</td>
<td>200 000</td>
</tr>
<tr>
<td>Waste transportation</td>
<td>5 000</td>
<td>100 000</td>
</tr>
<tr>
<td>Waste disposal or processing</td>
<td>10 000</td>
<td>200 000</td>
</tr>
<tr>
<td><strong>Overall costs (EUR)</strong></td>
<td><strong>315 000</strong></td>
<td><strong>500 000</strong></td>
</tr>
</tbody>
</table>

NB: Crude oil tank: diameter 50 to 80 m - floating roof - 2 000m³ oil sludge

**Driving force for implementation**
To reduce VOC emissions and tank bottom content.

**Example plants**
Examples exist of for applications in many EU refineries and tank farms.

**Reference literature**

**4.21.12 Colour of tanks**

**Description**
It is preferable to paint tanks containing volatile materials in a light colour to prevent for the reasons given below.

- To prevent increasing the evaporation because of increased product temperature.
- To prevent increasing the breathing rate of fixed roof tanks. A total heat reflectance coefficient of a minimum of 70 % should be ensured is recommended. This coefficient can be achieved by using colours with a low-coating factor, e.g. white (1.0) or aluminium silver (1.1). On the contrary, any of the other colours usually used, including light grey, show significantly higher factors (>1.3) which cannot allow to reach the above coefficient mentioned above.

**Achieved environmental benefits**
Reduction of VOC emissions.

**Cross-media effects**
Depending on the geographical landscape context, painting in light colours can result in tanks being more ‘visible’ which can have a negative visual effect. Emissions may occur during painting.

**Applicability**
Painting the roof and the upper part of the shell of a tank in the middle of a tank farm can be almost as effective as painting the entire tank.

**Driving force for implementation**
Using this technique is also a requirement of Directive 94/63/EC for gasoline tanks, except where there are derogations for visually-sensitive areas.

**Reference literature**
[262, Jansson, 2000], [268, TWG, 2001], [302, UBA Germany, 2000], [28, Tebert et al. 2009].
4.21.13 Other good storage practices

KOM conclusion 3.7: TWG to provide necessary information to update and complete BREF Section 4.21, in particular with regard to:

- the control (tightness) and maintenance of aerial and underground storage
- VOC reduction for storage (sealing, covering, leak detection, etc)

→ Info expected from CZ, DE/OMV (3rd seals), NL, NO, UK, FR, and CONCAWE

Description
Proper material handling and storage minimises the possibility of spills, leaks and other losses which result in waste, air emissions and emissions to water. Some good storage practices are listed below:

- Use larger containers instead of drums. Larger containers are reusable when equipped for top and bottom discharge, whereas drums have to be recycled or disposed of as waste. Bulk storage can minimise the chances of leaks and spills as compared to drums.
- Reduction of the generation of empty oil drums. Bulk purchasing (via tank trucks) of frequently used oils and filling tote bins as intermediate storage. Personnel could then transfer the oils from the tote bin to reusable drums, buckets, or other containers. This would reduce the generation of empty drums and their associated handling costs.
- Storage of drums off the floor to prevent corrosion through spills or concrete ‘sweating’
- Keeping containers closed except when removing material.
- Practise corrosion monitoring, prevention and control in underground piping and tank bottoms (related to the Sections 4.21.8 and 4.21.22).
- Tanks for storage of ballast water may cause large VOC emissions. They can be therefore equipped with a floating roof. These tanks are also relevant as equalizing tanks for the waste water treatment system.
- Passing of vents from sulphur storage tanks to pass to sour gas or other arrestment systems.
- Vent collection and ducting from tank farms to central abatement systems.
- Installation of self-sealing hose connections or implementation of line draining procedures.
- Installation of barriers and/or interlocking systems to prevent damage to equipment from the accidental movement or driving away of vehicles (road or rail tank cars) during loading operations.
- Implementation of procedures to ensure that arms are not operated until inserted fully into the container to avoid splashing where top loading arms are used.
- Application instrumentation or procedures to prevent overfilling of tanks.
- Installation level alarms independent of the normal tank gauging system.
## Achieved environmental benefits and Economics

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Emission factor for NM VOC (g/t throughput)</th>
<th>Abatement efficiency (%)</th>
<th>Size (diameter in m)</th>
<th>Cost (EUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed roof storage tanks (FRT)</td>
<td>7 – 80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>External floating roof tank (EFRT)</td>
<td>7 – 80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Internal floating roof tank (IFRT)</td>
<td>2 – 90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>External paint finish in a lighter shade</td>
<td>1 – 3 FRT</td>
<td></td>
<td>40</td>
<td>25 400</td>
</tr>
<tr>
<td>Installation of an internal floating roof in existing fixed-roof tank</td>
<td>97 – 99 FRT</td>
<td></td>
<td>40</td>
<td>32 500</td>
</tr>
<tr>
<td>Replacement of a vapour-mounted primary seal with a liquid-mounted primary seal</td>
<td>30 – 70 EFRT</td>
<td></td>
<td>40</td>
<td>4 600</td>
</tr>
<tr>
<td>Retrofitting secondary seals on an existing tank</td>
<td>90 – 94 EFRT</td>
<td></td>
<td>40</td>
<td>15 100</td>
</tr>
<tr>
<td>Improvement of primary seal, plus secondary seal and roof fitting control (pontoon and double deck)</td>
<td>98 EFRT</td>
<td></td>
<td>40</td>
<td>11 300</td>
</tr>
<tr>
<td>Installation of a fixed roof on an existing external floating-roof tank</td>
<td>96 EFRT</td>
<td></td>
<td>40</td>
<td>200 000</td>
</tr>
</tbody>
</table>

NB: Columns for abatement efficiency, size and cost are related to the techniques and not to each other. Costs are average costs for the two diameters and abatement efficiencies are ranges for the technique applied to different types of tanks.

### Reference literature


### 4.21.14 In-line blending

**Description**

Figure 4.39 shows a scheme of an in-line blending system for gas oils.
Achieved environmental benefits
The energy savings realised by in-line blending compared to batch blending can be substantial, especially in electric power consumption. Using in-line blending reduces the total number of handling operations with respect to feed and product streams—less filling and emptying of tanks and thus reduced the total emission to atmosphere. The numerous valves and pumps can be provided with double mechanical seals and can be regularly maintained in order to minimise fugitive VOC emissions. In-line blending generally creates more flexibility towards product specifications and product quantities, and represents a large savings by avoiding intermediate storage.

Cross-media effects
In-line blending systems contain many flange connections and valves, which could be sources of leakage, particularly during maintenance.

Operational data
Extreme care has to be taken to on-line in-line quality analysers to ensure the quality of the blended product.

Applicability
Optimising the blend ratios to meet all critical specifications is, to a certain extent, a trial-and-error procedure which is most economically accomplished with the use of a computer. There are usually permits a number of comparable solutions that give
roughly equivalent total overall cost or profit. Optimisation programs allow the computer to provide the optimum blend to minimise costs and maximise profit.

**Example plants**
In-line blending systems are normally applied for high volume feed and/or product streams.

**Reference literature**
[118, VROM, 1999].

### 4.21.15 Batch blending

**Description**
See Section 2.21.

**Applicability**
The reasons for batch blending are the minimum storage requirements for strategic reasons, fiscal and tax control, operating flexibility and tank dimensions.

**Example plants**
For a variety of the reasons given mentioned above, under ‘applicability’, batch blending of feed and product is still done to a certain extent.

### 4.21.16 Vapour recovery

KOM conclusion 3.7: TWG to provide necessary information to update and complete BREF Section 4.21, in particular with regard to:

- VOC reduction from handling (loading/unloading facilities)
  - Info expected from CZ, DE, NL, NO, UK, FR, and CONCAWE.

Vapour recovery/destruction systems and vapour return during loading applied to storage are included in Section 4.25.6.2.

Note to TWG: The text from this section has been merged in 4.25.6.2 for consistency

### 4.21.17 Vapour destruction/use

Text moved to Section 4.25.6.3

**Description**
Vapour destruction is also a technically viable option, which may include energy recovery. It also includes the destruction of vented products in process heaters, special incinerators or flares.

**Achieved environmental benefits**
Efficiency up to 99.2% can be achieved with conventional thermal oxidation (e.g., flares, furnaces). Catalytic combustions can achieve higher efficiencies of 99.9%. Efficiency of the flameless thermal oxidation can achieve removal efficiencies of 99.99% or greater. In the absence of a high-temperature, thermal NOx is typically less than 2 ppm v/v.

The heat generated in the combustion can be used to produce low-pressure steam or to heat water or air.

**Cross-media effects**
CO₂ is produced in the combustion process. CO and NOx may be also produced. Additional fuel is consumed in the combustion of streams with low concentrations and for the preheating of catalysts. Experience with existing units shows 19 – 82 kg/h of gasoil is used. Continuous
ignition source within the vapour system is a major safety concern that requires the implementation of systems to prevent ignition propagation.

Applicability
Vapour destruction used is applicable to reactor and process vents, tank vents, loading facilities, ovens and dryers, remediation systems and other manufacturing operations. Applicability is limited to very light hydrocarbons, methane, ethane and propylene.

Economics
The investment Costs (EUR million) is 2 – 25 and 3.2 – 16 for marine loading (EUR 0.1 – 0.23 million/ship for conversion). Operating Costs are in the range of: EUR 0.02 – 1.1 million Retrofit costs are very site specific.

Driving force for implementation
Reduce VOC emissions.

Example plants
Catalytic combustion processes have been applied in the chemical industry.

Reference literature
[181, HP, 1998], [118, VROM, 1999], [268, TWG, 2001]

4.21.18 Vapour balancing during loading processes

Description
In order to prevent emissions to atmosphere from loading operations, several options are available. Where loading takes place from fixed roof tanks, a balance line can be used. The expelled mixture is then returned to the liquid supply tank and so replaces the pumped-out volume. Vapours expelled during loading operations may be returned to the loading tank, if it is of the fixed roof type, where it can be stored prior to vapour recovery or destruction. This system can also be used for vessels and barges.

Achieved environmental benefits
This Vapour balancing greatly reduces the vapour volumes expelled to atmosphere. It can reduce VOC emissions by up to 80% of the VOC emitted.

Cross-media effects
Due to evaporation in the receiving vessel during transfer (vapour evolution by splashing), there is usually a surplus volume of vapours compared to the displaced liquid volume. The balancing line is not considered an efficient means of VOC abatement for the most volatile liquids.

Operational data
Where explosive mixtures can occur, it is important that safeguards are implemented to limit the risk of ignitions and ignition propagation. Tanks should remain closed to prevent emissions, so they may operate under a low pressure and ullaging and sampling should not be undertaken through open dispatches. Detonation arrestors require regular cleaning when vapours contain particulates (e.g. soot from badly-operated cargo tank inerting systems).

Applicability
Not all vapours can be collected. May affect loading rates and operational flexibility. Tanks which may contain incompatible vapours cannot be linked.

Economics
The investment required is costs are EUR 0.08 million per tank and the operating costs are low.
Driving force for implementation
Reduce VOC emissions.

Example plant(s)
LPG loading. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the refinery fuel gas system.

Reference literature
[115, CONCAWE, 1999], [268, TWG, 2001].

4.21.19 Bottom loading measures

Description
The loading/unloading pipe is flange-connected to a nozzle situated at the lowest point of the tank. A vent pipe on the tank can be connected to a gas balancing line, VRU or to a vent. In the last case, VOC emissions can occur. The flange connection in the filling line has a special design (‘dry connection’) which enables it to be disconnected with minimum spillage/emissions.

Achieved environmental benefits
It reduces VOC emissions reduction.

Driving force for implementation
European Directive 94/63/EC on the control of VOC emission prescribes requirements for gasoline loading for road tankers.

Reference literature
[80, March Consulting Group, 1991], [268, TWG, 2001].

4.21.20 Tightly sealed floors

Description
The handling of materials used in the refinery may result in accidental spills that could contaminate the soil, or rainwater, surface water or groundwater. This technique Paving and kerbing the area where materials are handled, for the collection of the possible spilled material.

Achieved environmental benefits
Avoid Prevention of soil pollution and directing any spillage of product to the slops. This would minimises the volume of waste generated and allows for the collection and reclamation of the material.

Driving force for implementation
Avoid To prevent soil and rainwater contamination.

Example plants
Many examples can be found in European refineries.

Reference literature
[80, March Consulting Group, 1991].

Section moved to Section 2.21

4.21.21 LPG odourant plant

Description
The design and operation of odorising facilities should be to a very high standard which minimises the risk of odorant leaks or spillages. To an extent, the operational aspects of this are
facilitated by the ease of detection of even the smallest odorant release, but this needs to be used as an aid to vigilance, not as a reason for lax control.

Odorising plants should be designed to minimise the potential for leaks, e.g. by having the minimum number of pumps/valves/filters/tank connections, etc., by using welded, not flanged, connections wherever possible and by protecting the plant from possible impact damage. All such items used need to be designed to a very high standard of sealing efficiency. Devices such as automatic self-sealing couplings for loading lines are preferred.

Plants should be designed to deal with the high vapour pressure of odorants and should use inert or pressure controlled natural gas blanketing of the vapour spaces above stored odorant. During deliveries into tanks any displaced vapour needs to be returned to the delivery vehicle, adsorbed on activated carbon or incinerated. The use of demountable semi-bulk containers avoids the generation of displaced vapours and is preferred where appropriate.

**Achieved environmental benefits**

In view of the nature and power of the odorants used, there should be no normal release of odorant to any environmental medium.

**Reference literature**

[18a, Irish EPA, 1992].

---

Section proposed to delete

### 4.21.22 Overground pipelines and transfer lines

**Description**

In overground pipelines it is easier to detect leakings.

**Achieved environmental benefits**

Decrease in the soil contamination.

**Applicability**

Its implementation is easier. Overground pipelines are easier to implement in new installations.

**Economics**

The replacement of existing underground pipelines is typically very expensive.

**Reference literature**

[19a, Irish EPA, 1993].
4.22 Visbreaking and other thermal conversions

4.22.1 Visbreaking

4.22.1.1 Hydrovisbreaking

**Achieved environmental benefits**
A modern technique, which increases the conversion rate of the feed by addition of H-donators and water without reducing the stability of the process.

**Economics**
Investment (based on: 750 kt/yr of topped heavy Canadian crude; battery limits including desalting, topping and engineering; 1994 US Gulf Coast). Information is given in Table 4.81.

<table>
<thead>
<tr>
<th>Process alternative</th>
<th>Normal visbreaker</th>
<th>Hydro visbreaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUR per t/yr</td>
<td>85 000</td>
<td>115 000</td>
</tr>
<tr>
<td>Utilities, typical per m³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel oil fired (80 % effic.) kg</td>
<td>15.1</td>
<td>15.1</td>
</tr>
<tr>
<td>Electricity, kWh</td>
<td>1.9</td>
<td>12.0</td>
</tr>
<tr>
<td>Steam consumed (produced), kg</td>
<td>15.1</td>
<td>30.2</td>
</tr>
<tr>
<td>Water, process, m³</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Hydrogen consumption, Nm³</td>
<td>NA</td>
<td>30.2</td>
</tr>
</tbody>
</table>

Example plants
Hydrovisbreaking was tested in a 2 Mt/yr visbreaker in a refinery in Curaçao.

Reference literature
[212, Hydrocarbon processing, 1998], [250, Winter, 2000].

4.22.1.2 Soaker visbreakers

**Description**
In this process, a soaker drum is added after the furnace, so the cracking takes place at lower furnace outlet temperatures, and longer residence time.

**Achieved environmental benefits**
The product yields and properties are similar but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption (30 – 35 %) and longer running times before shutting down to remove coke from the furnace tubes (running times of 6 – 18 months versus 3 – 6 months in coil cracking).

**Cross-media effects**
The above apparent advantage of reducing the number of clean-ups for soaker visbreakers is at least partially balanced by the greater difficulty in cleaning the soaking drum.

**Operational data**
Run times of 3 – 6 months are common for furnace visbreakers and 6 – 18 months for soaker visbreakers. Fuel consumption is around 11 kg FOE/t. Power and steam consumption is similar to the coil one. Operating temperature is 400 – 420 ºC at the soaker’s exit.

Example plants
Some soaker visbreakers exists in European refineries.
Chapter 5

4.22.2 Deep thermal conversion Thermal gas oil unit (TGU)
Text of description process transferred to Chapter 2

Description
Deep thermal conversion bridges the gap between visbreaking and coking. It maximizes yields of stable distillates and produces a stable residue, called liquid coke. The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gasoil and naphtha cuts produced, as shown in Error! Reference source not found.. After a first thermal cracking, the resulting products are separated in a cyclone. The gaseous phase is introduced in the flash zone of the main distillation column and separated according to desired boiling intervals. The heavy gas oil (HVGO) and the vacuum gas oil from the flash column (LVGO) are treated in a second thermal cracker and re-introduced into the column. Former Figure 4.39:Simplified process of a thermal gas oil unit has been transferred to chapter 2

The resulting vacuum flashed cracked residue (VFCR) has a high sulphur content and can only be used as fuel in the refinery power plant if equipped with an efficient and appropriately sized flue gas cleaning system.

For complete description see Section 2.22.2 on thermal gasoil unit.
The thermal gas oil unit (TGU) allows the conversion of the vacuum distillation residue by using a two-step thermal cracking and subsequent distillative separation into the gasoil and naphtha cuts produced.

Achieved environmental benefits
Increase the performance of visbreaking. Compared to a conventional visbreaker, the TGU process allows for a significantly higher conversion of the vacuum residue into lighter products. The conversion yield reaches about 40 % weight instead of 15 %, and the resulting products can be directly valorised in cut streams used for diesel, gasoline and naphtha production.

Cross-media effects
This process increases the site energy consumption and the related air emissions. The net energy necessary for the conversion is about XX GI/t of vacuum residue. It also generates additional heavily hydrocarbon-contaminated waste waters to be treated in the WWTP.

Operational data
A TGU unit has been operated at the OMV refinery in Schwechat since Spring 2009. The unit treatment capacity is 2000 t/day. The heat required for the process is provided by a natural gas-fired gas turbine with a rated thermal input of about 80 MW, which delivers a 27 MW_e of additional electrical energy to the refinery grid together with some process steam generated in the heat recovery unit of this plant.

Applicability
This process is fully applicable for new plants. On the contrary, the retrofitting of such process on existing visbreaking units is not possible.

Economics
The investment amounts to USD 2 400 to 3 000 (EUR 1 900 – 2 500) per bpd (barrel per day) installed, excluding treatment facilities and depending on the capacity and configuration (basis Europe: 1998 – 2004).

Driving force for implementation
Maximisation of the site conversion ratio towards a ‘no residue’ refining.
Example plants
Approximately 12 units are installed worldwide. One plant has been operated since 2009 by OMV in Schwechat (Austria)

Reference literature
[316, TWG, 2000] [ 54, Gallauner et al. 2009 ] [ 76, Hydrocarbon processing 2011 ].

4.22.3 Sour gas and waste water management

Description
The gas generated in the visbreaking may be sour and contain sulphur compounds, in which case a gas-sweetening operation, typically amine scrubbing, should be applied before the gas is recovered into products or used as refinery fuel gas. Visbreaking gas, apart from being amine scrubbed to remove H₂S, is further treated to remove approximately 400 to 600 mg/Nm³ of mercaptan sulphur (depending on the feed) in order to meet the refinery fuel gas sulphur-content specification.

The aqueous condensate is usually sour, and should pass to the sour water stripper in an enclosed system.

Achieved environmental benefits
Reduction in the sulphur content of products.

Cross-media effects
Need for chemicals and utilities to run the processes.

Driving force for implementation
Sulphur specifications of the products.

Example plants
These techniques, Sour gas use and waste water management are applied in many refineries.

Reference literature
[316, TWG, 2000].

4.22.4 Reduction of coke formation in visbreakers

Description
During the thermal cracking some coke formation is produced and deposits itself onto the furnace tubes. The coke should be cleaned when necessary. It exist in the market. Additives are available on the market to control the sodium content within the feedstock. The control of the addition of caustics or specific additives to the feedstock upstream can also be used.

Achieved environmental benefits
Reduction of the coke formation and as a consequence, reduction of cleaning waste.

Driving force for implementation
This technique is typically applied to prevent cleaning.

Reference literature
[268, TWG, 2001].
Chapter 5

4.23 New high conversion techniques (if any reported)

KOM conclusion 3.6: TWG to review existing/new ‘bottom end’ high conversion processes (for BREF Section 4.22, and eventually new sections)
KOM conclusion 3.6: TWG to review existing/new ‘bottom end’ high conversion processes.

Note for the TWG:
Data collected by EIPPCB on new conversion techniques have been gathered in Chapter 6

4.24 Techniques for the elimination or valorisation of external waste used as secondary raw material

KOM conclusion 2.4: TWG to provide info on such applied techniques.
→ info still expected, in particular from CZ, SK

No specific information was made available – Paragraph proposed to delete
Chapter 4

4.25 Waste gas minimisation and treatments

This section together with the following two sections (namely Sections 4.26 and 4.27) are dealing with the end of pipe processes that appear in a refinery. This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for air emissions of oil and gas refining.

For a given technique, the information provided here aims at completing, broadly, the operational data and material that have already been provided in previous sections where only specific results obtained from the application of this technique to a particular process or unit are reflected. The reason why these techniques are appearing here is to give an overall description of the techniques and to avoid repetition. Description of end of pipe techniques does not appear in the previous sections. Consequently, in this Sections (23 and 24), will notably be found in this section general information on environmental benefits, cross-media effects, operational data, and applicability, which will have not been repeated in other sections. Consequently the data included in these sections is broader and more general than the one appearing within the activities.

Complementing these techniques that may appear within the production activities, this section and the next one also contain end-of-pipe processes which concern the whole refinery and have also to be considered for applied and that are techniques to consider in the determination of BAT for refineries. Under this category are the sulphur recovery units, flares, and amine treatment or the waste water treatments. These techniques are only discussed here.

In case of need, further and deeper information about these techniques included in this section and next one can also be found in the Common Waste Water and Waste Gas Treatments BREF [6, EC 2003].

4.25.1 CO-abatement techniques

Note for the TWG: After considering TWG comments, mainly in favour of keeping this section the information is kept in.

Description

CO boilers and catalyst reduction of CO (and NOx). Good primary measures for the CO reduction are:

- good operational control
- constant delivery of liquid fuel in the secondary heating
- good mixing of the exhaust gases
- catalytic afterburning
- catalysts with oxidation promoters.

Achieved environmental benefits

Reduction of CO emissions. Emissions after the CO boiler: <100 mg/Nm³. In the case of conventional firings, a CO concentration below 50 mg/Nm³ is achievable at temperatures above 800 °C, at sufficient air delivery and sufficient retention times (see Table 4.37).

Applicability

FCC and in heavy residues fired. (Sections 4.10.4.10 and 4.5.5).

Reference literature

[316, TWG, 2000].
Chapter 5

4.25.2 CO₂ emission control options

Note to TWG: Updated data at the time of writing (2012) on this topic are gathered in Chapter 6 on emerging techniques.

Description
Unlike SO₂, treatment NOₓ or particulates treatment of flue-gases, as a feasible abatement technology for CO₂ is not available. CO₂ separation techniques are available but the problem is the storage and the recycling of the CO₂. Options for the refiner to reduce CO₂ emissions are:

1. effective energy management (topic discussed in Section 4.10.1) including:
   - improving heat exchange between refinery streams;
   - integration of refinery processes to avoid intermediate cooling of components (e.g. Section 4.19.1 Progressive distillation unit);
   - recovery of waste gases and their use as fuels (e.g. flare gas recovery);
   - use of the heat content of flue-gases;

2. use of fuels with high hydrogen contents (topic discussed in Section 4.10.2);
3. effective energy production techniques (see Section 4.10.3). It means the highest possible recovery of energy from fuel combustion;
4. the capture, transport and sequestration (CCS - Carbon Capture and Storage) of CO₂ emissions (see Chapter 6 Emerging Techniques).

As the CCS option is not yet available at site scale, choices for abatement techniques should be made taking into account the possibility to further use it.

Achieved environmental benefits
Reduction of CO₂ emissions.

Cross-media effects
Use of fuels with high hydrogen contents reduce CO₂ emissions from the refineries but overall will not reduce CO₂ as these fuels will not then be available for other uses.

Operational data
Rational energy use requires good operation to maximise heat recovery and process control (e.g. O₂ excess, heat balances between reflux, product temperature to storage, equipment survey and cleaning). To get optimum results, repeated operator training and clear instructions are necessary.

Reference literature
[252, CONCAWE, 2000], [268, TWG, 2001] [77, REF TWG 2010].

4.25.3 NOₓ-abatement techniques

The NOₓ emission level of an oil refinery or a natural gas plant is influenced by the refining scheme, the type of fuels used and the abatement techniques implemented. As the number of emission sources and their contribution to the overall emission level may vary greatly, one of the first techniques to consider is the precise quantification and characterisation of the emission sources in each specific case. For more information, see Section 3.26.

See also section 4.25.8 for information on the SNOₓ combined technique.
4.25.3.1 Low-temperature NO\textsubscript{x} oxidation

**Description**
The low-temperature SNO\textsubscript{x} oxidation process injects ozone into a flue-gas stream at optimal temperatures below 200\textdegree\textsuperscript{C}, to oxidise insoluble NO and NO\textsubscript{2} into highly soluble N\textsubscript{2}O\textsubscript{5}. The N\textsubscript{2}O\textsubscript{5} is removed in a wet scrubber by forming dilute nitric acid waste water that can be used in plant processes or neutralised for release. General information about this technique can be found in the Section CWW BREF.

**Achieved environmental benefits**
- Low temperature NO\textsubscript{x} oxidation can achieve 90 – 95\% removal of NO\textsubscript{x}, with consistent NO\textsubscript{x} levels as low as 5 ppm. Additional benefits are the heat-recovery from the fuel gas savings which remains fully possible. The entire process is controlled to produce no secondary gaseous emissions. Because ozone is used as an oxidising agent, emissions of CO, VOC and ammonia are also reduced.

**Cross-media effects**
Ozone should be produced on site, on demand, from stored O\textsubscript{2}. There is the risk of ozone slip. The system can increase nitrate concentration in the waste water.

**Operational data**
The use of ozone and the low optimal temperatures of the process provide stable treatment conditions. Energy consumption for the production of ozone range from 7 – 10 MJ/kg (2 – 2.8 kWh/kg) of ozone produced with a concentration of 1 – 3\% w/w with dry oxygen feed. Temperatures should be below 150\textdegree\textsuperscript{C} to minimise ozone decomposition. Heavy particulate-laden fuels may require additional equipment.

**Applicability**
This process has been developed and is known as SNERT (scrubber-based NO\textsubscript{x} emissions reduction technology). The NO\textsubscript{x}-removal performance is directly linked to the ozone injection rate and its real-time regulation in relation to the NO\textsubscript{x} outlet concentration target. The outlet NO\textsubscript{x} can be adjusted by varying the set point on the system controller.

This process can be used as a standalone treatment system or can follow other combustion modifications and post-combustion treatment systems, such as low-NO\textsubscript{x} burners, SCR or SO\textsubscript{x} removal, as a final polish step, including the treatment of ammonia slips. The process can be used either as a ‘stand alone’ treatment system or as a retrofit to an existing plant. It can also be used as a polishing system to other NO\textsubscript{x} removal technologies and for the treatment of ammonia slips.

**Economics**
This technique requires low maintenance and low operator interface. The relative capital cost and operating costs given by the technology providers claim that they are equal to, or less than SCR-type systems.

A prospective study for the potential control of existing major SO\textsubscript{2} and NO\textsubscript{x} industrial sources in Colorado (US) provides accumulative capital and operational annual cost data expressed per tonne of abated NO\textsubscript{x} for some industrial sectors. In refineries, the quoted application concerns FCC units with costs ranging from 1 391 – 1 595\textsuperscript(*) EUR/tonne (1884 – 2 161 USD/tonne 2007 values). As a comparison, other cost ranges are available for wet kilns 2303 – 2454 EUR/tonne (3 102 – 3 324 USD/tonne) and dry kilns 1 717 – 1 963 EUR/tonne (2 327 – 2 659 USD/tonne) in the cement industry.

\textsuperscript(*) Based on currency conversion rate of 0.73822 at 1/07/2007
Example plants
The process is in use on USA commercial installation for sectors as acid pickling, lead smelting, steam boilers and coal fired boilers. A trial is planned for is currently planned on a refinery FCC UNIT unit. A number of FCC units have been notably retrofitted with such technique in the US as well (see Section 4.5.8.5).

Driving force for implementation
To reduce the NOx emissions.

Reference literature
[181, HP, 1998], [344, Crowther, 2001], [268, TWG, 2001], [17, Jeavons and Francis 2008]

4.25.3.2 Selective non-catalytic reduction (SNCR)

Description
SNCR is a non-catalytic process for removing nitrogen oxides of nitrogen from the combustion flue-gases by gas phase reaction of ammonia or urea at high temperatures (generally between 850 and 1100 °C). This technique, also called thermal DeNOx, reduces NOx to nitrogen and water. To achieve a good mixing, the small amount of reactant is injected along with a carrier gas, usually air or steam. General information about this technique can be found in Waste water and wastegas BREF [312, EIPPCB, 2001] the CWW BREF [ 6, EC 2003 ] and in Section 3.4.2.2 of the LCP BREF [ 7, EC 2006 ].

Achieved environmental benefits
Reductions of 40 – 70 % can be achieved giving values of less than 200 mg/Nm³ by the use of this technique. Higher reduction figures (up to 80 %) can only be achieved under optimal conditions.

Cross-media effects
When the temperature lower In the case of risk of the temperature decreasing outside the optimal temperature window, it is may be needed necessary to reheat up the flue gas with the consequent use of energy.

The systems also need the equipment necessary for the storage of ammonia or urea. Disadvantages are also NH3 slip (5 – 40 mg/Nm³) and possible side reactions (N2O).

An intrinsic limitation of the SNCR technique is the emission of a small amount of unreacted NH3 (ammonia slip) in the flue-gas stream. The ammonia slip is typically in the range of 5 – 20 ppm (3 – 14 mg/Nm³), the higher values being associated with higher NOx reduction. The US EPA identified ammonia as the single largest precursor of fine particulate (2.5 microns in size and smaller) air pollution (2.5 microns in size and smaller) in the country.

A side reaction of particular concern is the formation of ammonium sulphates when firing sulphur-containing fuels such as liquid refinery fuel. Sulphates give rise to the fouling and corrosion of downstream equipment.

Aqueous ammonia, anhydrous ammonia, or urea can be used as a reactant in the SNCR system. The storage of gaseous or liquefied anhydrous ammonia has a great hazardous potential. Therefore, every time whenever possible, after an appropriate evaluation of the risks a liquid solution of ammonia (25 %) or urea should generally be preferred used.

N2O is a by-product formed during SNCR. Urea-based reduction generates more N2O than ammonia-based systems. At most, 10 % of the eliminated NOx is formed into N2O in the urea based systems [ 103, EPA 2002 ] However, ammonia injection produces significantly less N2O and CO side emissions than urea or other reagents.
Operational data
SNCR process needs to achieve temperatures of 800 °C to 1200 °C for efficient conversion. The NO\textsubscript{x} reduction rate depends very much on the possibility of matching the following temperature windows together with a minimum residence time of 0.2 – 0.5 s in the region of injection temperature window:

- 850 – 1000 °C for ammonia and caustic ammonia (optimum 870 – 950 °C)
- 800 – 1100 °C for urea (optimum 1000 °C)

Injection of reagent below this temperature window results in excessive ammonia slip. Injection of reagent above the temperature window results in increased NO\textsubscript{x} emissions. With the injection of hydrogen along with the NH\textsubscript{3} and carrier, optimum temperatures can be shifted to as low as 700 °C. In some applications, it has been suggested that chemical enhancers, such as hydrogen, are needed to help the reaction at lower temperatures, but this type of application is not reported within the refining industry.

The ammonia produced in the sour water stripping (see Section 4.26.4) can be used as a denox DeNO\textsubscript{x} agent. The effectiveness of this process is very temperature dependent.

It also depends on the NO\textsubscript{x} inlet concentration to be abated, because even under optimal thermal conditions, there is a lower limit to the technically achievable reduction yield and outlet concentration due to the particular mixing conditions and chemical kinetics.

Applicability
SNCR is typically applied to flue-gases from heaters and boilers. Only there are no or very small space requirements. Space requirements are mainly restricted concerning NH\textsubscript{3} storage. In some cases, operating and physical constraints can make retrofitting difficult: e.g. temperature window required may occur in the middle of the boiler tube bank and could lead to impingement of the injected chemical against the tubes.

Economics
Cost considerations include the initial capital costs for modifying the furnace or boiler, piping to inject the reactant, the reactant supply system and the recurring cost for ammonia or urea to react with the NO\textsubscript{x}. Cost estimates for the use of an SNCR after a power plant are reported in Section 4.10.4.6. Table 4.82 gives general cost effectiveness data ranges for the use of SNCR under different conditions. For more specific data, see in particular Sections 4.5.8.2 and 4.10.4.6.

<table>
<thead>
<tr>
<th>SNCR applied to:</th>
<th>Cost effectiveness in EUR/tonne NO\textsubscript{x} removed (includes capital charge of 15 %)</th>
</tr>
</thead>
</table>
| Fired Heaters and boilers firing refinery blend gas | 2000 – 2500  
1800 – 4300 |
| Boilers firing residual fuel oil      | 1500 – 2800  
1500 – 4300 |
| Fluid catalytic cracking units       | 1900 |

N.B: Details on the conditions are given in Annex IV.

Driving force for implementation
Reduction To reduce nitrogen oxide emissions.

Example plants
Applied to FCC\textsubscript{c} units, process furnaces and boilers.
4.25.3.3 Selective catalytic reduction (SCR)

Description
A further deNO\textsubscript{x} technique is also known as catalytic deNO\textsubscript{x}. The ammonia/urea vapour is mixed with the flue-gas through an injection grid before being passed through a catalyst to complete the reaction. Various catalyst formulations are available for different temperature ranges: zeolites for 300 – 500 °C, traditional base metals employed between 200 – 400 °C, and metals and activated carbon for the lowest temperature applications 150 – 300 °C metals and activated carbon are used. More information about this technique can be found in the Waste gas BREF [312, EIPPCB, 2001] the CWW BREF [6, EC 2003] and the LCP BREF [7, EC 2006].

Achieved environmental benefits
SCR is especially suitable for situations where emission standards are strict. With SCR, removal efficiencies of 80 to 95 % can be obtained generally for inlet concentration over 200 mg/Nm\textsuperscript{3}. Residual NO\textsubscript{x} stack levels of 10 – 20 mg/Nm\textsuperscript{3} can be obtained by application of SCR in gas-fired boilers and furnaces. When firing heavy residues, emissions of <100 mg/Nm\textsuperscript{3} (3 % O\textsubscript{2}, half-hourly mean value, efficiencies of up to 90 %) can be achieved.

Cross-media effects
SCR has some cross-media effects as NH\textsubscript{3} slip of less than <2 – 20 mg/Nm\textsuperscript{3} depending on the application and requirements or sulphate aerosols are controllable to very low levels. SCR operation at the end of its catalyst life may also entail bigger slip of NH\textsubscript{3}. This means a constraint in conversion efficiency. At the end of its life, some components of the catalyst can be recycled and the other are disposed of. The main cross-media effects can be summarised below.

- As for with SNCR, an intrinsic limitation of the SCR technique is the emission of a small amount of unreacted NH\textsubscript{3} (ammonia slip) in the flue-gas stream. The ammonia slip is typically in the range of 2 – 10 ppm (1.4 – 7 mg/Nm\textsuperscript{3} at 25 °C), the higher values associated to the with higher NO\textsubscript{x} reduction and, more specifically, to catalyst end-of-run conditions. It should be noted that ammonia slip is dependent on many factors, including NH\textsubscript{3} injection rate, catalyst activity, fluegas distribution, process controllability. The US EPA identified ammonia as the single largest precursor of fine particulate (2.5 microns in size and smaller) air pollution in the country.
- N\textsubscript{2}O generation can occur with some catalysts.
- The spent catalyst should be regenerated or eliminated disposed of properly.
- Storage of gaseous or liquefied anhydrous ammonia has a great hazard potential. Therefore, whenever possible, a liquid solution of ammonia (25 %) or urea should be preferred.
- As for SNCR, aqueous ammonia, anhydrous ammonia, or urea can be used as a reactant in the SCR system. The storage of gaseous or liquefied anhydrous ammonia has a great hazardous potential. Therefore, whenever possible, after an appropriate evaluation of the risks, a liquid solution of ammonia (25 %) or urea should be generally preferred.
- Another disadvantage of SCR is that A small amount of SO\textsubscript{2} is oxidised to SO\textsubscript{3} over the deNO\textsubscript{x} cat SCR catalyst and as consequence it can potentially create plume opacity problems. In sufficient amounts, SO\textsubscript{3} in fluegas may impact plume opacity.
- Additional fuel consumption may be needed to increase the furnace fluegas temperature to reach the one required by the catalyst. In this case, additional CO\textsubscript{2} emissions will be produced. (see infra Operational data and Economics).
Chapter 4

Operational data

The ammonia produced in the sour water stripping (see Section 0) can be used as denox agent. The catalytic deNOx process operates at low temperatures (250°C to 450°C). Operator and maintenance requirements are low for clean gas applications. More

The theoretical amount of reducing agent for removing 1 kg of NOx is 0.37 kg of ammonia or 0.65 kg of urea. The amount is dependent on the ratio of NO to NO2 in the combined NOx concentration, as reaction stoichiometry requires one mole of ammonia to reduce one mole of NO and 2 moles for one mole of NO2. Attention is required for applications where fouling substances like SO3 and soot or dust are present in the off-gas. The presence of SO3 and ammonia will lead to the formation of ammonium sulphates if the fluegas temperature drops below the ammonium salt deposition temperature. Ammonium sulphates may have a detrimental effect on the activity of the catalyst due to the masking of active sites and can and lead to fouling of downstream heat exchangers. Catalyst deactivation can be mitigated by ensuring that the process unit is operated above the ammonium salt deposition temperature. However sulphate deactivation can be avoided with a relevant temperature control. Reactivation of the catalyst can be executed by heating at 400°C, to counteract fouling a water washing step is generally applied. Soot has to be removed by blowing of the catalyst with steam or inert gas (e.g. nitrogen), while a ‘dummy’ layer can optionally be applied for extra protection of the catalyst. If the flue gas contain particulates containing metals, metal deactivation may occur.

The NH3 consumption is directly related to the NOx concentration in the flue gas and amounts to about 0.4 tonne NH3 per tonne of NOx removed. The amount of ammonia is normally dosify in a 10 % more than the stoquiometric needs. The catalyst has a general lifetime of 4 to 7 years for oil firing, and for gas firing 7 to 10 years for gas firing, but shorter lifetimes have been reported in particularly defavourable unfavourable conditions. For multifuel SCR catalyst treating, catalyst life is likely driving by the most severe fuel. The pressure drop of the catalyst bed will lead to a minor amount of additional power consumption from fans in the system or loss of efficiency in the case of a gas turbine application (equivalent to 0.5 - 1 % of the heat input). Additional fuel in the event of reheating the flue gas is necessary, corresponding to a loss of energy efficiency of 1 - 2 %. Common safety precautions need to be taken when using pure NH3. To avoid elaborate safety measures (required for larger volumes of NH3,) the trend is towards using aqueous NH3 or urea. The NH3 storage also varies in size allowing 1 - 3 week operational hold-up.

When a so-called ‘tail-end’ configuration is preferred (e.g. where the SCR is projected behind downstream to of a wet scrubber, or at the end of to a gas-fired unit where the flue gas has reached a temperature of less than 150 °C, it may be necessary to reheat the flue gases to have an adequate temperature for the reduction reaction. For these applications in line burners are required. If the required temperature rise is larger than 70 – 100°C heat recuperation by means of a gas-to-gas heat exchanger could be cost-effective. Flue-gas reheat may be required if the SCR is located downstream of wet scrubbing processes or in applications with low flue-gas temperatures. Minimum operating temperature for an SCR unit is dependent on catalyst type and composition and will be application specific. According to a study at API refinery (Italy), fuel gas required to increase temperature (around 270 °C) could lead to additional CO2 emissions in the order of magnitude of 5750 tonnes/yr for 100 tonnes of NOx abated.

Applicability

Selective catalytic reduction (SCR) has been applied to combustion flue-gases or process off-gases (e.g. FCC). The introduction of an SCR system into an existing installation is a challenge due to space, pressure and temperature problems. Creative solutions can often be found to reduce the retrofit costs. Higher operating temperatures reduce the catalyst size and costs but introduce retrofit complexity. Lower operating temperatures increase the required catalyst volume and costs but often allow for a more simple a simple retrofit.

So far, predominantly operating temperatures between 200 and 450 °C prevail. These temperatures are normally available before the economiser section or the air preheater of a boiler. Gas-fired refinery furnaces generally have a stack temperature of 150 – 300°C. Dependent on the flue-gas sulphur content a medium temperature (MT) or low temperature (LT)
catalysts can be applied in tail-end configuration. Zeolite-type catalysts have reached the market place. In the US a number of gas turbines have been fitted with these catalysts.

Some other applications also exist (such as the DESONOX). Combined techniques for both SO$_2$ and NO$_x$ removal use also such a catalyst: e.g. the DesoNO$_x$ process [7, EC 2006]. As for oil firing, only MT catalysts can be applied, because of the presence of sulphur and particulates. MT catalysts have been widely applied in coal-fired power plants predominantly under conditions where the flue-gas still contains all the fly-ash and SO$_2$ from the boiler. Two other configurations are low dust/high SO$_2$ level and low dust/low SO$_2$ level (tail-end configuration).

There is little experience with the use of SCR for units applying vacuum residue as fuel. However, the power plant of the refinery Mider refinery in Germany uses vacuum residue, visbreaker residue and FCC slurry as fuel in its three oil-fired heaters. An SCR plant in high dust configuration is installed after the heaters, cleaning the gas of the NO$_x$ to concentrations less than 150 mg/Nm$^3$ (see Section 4.10.4.7 for detailed datasets). The particular difference of oil firing represent lies in the nature of its fly ash. In contrast to coal, the fly ash is extremely fine (>90% fall in the category of PM$_{2.5}$), though the quantity is much less. The composition is also quite different. Coal fly-ash predominantly consists of silica compounds, with a minimum of unburnt HCs. Oil fly-ash contains metal oxides, soot and coke. Unabated fly-ash concentrations for oil firing are in the range of 100 – 600 mg/Nm$^3$ (with the highest values for vacuum residues). SCR applied under these conditions may suffer from clogging by fly-ash and sulphates (at coal firing the fly-ash by its sandblasting effect keeps the catalyst clean). The potential for sulphate precipitation is generally higher with vacuum residue, due to its high sulphur content (2.5 – 4%).

Pressure drop can be an important consideration when considering as to whether SCR can be applied to a flue-gas system. For this reason natural draft furnaces could probably not be fitted with it. See Section 4.25.8 for combined flue-gas desulphurisation and deNO$_x$ing.

![Figure 4.40: Some examples of SCR retrofit situations in refineries (clean gas situations)](image-url)
Economics

See applications in each section (Section 4.10.4.7 for the energy system, 4.5.8.1 for FCC units cat cracker and Section 4.7.9.5 for cokers). The investment costs of new SCR system depend largely on the flue-gas volume, its sulphur and dust content and the retrofit complexity. The total erection costs for an SCR system (including all material costs i.e. reactor system and first catalyst charge, NH₃ dosage and storage, piping and instrumentation, engineering and construction costs) for a flue-gas flow of 100 000 Nm³ are EUR 1 - 3 million for gas firing and between EUR 3 – 6 million for liquid fuel firing. For existing installations, the possible location of the catalyst bed is often constrained by space limitations, which will lead to additional retrofitting costs.

The installation of two SCR units were studied in 2007 at the API refinery (Italy) with the objective of reducing NOₓ emissions from gas furnaces: one at the thermal cracking unit, for an estimated investment cost (ammonia system, compressor, design and installation) of EUR 2.2 million and the other one at the pipestill furnaces, for EUR 3 million. Both SCR had designed performances of 85 – 87 % NOₓ abatement (from average 120 mg/Nm³ with current low Noₓ burners to 15 mg/Nm³) and a flue-gas flow around 55 000 Nm³/h. The project was not accomplished.

Operation costs comprise costs of energy, NH₃ and catalyst replacement. Specific costs for NH₃ and the catalyst charge are of the order of EUR 250 per tonne NH₃ respectively EUR 1 per Nm³ of flue-gas when firing gas and EUR 1.5 per Nm³ of flue-gas when firing oil (see Table 4.83).

Table 4.83: Cost range of an SCR treatment in function of the flue-gas flow

<table>
<thead>
<tr>
<th>Abatement technique</th>
<th>Plant size range</th>
<th>Approximate capital cost (in EUR million installed)</th>
<th>Approximate operating cost per year (EUR million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCR</td>
<td>Flue-gas flows 150 000 Nm³/h</td>
<td>5 – 8</td>
<td>0.87 (costs are mainly for ammonia)</td>
</tr>
<tr>
<td></td>
<td>650 000 Nm³/h</td>
<td>13 – 23</td>
<td></td>
</tr>
</tbody>
</table>

N.B: They are battery limit costs based on 1998 prices and include such items such as equipment, licensing fees, foundations, construction and commissioning. They are an in order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact on costs. In some cases, these factors might be expected to increase the costs by some 50 %.

Table 4.84 gives cost effectiveness of the use of SCR under different conditions:

Table 4.84: Data on the cost effectiveness of SCR retrofitting for various refining units

<table>
<thead>
<tr>
<th>SCR</th>
<th>Cost effectiveness in EUR/tonne NOₓ removed (includes capital charge of 15 %)</th>
</tr>
</thead>
</table>
| Fired Heaters and boilers firing refinery blend gas                | 8 300 – 9 800  
|                                                                    | 12 000  
|                                                                    | 4 200 – 9 000  |
| Boilers firing residual fuel oil                                    | 5 000 – 8 000  
|                                                                    | 4 500 – 10 200  |
| Gas turbines firing natural or refinery blend gas                  | 1 700 – 8 000  
| Fluid catalytic cracking units                                    | 2 800 – 3 300  |

N.B: Details on the conditions are given in Annex IV.

Driving force for implementation
Reduction To reduce NOₓ emissions.

Example plants
SCR has been applied to FCC off-gases, gas turbines, process boilers and process heaters. SCR It has been applied successfully on a large variety of applications: coal and oil-fired power
plants, waste incineration plants, diesel and gas engines, gas turbine plants, steam boilers and refinery furnaces (such us naphtha reformers, steam reformers, crude and vacuum distillations units, thermal cracking and hydroprocessing units) and FCC plants. Some examples are shown in Figure 4.10. Less There has been less experience is available with flue-gas from firing high-
sulphur residual oil.

SCR is used extensively on power plants in Japan, Germany, Austria and on gas turbine plants in the Netherlands, and in California in the USA. SCR are also widely used in waste incineration plants. To date, SCR has been successfully applied worldwide in refinery processes as power plants and the FCCs. For example, at refineries in Japan, SCR applications are common. In European refineries, more than 6 applications have been found (Austria, the Netherlands and Sweden).

Reference literature
[302, UBA Germany, 2000], [211, Ecker, 1999], [118, VROM, 1999], [257, Gilbert, 2000], [175, Constructors, 1998], [181, HP, 1998], [115, CONCAWE, 1999], [268, TWG, 2001] [ 77, REF TWG 2010 ] [ 105, EPA 2002 ].

4.25.4 Particulates

Particulate Matter (PM) emissions from refinery units entail particles present in the flue-gas from furnaces, particularly soot, catalyst fines emitted from FCC regeneration units and other catalyst-based processes, from the handling of coke and coke fines and ash generated during the incineration of sludges. Particulates generated in the refinery contain metals. Then, Therefore, a reduction in the particulate content reduces the metal emissions from the refinery. The particles may range in size from large molecules, measuring a few tenths of a nanometer, to the coarse dusts arising from the attrition of catalyst. Distinction is usually made between aerosols, <1 - 3 µm, and larger dust particles. The avoidance of fine particulates (PM<sub>10</sub>) is particularly important for health reasons.

The available dust removal techniques can be subdivided into dry and wet techniques or a combination of the two. The usually usual techniques applied at refineries applied techniques for dust emission reduction are briefly discussed below. The main dusting processes dry techniques are include cyclones, electrofilters and filtration including cyclones, electrostatic precipitators and bag filters. Some wet techniques such as scrubbers may also be used mainly as finishing treatment. More information can be found in the CWW BREF [ 6, EC 2003 ]. See also Section 4.25.8 for information on the SNO<sub>x</sub> combined technique

4.25.4.1 Cyclones

Description
The principle of cyclone separation is based on centrifugal force, whereby the particle is separated from the carrier gas. More information can be found in the waste gas BREF [312, EIPPCB, 2001]. Data on application of cyclones to FCC units is available in Section 4.5.9.1.

Achieved environmental benefits
Cyclones are used to reduce dust concentrations in the 100 - 500 mg/Nm<sup>3</sup> range. A novel cyclone design, called the rotating particulate separator (RPS), is able to effectively remove particles of >1 µm; this design, however, has a limited capacity compared to the conventional cyclone. Third cyclones achieve a 90 % reduction of particulate emissions (100 - 400 mg/Nm<sup>3</sup>). Modern multicyclones used as third-stage cyclones achieve an 80 % reduction of particulate emissions to about 50 mg/m<sup>3</sup>. Particulate concentrations below 50 mg/Nm<sup>3</sup> are only achievable in combination with specific catalysts.
**Cross-media effects**
By nature, cyclones are efficient for bigger larger particulates but do not separate and retain the finest part of emitted dust. Furthermore, a reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem.

**Operational data**
Cyclones can be designed for high temperature and pressure operation. Dust collection equipment is normally simple to operate and is fully automated. For the dry separation, no utilities are needed. For dust removal normally no additives are used. Sometimes the collected dust needs rewetting to avoid the spreading of dust during handling.

**Applicability**
Multi-cyclones as employed in FCC units, cokers are not able to remove fine particulate matter \((\text{PM}_{10} = \text{dust} < 10 \, \mu \text{m})\) and therefore they are mainly used as a pre-separation step.

**Driving force for implementation**
Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalytic fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

**Example plants**
In refineries, multi-cyclones and ESPs are employed, often together with ESPs, in FCC and RCC heavy oil and residue cracker units.

**Reference literature**
[250, Winter, 2000], [118, VROM, 1999].

### 4.25.4.2 Electrostatic precipitator Electrofilters or (ESP)

**Description**
The basic principle of operation for electrostatic precipitators (Electrostatic precipitator – ESP or electrofilter) is simple. Flowing gas is ionised as it passes between a high-voltage electrode and an earthed (grounded) electrode. The dust particles become charged in the electric field that is generated and are attracted to the earthed electrode. The precipitated dust is removed from the electrodes mechanically, usually by vibration force (dry ESP), or by washing in so called ‘wet electrofilters’ water wash (wet ESP).

**Achieved environmental benefits**
ESP are capable of collecting bulk quantities of dust including very fine particles \(<2 \, \mu \text{m}\) at high efficiencies. ESPs can achieve values of \(<10 - 50 \, \text{mg/Nm}^3\) (95 % reduction or higher with higher inlet concentrations only). However, a penetration ‘window’ exists in the submicron (0.1 – 1 \, \mu \text{m}) size range where the collection efficiency lowers.

**Cross-media effects**
A high voltage in an ESP introduces a new safety risk in refineries. A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emission problem to a waste problem. Electricity consumption, dust disposal, and in some cases ammonia emissions. In addition the high voltage in an ESP introduces a new hazard in refineries. For some installations, ammonia may be injected to improve ESP performance. For these installations, ammonia emissions result from ammonia slip through the ESP. The dust collected in an ESP requires disposal if a useful outlet is not found.
Chapter 5

Operational data
An ESP uses some electricity. For dust removal, normally no additives are used. Sometimes the collected dust needs rewetting to prevent the spreading of dust during handling.

Applicability
The application of ESPs can be found in FCC units, FGD processes, power plants and incinerators. It may not be applicable for some particulates with high electric resistance. They typically can be installed in new and existing plants.

Economics
Operating costs are in the order of EUR 0.5 to 10 per 1000 Nm\(^3\) treated flue gas. Some recent examples of ESP costs for FCC units are available in Section 4.5.9.2. Generally inclusion of fines disposal costs are not included and need to be taken into account for the total cost. gives figures 2.5 – 3 times higher than the ones specified in the above table Table 4.85 and 10 times higher the operating cost.

Table 4.85: Cost data for electrostatic precipitators – To be updated

<table>
<thead>
<tr>
<th>Abatement technique</th>
<th>Plant size range</th>
<th>Approximate capital cost (in EUR million installed)</th>
<th>Approximate operating cost per year (in EUR million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic precipitator</td>
<td>Flue-gas flows</td>
<td>1.9</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>150 000 Nm(^3)/h</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650 000 Nm(^3)/h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.B: They are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, construction and commissioning. They are an in order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact on costs. In some cases, these factors might be expected to increase the costs by some 50%.

Driving force for implementation
Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
In refineries, multi-cyclones and ESPs are employed in FCC units and in heavy oil and residue cracker units.

Reference literature

4.25.4.3 Filtration

Description
Fabric and solid bundle blow-back filters (see also Section 4.5.9.3.)

Achieved environmental benefits
Fabric and solid bundle blow-back filters can achieve values less than 5 mg/Nm\(^3\). They are more efficient than cyclones and ESPs on the finest particulates. Solid bundle filters can allow a filtration guaranteed for particulates above a minimal granulometry of 0.8 – 1 \(\mu\)m.

Cross-media effects
As for all other dry separation techniques, a reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emissions problem to a waste problem. In the case of conventional fabric bundles, filter material life is limited (1 - 2 years) and may add create a
disposal problem. In the case of solid ceramic/alloy bundles, the lifetime is much longer but bundles may need a chemical cleaning from time to time if an eventual progressive increase of the pressure drop due to plugging is experienced, generating another issue of waste elimination.

Operational data
Dust collection equipment is normally simple to operate and is fully automated. For the dry separation, only limited utilities are needed.

Applicability
Fabric filters are effective, except in applications with sticky dust or at of temperatures of over 240 ºC. Depending on the flow rate design parameters, they can reach significant volumes and space needs.

Solid bundle filters are much more compact, and can resist much higher temperatures, up to 800 ºC depending on the metallurgy of the bundles constituent.

Filters are typically used for the cleaning of flue-gases with an output volume of <50000 Nm³/h, even if they are also used for the treatment of much higher flow rates in the metallurgy. They are well adapted for processes likely to deliver variable flue-gas flows and dust concentrations.

Driving force for implementation
Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors and turbo expanders. Toxic and other hazardous substances (e.g. coke fines and heavy-metal containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Reference literature
[250, Winter, 2000], [118, VROM, 1999].

4.25.4.4 Wet scrubbers

Description
In wet scrubbing, the dust is removed by counter-current washing with a liquid, usually water, and the solids are removed as slurry. Venturi and orifice scrubbers are simple forms of wet scrubbers. The electro dynamic venturi (EDV) washer is a recent development which reduces the dust emission to 5 mg/Nm³. The technique combines venturi with electrostatic dust separation. EDV is sometimes reported to be used in the flue-gas treatment of combustion installations and incinerators. More information is available in the CWW WI BREF [EC 2003]. [82, COM 2006].

Achieved environmental benefits
Particles sizes down to 0.5 µm can be removed in well designed scrubbers. A hypothetical curve (US-EPA) illustrating particle size and collection efficiency for wet scrubber is shown in Figure 4.41. Wet scrubbers reduce between 85 - 95 % of the particulates and can achieve values of particulate concentration of <30 - 60 mg/Nm³. In addition to solids removal, wet scrubbers can be used to simultaneously cool the gas and neutralise any corrosive constituents. The collecting efficiency can be improved by the use of plates or packings at the expense of a higher-pressure drop.
Cross-media effects
A reduction of the environmental impact is best achieved if a useful outlet is found for the collected solid dust material. Dust collection is essentially a shift of an air emissions problem to a waste problem. Cross-media issues related to water also need to be considered. Scrubbers for dust removal may also be effective for SO₂ reduction. Wet scrubbing requires pumping energy as well as water and alkali.

Operational data
Dust collection equipment is normally simple to operate and is fully automated. Wet scrubbing requires pumping energy as well as water and alkali.

Applicability
Spray towers have a low pressure drop but are not suitable for removing particles below 10 µm. Venturi and packed bed washers have been installed for sludge incinerators.

Economics
Operating costs are in the order of EUR 0.5 to 10 per 1000 Nm³ treated flue-gas.

Driving force for implementation
Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Toxic and other hazardous substances (e.g. coke fines and heavy metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
Some FCC units are equipped with scrubbers.

Reference literature
[250, Winter, 2000], [118, VROM, 1999].
4.25.4.5 Washers Other wet techniques

Description
Centrifugal washers combine the cyclone principle and an intensive contact with water, like the venturi washer.

Achieved environmental benefits
Dust emissions can be reduced to 50 mg/Nm³ and below if very large quantities of water are used such as in an absorber used in for a two-stage scrubbing system. Depending on the operating pressure and the construction, dust emissions can be reduced below 10 mg/Nm³ with centrifugal washers or venturi washers.

Operational data
Dust collection equipment is normally simple to operate and is fully automated. Venturi washers need to be operated at sufficient pressure and at full water saturation of the gas phase to reduce the dust emission.

Applicability
Wash columns, or absorbers with packing are applied in various processes.

Driving force for implementation
Process gas streams must often be cleaned up to prevent the contamination of catalysts or products, and to avoid damage to equipment, such as to compressors. Toxic and other hazardous substances (e.g. coke fines and heavy-metal-containing catalyst fines) have to be removed to comply with air-pollution regulations and for reasons of hygiene.

Example plants
Venturi washers: they are mostly applied for removal of a combination of dust, acidic components (HCl and HF) at for example cokers and incinerators. For SO₂ removal scrubbing at pH ± 6 with caustic or lime is necessary.

Reference literature
[118, VROM, 1999]

4.25.4.6 Combination of particulate abatement techniques

Often a combination of techniques is applied, such as cyclone/ESP, ESP/venturi/wash column or a cyclone/venturi/absorber leading to a >99 % dust elimination.

4.25.5 Techniques for sulphur recovery and SO₂ abatement

Sulphur is an inherent component of crude oil. Part of this sulphur leaves the refinery in its products, part of it is emitted to the atmosphere (already described in all the processes) and part of it is recovered by some processes located in the refinery for this purpose (more information about the sulphur split in a refinery can be found in Section 1.4.1). Sulphur is an environmental issue that cannot be addressed in an integrated manner if the sulphur coming out with the products is not considered. In other words, decreasing emissions from a refinery may result in the production of fuels (products) that may later be burned in a way that is not environmentally efficient, thereby jeopardising the environmental effort made by refineries. This is addressed trough other type of both European and national legislations.

Because it is such an integrated issue, proper sulphur management (see Annex VI) should also consider other topics that may not be within the objectives of this document. For example, a global environmental impact assessment of sulphur dioxide emissions should consider items listed below:
Chapter 5

1. Atmospheric emissions from processes generating SO\textsubscript{x} (furnaces, boilers, FCC, etc.). These issues are in fact included in this document in each of the process sections.

2. Atmospheric emissions from sulphur recovery units or of gases containing sulphur in an H\textsubscript{2}S form before incineration. This category of sulphur is normally recovered, as shown in Section 4.23.5.2.

3. Atmospheric emissions generated by sulphur contained in products for which more stringent specifications already exist, such as gasolines, gasoils, etc. These emissions cannot be considered here because they do not fall within the scope of IED legislation, but they should be considered as part of an integrated approach.

4. Atmospheric emissions generated by products with less stringent specifications (bunkers, coke, heavy fuel oil). Typically, these products (heavy residues) contain high quantities of sulphur. If they are not used in a proper way from an environmental point of view, the emissions can jeopardise the integrated approach to reducing sulphur emissions from the refinery sector. Another threat to this integrated approach is the exporting of these products to countries with less environmental control.

5. Sulphur contained in non-fuel products such as bitumen or lubricants is typically not identified as a problem.

In principle refiners have the following options given below and combinations thereof. In order to reduce the SO\textsubscript{2} emissions of the refinery level the operator needs to set a global strategy and may have recourse to combinations of the following types of actions:

- selection of fuels and raw material with low sulphur content such as:
  - To increasing the use of non-sulphur-containing gas (LPG, natural gas, etc.) discussed in see Section 4.10 on Energy systems.
  - To using low-sulphur crudes as discussed in (Sections 4.10)

- increase the efficiency of the various abatement techniques such as:
  - SRU as discussed in (see Section 4.25.5.2);
  - To lower the sulphur content of the fuels used Fuel gas desulphurisation (reduce the H\textsubscript{2}S reduction content in the refinery fuel gas with amine treating (see Section 4.25.5.1) or other techniques for FGD (see Section 4.25.5.4 and Sections 4.5.10 implementation to FCC units and 4.10.6 implementation to the energy system), gasification of heavy fuels (see Section 4.10), hydrotreatment of fuels in (see Section 4.13.2).
  - To apply end-of-pipe techniques to capture the SO\textsubscript{2} from the fumes (namely flue-gas desulphurisation – FGD), as these techniques are the ones discussed in Section 4.25.5.4 and have been considered in Sections 4.5.10 (implementation to FCC units) and 4.10.6 (implementation to the energy system).

- Reduce SO\textsubscript{2} emissions from typically small contributors when they become a significant part of the total emissions. For example, in the case of a gas firing refinery, the overall picture of the sulphur emissions changes because small contributors in liquid-fired refineries become significant.

In this section, only these processes dealing with the recovery of sulphur is going to be are considered. Between 17 to and 53 \% (on average 36 \%) of the sulphur is recovered in European refineries. H\textsubscript{2}S formed at various processes such as hydrotreating, cracking, and coking in a refinery, finally ends up as contaminant in refinery fuel gas and treat other gas streams. In addition to H\textsubscript{2}S, these gases also contain NH\textsubscript{3} and to a lesser extent CO\textsubscript{2} and traces of COS/CS\textsubscript{2}. H\textsubscript{2}S removal from these gases is achieved by extraction with an amine solvent. After regeneration of the solvent, the H\textsubscript{2}S is released and sent to a sulphur recovery unit (SRU). See also Section 4.25.8 for information on the SNO\textsubscript{X} combined technique.
4.25.5.1 Amine treating

Description
Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulphide. This is typically accomplished by dissolving the hydrogen sulphide in a chemical solvent (absorption). Solvents most commonly used are amines. Dry adsorbents such as molecular sieves, activated carbon, iron sponge and zinc oxide may also be used. In the amine solvent processes, amine solvent is pumped to an absorption tower where the gases are contacted and hydrogen sulphide is dissolved in the solution. The fuel gases are removed for use as fuel in the process furnaces or other refinery operations. The amine-hydrogen sulphide solution is then heated and steam stripped to remove the hydrogen sulphide gas. In Figure 4.42 a simplified process flow diagram of an amine treating unit is shown.

Figure 4.42: Simplified process flow diagram of an amine treating unit

The main solvents used are MEA (monoethanolamine), DEA (diethanolamine), DGA (diglycolamine), DIPA (disopropanolamine), MDEA (methyl diethanolamine) and a number of proprietary formulations comprising mixtures of amines with various additives. One important issue concerning the selection of the type of amine is the selectivity concerning H2S and CO2.

1. MEA has had a widespread use, as it is inexpensive and highly reactive. However, it is irreversibly degraded by impurities such as COS, CS2 and O2, and therefore is not recommended to use when gases from cracking units are present.
2. DEA is more expensive than MEA but is resistant to degradation by COS and CS2 and has obtained a widespread use.
3. DGA is also resistant to degradation by COS and CS2 but is more expensive than DEA and has the disadvantage of also absorbing high hydrocarbon solubility into the solution.
4. DIPA, which is used in the ADIP process, licensed by Shell. It can be used for selective H2S removal in the presence of CO2 and is also effective in removing COS and CS2.
5. MDEA is nowadays most widely used, MDEA and has a similar characteristic as to DIPA, i.e. it has a high selectivity to H2S, but not to CO2. As MDEA is used as a 40 - 50 % solution (activated MDEA) in water, this also has the potential energy savings. Because of the low selectivity for CO2 absorption, DIPA and MDEA are very suitable for use in ClausTail gas amine absorbers, as these do not tend to recycle CO2 over the Claus unit. MDEA is applied as a single solvent or as in proprietary formulation comprising mixtures.
Achieved environmental benefits

Sulphur is removed from a number of refinery process off-gas streams (sour gas or acid gas) in order to meet the SO\(_x\) emission limits of the applicable regulation and to recover saleable elemental sulphur. The amine-treating unit produces two streams for further use/processing in downstream units:

- the treated gas stream can usually contain between 20 and 200 mg/Nm\(^3\) H\(_2\)S (H\(_2\)S content depends on absorber operating pressure; at only 3.5 bar H\(_2\)S level is 80–140. At higher pressures as 20 bars the H\(_2\)S level is around 20) with a residual H\(_2\)S content normally in the ranges displayed in Table 4.86;
- and the concentrated H\(_2\)S/acid gas stream, which is routed to the SRU for sulphur recovery (discussed in Section 4.25.5.2).

<table>
<thead>
<tr>
<th>Residual (\text{H}_2\text{S}) concentration achievable in the refinery fuel gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical amine-scrubbing pressure</td>
</tr>
<tr>
<td>(absolute bar)</td>
</tr>
<tr>
<td>3.5</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>50</td>
</tr>
</tbody>
</table>

Source: CONCAWE 4/09 report-Daily average values

Cross-media effects

They are summarised in Table 4.87. Energy consumption must also be considered (see above).

<table>
<thead>
<tr>
<th>Overview of the cross-media effects related to some aspects of amine treating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
</tr>
<tr>
<td>Effluent: amine blowdown</td>
</tr>
<tr>
<td>Waste 1: Amine filter cleaning residue</td>
</tr>
<tr>
<td>Waste 2: Saturated activated carbon from skid-mounted unit</td>
</tr>
</tbody>
</table>

Operational data

The use of selective amines should be considered, e.g. for a stream containing carbon dioxide. Measures should be taken to minimise hydrocarbons entering the sulphur recovery system; operation of regenerator feed drums should be controlled to prevent hydrocarbon accumulation in, and sudden release from, the amine regenerator as this is likely to lead to an emergency shutdown of the SRU.
Utility consumption per tonne of H₂S removed in an amine treating unit is approximately:

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Cooling water (m³/t, ΔT =10 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 – 80</td>
<td>1 500 – 3 000</td>
<td>25 – 35</td>
</tr>
</tbody>
</table>

Usually a fresh solvent make-up rate of 10 - 50 t/yr is required to maintain solvent strength for a 5 Mt/yr refinery.

Amine solutions should be reused wherever possible and where necessary, suitably treated before disposal which should not be to land properly disposed of. Recycling of monoethanoleamine-solutions: corrosive salts, which concentrate during recycling, can be removed via ion exchange or thermal reclaiming techniques. Some proprietary solutions may be biodegradable under suitable conditions.

It is also important also that the amine processes have sufficient capacity to allow for maintenance activities and upsets. This sufficient capacity can be achieved by having redundancy equipment, or by applying load shedding, emergency amine scrubbers or multiple scrubber systems.

**Applicability**

Process off-gas streams from the coker, catalytic cracking units, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulphide mixed with light refinery fuel gases. Emergency H₂S scrubbers are also important.

**Economics**

The cost of upgrading the refinery amine treatment system (2 %) to meet 0.01 to 0.02 % v/v of H₂S in fuel gas is around EUR 3.75 to 4.5 million. This cost is battery limit costs based on 1998 prices and include such items such as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.

**Driving force for implementation**

Reduce the sulphur content of flue-gases.

**Example plant(s)**

Common technology technique used all over the world

**Reference literature**

[118, VROM, 1999], [211, Ecker, 1999], [19a, Irish EPA, 1993], [268, TWG, 2001]

**4.25.5.2 Sulphur recovery units (SRU)**

H₂S-rich gas streams from amine treating units (see section 4.25.5.1) and sour water strippers (see section 4.26.4) are treated in a sulphur recovery unit (SRU) normally which most often consists of a Claus process for bulk sulphur removal and subsequently in a tail gas Clean-up treatment unit (TGU) (see later in this section) for trace remaining H₂S removal. Other components entering the SRU may include NH₃, CO₂ and, to a minor extent, various hydrocarbons.

Add
4.25.5.2.1 Increased efficiency of the Claus Process

Description
The Claus process consists of the partial combustion of the hydrogen-sulphide-rich gas stream (with one-third of the stoichiometric quantity of air) and then reacting the resulting sulphur dioxide and unburned hydrogen sulphide in the presence of an activated alumina catalyst to produce elemental sulphur. As shown in Figure 4.43, the Claus unit then consists of a reaction furnace followed by a series of converters and condensers, where:

- the partial combustion and a part of the sulphur formation \( 2H_2S + 2O_2 \rightarrow SO_2 + S + 2H_2O \) occurs in the primary reactor;
- the main of Claus reaction for sulphur formation \( 2H_2S + SO_2 \rightarrow 3S + 2H_2O \) takes place in the different catalytic converters;
- and liquid elementary sulphur is collected from the various condensers in a common pit, as shown in Figure 4.43.

Side reaction effects also occur that produce carbonyl sulphide (COS) and carbon disulphide (CS₂), which have raised problems in many Claus plant operations because they can not be easily converted to elemental sulphur and carbon dioxide.

The overall capacity of the Claus plants can be increased with the use of oxygen enrichment technologies instead of air (e.g. OxyClaus process). However, this has not had any beneficial effect in the sulphur-recovery efficiency of the Claus plant. The use of this process can increase the unit capacity up to 200 % in existing Claus sulphur-recovery units, or can be an option for a more economical design of new Claus sulphur units.

The techniques given below can be used and retrofitted to existing SRUs for increasing the Claus process efficiency.

- An improved unique burner system and enhanced combustion conditions to reach a minimum temperature of 1350 °C which allows a better destruction of ammonia and mercaptans in the combustion chamber, and a reduction of the Claus catalytic bed plugging by ammonium salts [Questionnaire n° 31].
- High-performance catalysts process (e.g. Selectox), which can be used in combination with the first stage of the Claus unit to promote the oxidation of \( H_2S \) to \( SO_2 \) without the use of a flame. They allow for a significant increase in the sulphur-recovery efficiency.
Achieved environmental benefits

The SRU is characterised by its sulphur-recovery efficiency, calculated as the fraction of sulphur in the feed which is recovered in the liquid sulphur stream routed to the sulphur collection pits. This fraction includes the dissolved H$_2$S (typically 200 – 500 ppm weight) which must be removed from the liquid sulphur at a later stage of the process (see Section 4.25.5.2.4 on sulphur degassing).

The sulphur-recovery efficiency of an SRU closely depends on the number of Claus reactors that are operated in series in the sulphur recovery unit chain, as shown in Table 4.88.

Table 4.88: Sulphur-recovery efficiency of the Claus process SRUs in European sites

<table>
<thead>
<tr>
<th>Number of Claus reactors</th>
<th>Number of datasets</th>
<th>Sulphur recovery efficiency (% H$_2$S converted)</th>
<th>Observed range</th>
<th>Median</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Observed range</td>
<td>Median</td>
<td>Typical</td>
</tr>
<tr>
<td>1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>87</td>
<td>92.4 - 97.8</td>
<td>96.1</td>
<td>94 – 96.95 – 96.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>96.0 - 98.4</td>
<td>97.0</td>
<td>97–98 96.5 – 98</td>
<td></td>
</tr>
</tbody>
</table>

Sources: [36, CONCAWE n°4/09 2009]

Most recent or recently refurbished units have 3 – 4 stage units (including SuperClaus), meaning that they have 3 to 4 sets of converters and condensers.

Furthermore, state-of-the-art oxidation catalysts (e.g. Selectox or Criterion – these types of catalysts are suitable for promoting the Claus reaction) have been used in North American refineries with significant increased efficiency rates reported [25, Pham et al. 2009] specifically:

- from 90 to 97 % at 1st Claus stage level
- from 96 – 97 % to 99.8 – 99.9 % for a full three-stage Claus unit.

Cross-media effects

The reduction of SO$_2$ leads to an increase of the CO$_2$ emission. For example for a 100 t/d sulphur Claus plant, the application of three reactors would lead to an emission of 4.8 tonnes of sulphur per day at a cost of 8.5 tonnes of CO$_2$ per day. Table 4.89 shows indicative estimates of the incremental emission of CO$_2$ which will be associated with the marginal incremental reduction of SO$_2$ achieved for various SRU+TGTU configurations. It is assumed that the low pressure steam generated on the SRU can be fully valorised as energy, which goes against the amine-based TGTU but this does not necessarily reflect real case situations.

Table 4.89: CO$_2$ incremental emissions for the main categories of SRU+TGTU techniques

<table>
<thead>
<tr>
<th>SRU technology</th>
<th>Incremental t CO$_2$ per incremental t SO$_2$ reduced (compared to a base two stage Claus (1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two stage Claus + 3rd stage Claus</td>
<td>0.25</td>
</tr>
<tr>
<td>Two stage Claus + Superclaus</td>
<td>0.25</td>
</tr>
<tr>
<td>Two Stage Claus + Catalytic Oxidation</td>
<td>0.31</td>
</tr>
<tr>
<td>Two stage Claus + sub-dewpoint TGCU</td>
<td>0.55</td>
</tr>
<tr>
<td>Two stage Claus + amine based TGCU</td>
<td>0.75</td>
</tr>
</tbody>
</table>

(1) Based on a 100 t/d SRU fed with 80 % acid gas feed (95 % H$_2$S) and 20 % gas from the sour water stripper (56 % H$_2$S, 43 % NH$_3$).
Operational data

- Feed/air ratio control, temperature control of the furnace, reactors and condensers and good demisting of liquid sulphur, especially from the final condenser exit gas stream are important parameters in obtaining maximum sulphur recovery. Good control and availability is crucial as a technique, to deliver any design targets. In this line, the use of state-of-the-art control and monitoring systems can be seen as an important technique. Use of a tail gas analyser linked to the process control system (feedback control) will aid optimum conversion during all plant operating conditions, including changes to sulphur throughput.

- To have an SRU configuration with sufficient capacity for the H₂S feed to the unit including the sour crude oil to be used is important. The duplication of the SRU capacity is important to consider to obtain low sulphur emissions. This capacity also should consider should also be large enough to allow the scheduled maintenance activity to proceed every two years, without a significant increase of sulphur emissions.

- To have utilisation factors close to 100% increases how efficiently the units are used. These capacity factors should also must also include the impact of major turnaround maintenance.

- Use a good furnace burning-zone design and effective furnace temperature and oxygen control systems where sour water stripper off-gases are a feed stream, because the process must also be designed and operated to complete the destruction of ammonia. Ammonia breakthrough may lead to deposition and blockages of catalyst beds by ammonium salts (e.g. carbonate/sulphate) and these SRUs need to be monitored for evidence avoidance of this.

Typical emissions and utilities necessary in for the a 20 000 t/yr SRU are summarised in next Table 4.90 and Table 4.91 below.

**Table 4.90: Typical impact of a 20 000 t/yr SRU**

<table>
<thead>
<tr>
<th>Type</th>
<th>Source</th>
<th>Flow</th>
<th>Composition min/max</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air emissions:</td>
<td>Incinerator off-gas</td>
<td>0.2 % of the total H₂S-load to the SRU</td>
<td>SO₂: 1500 mg/Nm³ Through presence of NH₃ non-catalytic deNOₓing takes place</td>
<td>Amount of SO₂ released depends on total sulphur production and overall sulphur recovery or conversion</td>
</tr>
<tr>
<td>CO₂, SO₂, NOₓ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid effluents:</td>
<td>Knock-out drum for water in SWS off-gas</td>
<td>0.02 m³/h</td>
<td>H₂S: 50 mg/l; Phenol: 100 mg/l; NH₃: 2000 mg/l</td>
<td>To be treated in the SWS</td>
</tr>
<tr>
<td>Solid waste:</td>
<td>Spent SRU catalyst</td>
<td>Plant specific</td>
<td>Mainly Al₂O₃ depending on the catalyst composition</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.91: Typical utility consumption**

<table>
<thead>
<tr>
<th>Fuel (MJ/t)</th>
<th>Electricity (kWh/t)</th>
<th>Steam produced (kg/t)</th>
<th>Cooling water (m³/t, ΔT=10 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 – 1600</td>
<td>60 – 75</td>
<td>1500 – 2000</td>
<td>0 – 20</td>
</tr>
</tbody>
</table>

In some cases, the SRU needs a pilot flame to co-fire natural or fuel gas when the H₂S concentration is so low that a stable flame cannot be achieved.
Applicability
Fully applicable. The OxyClaus process and other oxygen enrichment technologies increase the plant flexibility, as they allow the treatment of feed gases for a wide H₂S content range of 20 – 100 % (volume). Temporary higher, lower of fluctuating amounts of hydrogen sulphide can be handled by automatic changeover from air to oxygen operation and vice versa. Higher hydrocarbon contents can also be processed, and an almost complete combustion of the ammonia contained in sour water stripper off-gases provided the reaction furnace temperature is above 1350 °C, there is adequate residence time, and a properly designed burner.

Economics

Table 4.92: Cost examples of two typical upgrading projects for an existing 2 two-stage 100 t/d SRU

<table>
<thead>
<tr>
<th>Abatement Upgrading project</th>
<th>Plant size range</th>
<th>Approximate capital cost (EUR million installed)</th>
<th>Approximate operating cost per year (EUR million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upgrade SRU with O₂ enrichment to increase throughput from 100 t/d to 170 t/d (₁)</td>
<td>100 t/d</td>
<td>2.1 – 5.3</td>
<td>1.6 (oxygen consumption)</td>
</tr>
<tr>
<td>Addition of a 3rd stage Claus reactor (₂)</td>
<td>100 t/d</td>
<td>2.0 – 3.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

(₁) There are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, erection, tie-ins to existing plant and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.

(₂) Capacity of the process: 30 000 t/yr of sulphur production. Volume of gas to be treated: 60 million m³/yr. Pollutant initial concentration: 34000 mg SO₂/m³ (1.2 % molar or 2.3 % weight, the rest considered as air) – 1998 prices

Another example of the upgrade of SRU with oxygen enrichment (Oxyclaus)
Economics: For a reference 200 t/d sulphur recovery unit (Claus and tail gas unit) requiring 99.9 % overall sulphur recovery, capital cost savings of $2 – 3 million are achievable with oxygen enrichment as compared to an air only design. Based on typical pipeline oxygen costs of $35 per tonne, even if oxygen enrichment were used 100 % of the time, it would take over 8 years for oxygen costs to equal the incremental capital saving.

Example of the economics of the installation of a third Claus reactor.
Capacity of process: 30000 t/yr sulphur production (sulphur recovery efficiency 91 – 96 % for a two stage unit). Volume of gas: 60 million m³/yr. Pollutant initial concentration: 34000 mg SO₂/m³ (1.2 % molar or 2.3 % weight, rest considered as air). The investment cost to build a new third reactors is between EUR 2 and 3 million and the operating cost around EUR 0.1 million per year.

Driving force for implementation
Reduction of To reduce sulphur emissions.

Example plants
In the market, it exists more than five licensors of this process exist. The Claus process is public domain and virtually applied at any refinery virtually. Two stages Claus process is the most common in Europe. More than 30 35 OxyClaus systems (4 – 270 t/day) are in operation in the world.

Reference literature
4.25.5.2.2 Tail gas treatment units (TGTUs)

Description
Current methods for removing sulphur from the hydrogen sulphide gas streams are typically a combination of two processes: the Claus process (See Section above 4.24.5.2.1) followed by a tail gas clean-up or treatment unit. Since the Claus process by itself removes only about 94 – 96 % (2-two stages) or 96 – 98 % (three stages) of the hydrogen sulphide in the gas stream, the TGTU processes are often must be used to further recover sulphur.

More than 20 A large number of processes for TGTUs have been developed in order to enhance the recovery of sulphur compounds from natural gas and/or refinery sources. The most frequently operated TGTU processes (see Figure 3.35 in Section 3.25.2) can be broadly divided into the following four categories according to the principles applied:

The first and third categories can further be divided in sub-categories depending on the sulphur recovery method used. It should be noted that a strict distinction between dry beds and liquid scrubbing processes may become uneasy as some arrangement combine the capabilities of both types of processes. Some processes belonging to the four groups above mentioned are further explained below; this list is not intended to be exhaustive.

- direct oxidation to sulphur
- continuation of the Claus reaction
- oxidation to SO2 and recovering sulphur from SO2
- reduction to H2S and recovering sulphur from this H2S

I. Direct oxidation to sulphur Dry bed catalytic direct oxidation processes where the main process step is achieved on a solid catalyst. In particular: Two paths have been followed within this group: a) Extend Claus reaction on a solid bed, b) Oxidise sulphur compounds to SO2 prior to absorption, or reaction:

a. PRO-Claus stands for Parson RedOx Claus. It is a dry catalytic process that contains three additional stages (one reduction and two oxidations). In the 1st stage, a highly-selective catalyst developed by the US Lawrence Berkeley National Laboratory is used for the reduction of SO2 to elemental sulphur. In the 2nd stage, the remaining H2S is then oxidised to also form elemental sulphur under the presence of another highly specialised catalyst. The remainder is sent to a thermal oxidiser.

b. The SUPERCLAUS process is by far the most commonly used in this category. It is based on two principles: a) operating the Claus plant with excess H2S to minimise the SO2 content in the Claus tail gas, and to simplify and make more flexible the air ratio control, and b) to oxidise selectively the remaining H2S in the Claus tail gas by means of a specific catalyst which efficiently converts the remaining H2S in the presence of water vapour and excess oxygen into elemental sulphur only. This reaction takes place in a specific converter (an oxidation reactor), downstream of a two or three reactors in the traditional Claus unit. The catalyst used is an alumina-based catalyst coated with iron oxide and chromium oxide layers.

II Continuation of the Claus reaction Liquid phase sub-dewpoint processes, consisting of extending where the Claus reaction is extended over a bed of standard Claus catalysts or a non-volatile organic solvent under sub-dewpoint conditions in the liquid phase. In particular:

a. The CBA (cold bed absorption) process is very similar to the Sulfreen process except in the fact that the CBA process uses a hot process stream indigenous to the Claus process to accomplish regeneration of the sulphur loaded catalyst bed. The hot process stream is part of the effluent of the first Claus reactor. Several configurations are available depending on the number of Claus converters.
b. The CLAUSPOL is a process where the tail gas is put into contact with a solvent (polyethylene glycol) and the reaction of H$_2$S and SO$_2$ is catalysed by a dissolved catalyst. (sodium salt of an inorganic acid, e.g. sodium salicylate) which is a solvent for H$_2$S and SO$_2$, but not for liquid sulphur. The Claus reaction can therefore proceed at low temperatures (120 °C) and is shifted further to the right as the produced sulphur is removed from the reaction medium, as it is not soluble and separates.

c. The SULFREEN process is a dry-bed, sub-dew point absorption process based on the extension of the Claus reaction, i.e. catalytic oxidation of H$_2$S to S. This basically consists of two (occasionally three for large capacities) Sulfreen reactors in series with the Claus reactors. Activated alumina is used as a catalyst. Regeneration is needed since the sulphur accumulates on the catalyst decreasing its activity. Sulphur from the hot regeneration stream is condensed in a dedicated condenser. Several variations are used:

- The HYDROSULFREEN adds a conversion step upstream of the first sulfreen reactor, to perform the hydrolysis of COS and CS$_2$ to H$_2$S with the help of an activated titanium oxide Claus catalyst in order to adjust more precisely the H$_2$S/SO$_2$ ratio more precisely. The Claus reaction takes place in the HydroSulfreen reactor and produced sulphur is condensed in a dedicated condenser
- The DOXOSULFREEN concept is based on two ideas: the upstream units are operated to get a slight excess of H$_2$S, compared to the quantity necessary to maintain the Claus ratio, therefore a nearly total SO$_2$ conversion takes place on the conventional Sulfreen catalyst; then the remaining H$_2$S is directly oxidised to elemental sulphur
- The MAXISULF is a simplified sulfreen process, including basically a one-stage (one absorber, one regenerator) unit with an open regeneration loop. The regeneration gas is fed to the absorber together with the Claus tail gas.

III. Reduction to H$_2$S and recovering sulphur from this H$_2$S-amine scrubbing processes

There are two main categories, H$_2$S scrubbing processes and SO$_2$ scrubbing processes. In the most commonly applied configurations, H$_2$S or SO$_2$ are recycled this process takes place after catalytic conversion of all sulphur species to H$_2$S, with amine scrubbing processes for recycling to the upstream Claus Unit. In particular:

a. The FLEXSORB process has been developed by Exxon Mobil as an alternative to the MDEA amine treatment process. It uses a variety of solvents specifically designed to absorb and convert H$_2$S and organic sulphur to elemental sulphur. A specific solution is used to remove H$_2$S from the tail gas after conversion of sulphur compounds to H$_2$S has been performed. The absorbed H$_2$S is recycled back to the Claus plant for sulphur recovery.

b. The HCR (High Claus Ratio) process is directly derived from the SCOT and designed by Siirtec Nigi.

c. The RAR (Reduction, absorption, recycle) is a MDEA reductive treatment allowing the use of plain MDEA or specifically-formulated MDEA-based solutions. It is was originally designed for Claus tail gas treatment, but can also be applied to other, more complex, hydrogen sulphide-containing gas streams which are either too diluted or too contaminated for direct processing through normal Claus units.

d. The SCOT (H$_2$S Scrubbing) process is by far the most widely applied in this category. SCOT stands for Shell Claus off-gas treatment. As shown in Figure 4.44, the concept underlying H$_2$S scrubbing processes are:

- hydrogenation and hydrolysis of all sulphur compounds to H$_2$S passing it through a cobalt-molybdenum catalyst at 300 °C with the addition of a reducing gas;
- absorption of H$_2$S by an amine solution (generic amine or specialty amine)
- regeneration of the amine solution and recycle of the H$_2$S to the upfront Claus reaction furnace.
e. The BSR/MDEA process family where, in a first step, sulphur compounds are catalytically (cobalt-molybdate based) converted into H\textsubscript{2}S through an hydrogenation/hydrolysis reaction at high temperature (300 – 400°C). In a second step, H\textsubscript{2}S is removed by chemical solution (amines process).

- with other recovery process such as

Several licensors currently propose variations on the H\textsubscript{2}S scrubbing process, using solvents available on the market place, or in some instances proprietary solvents.

\section*{IV Liquid redox processes process. Liquid phase oxidation to absorb H2S used for a direct H2S absorption. In particular: There are two types of processes} 

\paragraph{a. The BEAVEN process.} where the hydrogen sulphide in the relatively low concentration gas stream from the Claus process can be almost completely removed by absorption in a quinone solution. The dissolved hydrogen sulphide is oxidised to form a mixture of elemental sulphur and hydroquinone. The solution is injected with air or oxygen to oxidise the hydroquinone back to quinone. The solution is then filtered or centrifuged to remove the sulphur and the quinone is then reused. The Beaven process is also effective in removing small amounts of sulphur dioxide, carbonyl sulphide, and carbon disulphide that are not affected by the Claus process. These compounds are first converted to hydrogen sulphide at elevated temperatures in a cobalt molybdate catalyst prior to being fed to the Beaven unit.

The \textit{LO-CAT} process is a liquid redox system that uses a chelated iron solution to convert H\textsubscript{2}S. Absorption and regeneration are performed in a single vessel divided into two sections: the centerwell and the outer space where aeration with air is performed. The purpose of the centerwell is to separate the sulphite ions from air in order to minimise by-product formation (e.g. thiosulphate). The difference in aeration (and therefore of density) between the centerwell and the outer space give sufficient driving force for solution circulation between the absorption and the regeneration zones without the need of a specific pump. The last type of processing scheme is called the ‘aerobic unit’ and is used to treat air contaminated with H\textsubscript{2}S. All reactions take place in the same vessel, at the expense of increased by-product formation, but with the advantage of a reduced capital cost.

\textbf{MODOP or BSR/SELECTOX} processes use direct oxidation after reduction to H\textsubscript{2}S.

\section*{IV Oxydation to SO\textsubscript{2} and recovering sulphur from SO\textsubscript{2} by process such as the following (for more details see also Section 4.25.5.4 on Sulphur dioxide abatement techniques)
a. **WELLMAN LORD** process where sodium sulphite reacts with SO$_2$ in the flue-gases forming sodium bisulphite. The concentrated solution is collected and evaporated for regeneration. In the regeneration step, using steam, the sodium bisulphite is broken down, to release the sodium sulphite, to be recycled back to the flue-gases.

b. **CLINTOX** process where the sulphur species are burnt to be converted to SO$_2$, which is then absorbed in a physical solvent, stripped from the solvent and returned to the Claus plant to replace oxygen in the air and contribute to increase the sulphur capacity of the Claus furnace unit.

c. **LABSORB** process based on an absorption/regeneration cycle including the use of an absorbing solution containing caustic soda and phosphoric acid to capture SO$_2$ as sodium bisulphite.

c. The SO$_2$ abatement from the Claus plant is a process that uses a physical scrubbing mechanism to remove SO$_2$ from the incinerated tail gas of a Claus plant. The recovered SO$_2$ is recycled to the inlet of the Claus plant unit. Question for TWG: is this 'mechanical scrubbing' something specific to be mentioned here or are we talking about scrubbing techniques already referred to in the document (in particular in 4.25.5.2.3)?

**Achieved environmental benefits**

Tail gas treatment units increase the overall recovery of H$_2$S and decreasing decrease the sulphur emissions from the refinery. For example, if a refinery has a 100 t/d SRU, with a two-stage Claus reactor, this SRU will emit around 5 t/d (1750 t/yr) of sulphur, being most probably one of the major SO$_2$ emission sources of the site. If a tail gas clean-up process is included in such a refinery, the emissions of sulphur may be reduced to 0.5 t/d, representing a reduction of 90% of the sulphur emissions from the sulphur recovery units, and saving 1575 t/yr of SO$_2$.

Table 4.93 shows the expected overall sulphur recovery yield, the resulting additional recovered sulphur and the dry basis sulphur emission (in the form of SO$_2$ species) after incineration, of a selection of the tail gas treatments considered in this section.
Table 4.93: Expected performances of SRU for various TGTU processes and configurations

<table>
<thead>
<tr>
<th>Added process:</th>
<th>Expected sulphur recovery yield (1)</th>
<th>Expected additional sulphur recovered (2)</th>
<th>Expected SO2 emissions after incineration (dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base (two-stage Claus)</td>
<td>95 – 96.5</td>
<td>96.01</td>
<td>13 652</td>
</tr>
<tr>
<td>+ 3rd stage Claus</td>
<td>96.5 – 98</td>
<td>1.00 – 2.00</td>
<td>9 000</td>
</tr>
<tr>
<td>+ 3rd stage Claus and Selectox</td>
<td>99.8 – 99.9</td>
<td>NA</td>
<td>22 – 28 ppmv (0 % O2)</td>
</tr>
<tr>
<td>+ Beavon</td>
<td>99 – 99.9</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>+ CBA (cold bed absorption)</td>
<td>99 – 99.50</td>
<td>3.65</td>
<td>1 726</td>
</tr>
<tr>
<td>+ Clauspol (3)</td>
<td>NA</td>
<td>3.75</td>
<td>1 382</td>
</tr>
<tr>
<td>+ Flexsorb</td>
<td>99.9</td>
<td>4.16</td>
<td>NA</td>
</tr>
<tr>
<td>+ LO-CAT II (4)</td>
<td>99.99</td>
<td>4.10</td>
<td>242</td>
</tr>
<tr>
<td>+ RAR</td>
<td>99.94</td>
<td>4.10</td>
<td>242</td>
</tr>
<tr>
<td>+ SCOT</td>
<td>99.5 - 99.99</td>
<td>NA</td>
<td>13 ppmv SO2, 0.1 ppmv H2S</td>
</tr>
<tr>
<td>+ Superclaus</td>
<td>99.64 – 99.93 (5)</td>
<td>2.77</td>
<td>4 631</td>
</tr>
<tr>
<td>+ Maxisulf</td>
<td>98.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ 3rd stage Claus + Maxisulf</td>
<td>99.0 – 99.5</td>
<td></td>
<td>2 000</td>
</tr>
<tr>
<td>+ Sulfreen</td>
<td>99.42 – 99.0 – 99.2</td>
<td>3.56</td>
<td>2 010</td>
</tr>
<tr>
<td>+ 3rd stage Claus + Sulfreen</td>
<td>99.2 – 99.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ DoxoSulfreen (6)</td>
<td>99.88</td>
<td>4.04</td>
<td>414</td>
</tr>
<tr>
<td>+ HydroSulfreen (7)</td>
<td>99.67 – 99.5 – 99.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ SO2 abatement</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) For the whole treatment train (SRU + TGTU).
(2) From the TGTU step only.
(3) Sulfreen reactors and hydrolysis section.
(4) Sulfreen reactors, hydrolysis section and DoxoSulfreen reactors.
(5) As LO-CAT II tail gas cannot be incinerated, sulphur is in the form of H2S species.
(6) See present section under applicability information.
(7) Upper level is guaranteed by the provider – lower level from HP 1998.
(8) Upper level requires COS and CS2 to be hydrolysed down to 300 ppmv of S through the catalytic stage.
(9) No incineration step required for this technique.

Cross-media effects
As already mentioned, the reduction of SO2 leads to an increase in the CO2 emissions (see Table 4.89 in Section 4.25.5.2.1). For instance the application of a tailing gas treatment would lead to a SO2 reduction of 96 % (if compared with the three reactor option), however at an increase for in CO2 of 110 %. For example for a 100 t/d sulphur Claus plant with three reactors, the application of a TGTU would reduce the emissions of SO2 to 0.1 t/d but at a price of increasing the CO2 emissions to 18 t/d.

Table 4.94: Cross-media effects associated with some of the TGTU

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow</th>
<th>Composition min/max</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effluents</td>
<td>Sour water from quench column for SRU off-gas</td>
<td>H2S: 50 mg/l; Phenol: 100 mg/l; NH3: 2 000 mg/l</td>
<td>To be treated in the SWS</td>
</tr>
<tr>
<td>Waste: SCOT</td>
<td>Spent TGTU catalyst</td>
<td>Regeneration and disposal 20 – 100 t/yr</td>
<td>Spent Claus catalyst is pyrophoric and needs purging with N2</td>
</tr>
</tbody>
</table>
Operational data
Good control and availability is crucial as a technique, to deliver any design targets.
The actual sulphur recovery yield from the SRU associated with its TGTU depends on the feed
composition, the catalyst run time (for catalytic oxidation TGTU), and the progressive fouling
during the operation run. Table 4.95 is based on actual sulphur recovery measurements taken in
more than 40 European refineries between 2004 and 2008. Measurement campaigns have been
carried out during a limited period of time (1 – 2 days) at various given times in the catalyst
cycle, then reflecting a wide range of unit operating conditions and catalyst lifetime situations.

Table 4.95: Expected range of recovery efficiencies for main TGTU categories

<table>
<thead>
<tr>
<th>TGTU categories</th>
<th>Number of datasets</th>
<th>% Recovery efficiency (% H2S converted) as daily average for the whole SRU+TGTU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed range</td>
<td>Median</td>
</tr>
<tr>
<td>Catalytic direct oxidation</td>
<td>26</td>
<td>95.5 – 99.3</td>
</tr>
<tr>
<td>Sub-dew point</td>
<td>16</td>
<td>98.0 – 99.8</td>
</tr>
<tr>
<td>Amine-based</td>
<td>19</td>
<td>98.7 – 99.99</td>
</tr>
</tbody>
</table>

Source: CONCAWE

Another set of site data recovery efficiency has been made available for 8 SRU from five
German refineries and is showed in Table 4.96.

Table 4.96: Range of sulphur recovery measured after TGTU in 5 German refineries

<table>
<thead>
<tr>
<th>Refinery/installation number</th>
<th>TGTU process</th>
<th>Sulphur capacity (t/d)</th>
<th>Operating grade (t/d)</th>
<th>Measured % recovery efficiency (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref 2 – Claus 1</td>
<td>Incineration</td>
<td>34.7</td>
<td>18.1</td>
<td>98</td>
</tr>
<tr>
<td>Ref 3 – Claus 1</td>
<td>Incineration</td>
<td>16</td>
<td>Na</td>
<td>98</td>
</tr>
<tr>
<td>Ref 3 – Claus 2</td>
<td>Incineration</td>
<td>17</td>
<td>Na</td>
<td>98</td>
</tr>
<tr>
<td>Ref 1 – Claus 1</td>
<td>Sulfreen</td>
<td>55</td>
<td>26.4</td>
<td>99.6</td>
</tr>
<tr>
<td>Ref 4 – Claus 2</td>
<td>Sulfreen</td>
<td>69.9</td>
<td>55.2</td>
<td>99.5</td>
</tr>
<tr>
<td>Ref 1 – Claus 2</td>
<td>SCOT</td>
<td>170</td>
<td>Na</td>
<td>99.9</td>
</tr>
<tr>
<td>Ref 5 – Claus 1</td>
<td>SCOT</td>
<td>128.6</td>
<td>80</td>
<td>99.7</td>
</tr>
<tr>
<td>Ref 2 – Claus 2</td>
<td>Clauspol II</td>
<td>33.6</td>
<td>10.2</td>
<td>98.8</td>
</tr>
</tbody>
</table>

(*) Estimated as efficiency = 1-SER (sulphur emission ratio) - Daily average.

Applicability
TGTUs are applicable to both new and existing plants. Capacities range from 2 to more
than 2000 tonnes of sulphur per day from the combined Claus/tail gas treatment units. However,
areas occupied by such units can be significant. As an example, a new TGT unit (540 t/day gas
treatment capacity – 10 t/day sulphur recovery) including a third Claus stage and a Sulfreen
Maxisulf TGT was built in 2008 on a French site and occupies a 960 m² area.

Significant difficulties have been reported concerning the poor utilisation factor of 2 Clauspol
units (0 – 25 %), due to side reactions favouring the formation of sodium salt precipitates and
highly corrosive components (native SO 3 and NH4HSO4). Furthermore, shut downs for cleaning
and maintenance generate large quantities of heavily polluted waste waters contaminated with
sulphur and PE.G (DCO 200 g/l).

Economics
The cost of the SRU depends strongly on the type of tail gas treatment. Following several tables
show some examples of economics of the TGTUs.
The estimate of operating costs, including sulphur produced, utilities and chemicals as well as
additional manpower expense are given in the following Table 4.97:
Chapter 5

Table 4.97: Operating costs of some TGTU units

<table>
<thead>
<tr>
<th>Abatement</th>
<th>Recovery yield objective</th>
<th>Plant size range</th>
<th>Approximate capital cost (EUR million installed)</th>
<th>Approximate operating cost (EUR per year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional 3rd stage Claus + TGTU (Maxisulf) to give &gt;98.5 %</td>
<td>540 t/d</td>
<td>31 (2008)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>New Sulfreen TGT (Sulfreen) on existing SRU to give 99.5 %</td>
<td>175 t/d</td>
<td>18 (2006)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Additional 3rd stage Claus + TGTU (Superclaus) to give &gt;98.5 %</td>
<td>210 t/d</td>
<td>26 (2005)</td>
<td>600 000 (2005)</td>
<td></td>
</tr>
<tr>
<td>New SRU including TGTU to give &gt;99 % S recovery (1998)</td>
<td>50 t/d</td>
<td>12</td>
<td>New SRU operating cost approximately equal to existing costs; NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 t/d</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 t/d</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tail gas treatment unit to improve existing SRU recovery to 99 % (1998)</td>
<td>50 t/d</td>
<td>1.6</td>
<td>Operating cost relatively low; NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 t/d</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 t/d</td>
<td>2.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tail gas treatment unit to improve SRU existing recovery to 99.8 % (1998)</td>
<td>50 t/d</td>
<td>3.5</td>
<td>Operating cost relatively low; NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 t/d</td>
<td>4.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 t/d</td>
<td>6.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NB: They There are battery limit costs based on 1998 prices and include such items as including equipment, licencing fees, foundations, erection, tie-ins to existing plant and commissioning. They are an in order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plants could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %.

Usual practice is to relate the capital cost of the TGCU to the one of the up front Claus unit. The following table gives estimate of such ratio, for a 100 t/d Claus unit (including catalyst) in a refinery environment.
Table 4.99: Relative capital cost for the upgrading of an existing 100 t/d SRU

<table>
<thead>
<tr>
<th>SRU upgrading technology option</th>
<th>Relative capital cost in 2009 ((^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-stage Claus</td>
<td>100</td>
</tr>
<tr>
<td>Two-stage Claus + 3rd stage Claus</td>
<td>109</td>
</tr>
<tr>
<td>Two-stage Claus + sub-dewpoint TGT (e.g. CBA)</td>
<td>120</td>
</tr>
<tr>
<td>Two-Stage Claus + catalytic direct oxidation TGT (e.g. SuperClaus)</td>
<td>130</td>
</tr>
<tr>
<td>Two-stage Claus + advanced Sulfreen TGT</td>
<td>140</td>
</tr>
<tr>
<td>Two-stage Claus + amine-based TGT</td>
<td>194</td>
</tr>
</tbody>
</table>

\(^1\) Based on a 100 t/d SRU fed with 80% acid gas feed (95% H\(_2\)S) and 20% gas from the sour water stripper (56% H\(_2\)S, 43% NH\(_3\)).

The reference to the upstream sulphur unit is indicative and corresponds to the way this kind of comparison is usually presented in the literature. This comparison should be taken with care when comparing with other studies, as the capital cost of a sulphur unit may vary greatly around fluctuate +/- 30%.

A particular example of the cost of a three-stage Claus for the upgrading of a two-stage Claus plant with a 3rd stage Claus + TGTU Superclaus process is shown in the following Table 4.100.

Note for TWG: Table proposed to delete
Another example of the cost of a TGTU unit reports that for a Clauspol unit treating a typical Claus unit tail gas, combined production of 100 tonnes of sulphur per day (ISBL, 1998 Gulf Coast location), the investment (excluding engineering and license fees) came up to 3 million USD.

Operating costs for two Hydrosulfreen units of total maximum capacity 15.2 t/h (440 00 Nm³/h) are estimated in Table 4.101. Costs are given for an utilisation factor of 82 % for each unit.

<table>
<thead>
<tr>
<th>Catalyst and utility consumption</th>
<th>Consumption</th>
<th>Cost (EUR/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts and activated carbon</td>
<td>5 year lifetime basis (assumed)</td>
<td>9.13</td>
</tr>
<tr>
<td>Fuel gas to incinerator</td>
<td>0.68 t/h</td>
<td>222.4</td>
</tr>
<tr>
<td>Combustion air to incinerator</td>
<td>17.32 t/h</td>
<td>10.8</td>
</tr>
<tr>
<td>LP Steam</td>
<td>0.70 t/h</td>
<td>11.5</td>
</tr>
<tr>
<td>Boiler feed water</td>
<td>8.81 t/h</td>
<td>26.4</td>
</tr>
<tr>
<td>Air + nitrogen</td>
<td>50 + 25 m³/h</td>
<td>1.7</td>
</tr>
<tr>
<td>Electricity</td>
<td>330 kW installed</td>
<td>12.4</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td><strong>294.33</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Utility production</th>
<th>Consumption</th>
<th>Cost (EUR/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP Steam production</td>
<td>8.39 t/h</td>
<td>-143.7</td>
</tr>
<tr>
<td>LLP Steam production</td>
<td>2.90 t/h</td>
<td>-41.8</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td><strong>-185.5</strong></td>
</tr>
<tr>
<td><strong>Net cost:</strong></td>
<td></td>
<td><strong>109</strong></td>
</tr>
</tbody>
</table>

Finally, the following Table 4.102 shows specific cost data for SO₂ abatement under the assumptions outlined in Annex IV. Proposed to delete.

<table>
<thead>
<tr>
<th>Name of the technique</th>
<th>EUR/tonne SO₂ abated (¹)</th>
<th>EUR/tonne SO₂ abated (²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd Claus reactor</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Standalone SCOT</td>
<td>321 – 538</td>
<td>32</td>
</tr>
<tr>
<td>Cascade SCOT regenerator</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>SuperClaus</td>
<td>155 – 228</td>
<td>32 – 161</td>
</tr>
<tr>
<td>3rd Stage Claus + SuperClaus</td>
<td>32 – 160</td>
<td></td>
</tr>
<tr>
<td>Clauspol</td>
<td>198 – 330</td>
<td>32</td>
</tr>
<tr>
<td>Sulfreen</td>
<td>174 – 288</td>
<td>32 – 160</td>
</tr>
<tr>
<td>HydroSulfreen</td>
<td>253 – 417</td>
<td>32 – 160</td>
</tr>
<tr>
<td>CBA/AMOCO cold real absorption</td>
<td>169 – 300</td>
<td>NA</td>
</tr>
</tbody>
</table>

(¹) [346, France, 2001]. Bases for calculation in Annex IV.
(²) [115, CONCAWE, 1999] Bases for calculation in Annex IV.
Driving force for implementation
Reduction of sulphur emissions and recovery of sulphur.

Example plants

Table 4.103: Approximate number of commercial installations in the world

<table>
<thead>
<tr>
<th>Technique</th>
<th>Number of installations all over the world</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beaven</td>
<td>More than &gt;150 installations</td>
</tr>
<tr>
<td>Clauspol</td>
<td>More than &gt;50 units</td>
</tr>
<tr>
<td>Sulfreen/hydrosulfreen</td>
<td>More than &gt;150 units in operation</td>
</tr>
<tr>
<td>Superclaus</td>
<td>More than &gt;70 commercial plants</td>
</tr>
</tbody>
</table>

Reference literature
[195, The world refining association, 1999], [112, Foster Wheeler Energy, 1999], [309, Kerkhof, 2000], [257, Gilbert, 2000], [115, CONCAWE, 1999], [107, Janson, 1999], [181, HP, 1998], [114, Ademe, 1999], [45a, Sema and Sofres, 1991], [346, France, 2001] [ 33, Lurgi 2005 ] [ 36, CONCAWE no/4/09 2009 ] [ Questionnaire no/11, 14, 18, 28 (specific attachments) ] [ 107, Kohl 1997 ].

4.25.5.2.3 Wet gas scrubbing of the SRU offgas

Other techniques than additional tail gas treatment of the SRU offgas may be used such as the SNOxi (a combined NOx and SOx abatement technique-see Section 4.25.8) or scrubber techniques as presented in this section.

Description
As an alternative to an additional TGTU, some refineries have installed non-regenerative or regenerative scrubbers in order to abate sulphur emissions from their SRUs.

- Non regenerative scrubbers used for this application can be of any type such as a jet ejector venturi, high energy venturi, magnesium-based or seawater scrubber. One type of scrubber that has been applied is a two-stage caustic scrubbers (DynaWave) with specific technologies for the enhancement of quenching and frothing effects in order to maximise the turbulent mixing and the gas absorption. These scrubbers are equipped with a droplet removal section and, optionally, brinks mist eliminators.
- The regenerative scrubber used for this application was based on the Cansolv technology, also used for the desulphurisation of waste gas in sulphuric acid plants and power plant boilers.

Achieved environmental benefits
The sulphur removal efficiency of the DynaWave non-regenerative scrubber is reported to be above 99.99 % for this particular application. In related refineries, SRU sulphur recovery/removal efficiency reaches a 99.95 % rate.

Cross media effects
Water, reagent and energy consumption.

Economics and operational data
Not available.

Applicability
A DynaWave non-regenerative caustic scrubber has been in operation in two US refineries since 2004, and in another one since 2006.
A regenerative scrubber was installed during four months in 2006, and then it was shut down due to technical problems (independent from the Cansolv section).

**Examples plants**
Sinclair Oil Corporation-Sinclair, Casper and Tula refineries (US)
BP-Cherry Point refinery (US)

**Driving force for implementation**
TGTU as described in Section 4.25.5.2.2 produce a concentrated H\(_2\)S stream which shall be recycled to the front end of SRU units for treatment. While this approach typically increases the sulphur-recovery efficiency, it also tends to reduce the amount of fresh acid gas that can be potentially treated by the Claus process. Therefore, non-regenerative scrubbing is preferred for undersized or critical capacity SRUs, in order to avoid the SRU capacity decrease generated by the additional TGTU recovery capacity. With this approach, there is no concentrated H\(_2\)S stream recycled to the front end of the SRU.

### 4.25.5.2.4 Stored sulphur degassing storage

**Description**
In order to reduce the emissions of H\(_2\)S from the storage and transport of liquid sulphur, and to improve the product quality, the amount of H\(_2\)S and polysulphides in the sulphur can be reduced to <10 ppm by oxidation or treatment with a suitable additive.

**Achieved environmental benefits**
Lowering H\(_2\)S concentrations in the gaseous phase of sulphur tanks reduces air releases during handling and improves operator safety. There are a number of techniques for sulphur degassing (SNEA or Aquisulf, Shell, Exxon and Texasgulf). With the Aquisulf degassing process for example, residual H\(_2\)S in liquid sulphur can be brought down to less than 10 mg/kg ppm by weight.

**Cross-media effects**
None in particular. Moreover, the reduction of H\(_2\)S in the liquid sulphur has a positive effect on the solidity of formed sulphur, and particularly on sulphur slate strength.

**Operational data**
Not available.

**Applicability**
Fully applicable.

**Driving force for implementation**
To reduce operational hazards (toxicity and explosivity) and environmental nuisances due to H\(_2\)S desorbed and accumulated in the gaseous phase of fixed and transportation tanks.

**Examples plants**
There were more than 50 Aquisulf sulphur degassing units for capacities 20 – 3 600 t/day in operation at the end of 2005.

**Reference literature**
[268, TWG, 2001] [33, Lurgi 2005]
Chapter 4

4.25.5.3 Hydrogen sulphide and light mercaptan removal

Description
The system works with a fixed-bed or batch-type granular reactant where iron compounds (Fe₃O₄ and Fe₂O₃) react with H₂S to form FeS₂ (pyrite).

Achieved environmental benefits
Processes for odour and low emission control features.

Applicability
Applications to waste water systems, land oil tanker vent, oil storage and transportation, and bitumen plants. Final polishing for odour control may be required to remove higher mercaptans and dimethyl disulfide.

Driving force for implementation
Processes for odour and emission control features.

Example plants
More than 1000 applications worldwide. Processes are licensed under SulfaTreat name.

Reference literature
[181, HP, 1998]

4.25.5.4 Sulphur dioxide abatement techniques

In refinery flue-gases or waste gases, SO₂ may have unabated concentration levels of 1500 – 7500 mg/m³. Flue-gas desulphurisation (FGD) is a technique by which SO₂ is removed from flue gases or other waste gases. FGD processes often involve an alkaline sorbent which captures SO₂ and transforms it to a solid product. Various FGD methods exist with varying SO₂ removal efficiencies. The FGD market is dominated by lost solvent processes, in particular by the so-called wet lime/limestone process followed by spray dry scrubbers and the application of sorbent injection. Recent years also show the development of solvent/catalyst regenerative processes, in which the absorbing/concentrating medium is regenerated and reused. More information can be found in the CWW BREF [6, EC 2003].

Systems either of the regenerative type or the non-regenerative type exist for SO₂ removal only, and also for the simultaneous removal of dust and NOₓ. Most of these combined processes are still in the development phase, but some are commercially available already. They are or may become competitive with systems consisting of separate units for SO₂ elimination (i.e. wet scrubbers) and NOₓ removal (i.e. SCR).

NB: Some relevant parts of the text have been moved from Section 4.10.6.2.

Description of the non-regenerative processes
Additive injection (AI) and spray dry absorber (SD) are scrubbing processes that remove SO₂ according to the same principle as Wet Limestone Scrubber (WS). They involve a reaction with a Ca-based sorbent however, without the complicating requirements for producing a high-grade gypsum by-product (i.e. prescrubbing and oxidising). The by-product is a mixture of sulphites, sulphates and fly ash for which there are few or no useful applications. The AI process provides moderate SO₂ removal at relatively low sulphur loads. A dry sorbent is injected into the furnace. The sorbent used is limestone or hydrated lime (for small boilers, more active sodium bicarbonate (NaHCO₃) is injected in the flue-gas duct).

Seawater scrubbing uses the natural alkaline – bicarbonates – of seawater to remove SO₂. This implies a potential for high removal efficiencies. The discharge will contain sulphate and chlorine ions - which are a natural constituent of seawater.
Walther (WA) is a process where SO\textsubscript{2} is absorbed by spray injection of aqueous ammonia, yielding ammonium sulphite. The sulphite is subsequently oxidised to sulphate. The ammonium salt solution from the scrubbing section is concentrated in an evaporation unit and granulated. The end-product is a marketable fertiliser.

Wet limestone scrubber (WS) systems have been very much improved recently and have become less complex than the earlier systems. Generally a limestone/water slurry is used as the sorbent. Gypsum is produced by oxidation (aeration) in the sump of the absorber.

**Description of the regenerative processes**

Regenerative processes have been widely applied in refineries for SO\textsubscript{2} abatement. The first was the Wellmann-Lord, then the Cansolv and the Labsorb process.

Following text has been moved from below in same section

**Wellman Lord (WL)** is the most widely used regenerative process. The process is based on sodium sulphite/bisulphite equilibrium. The first step is the absorption of SO\textsubscript{2} in a sodium sulphite aqueous solution, forming sodium bisulphite (NaHSO\textsubscript{3}). By decreasing the temperature, sodium bisulphite is then converted into sodium pyrosulphite (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{5}) which precipitates, due to its much lower solubility:

\[
\text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]

\[
2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{S}_2\text{O}_5 \downarrow + \text{H}_2\text{O}
\]

By reheating this precipitate with water, the reversed reactions can occur, allowing the regeneration of SO\textsubscript{2}, and the recycling of sodium sulphite into the process.

\[
\text{Na}_2\text{S}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]

\[
2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O}
\]

In US oil refineries where this process is operated for the treatment of SRU tail gases, the regenerated SO\textsubscript{2} is sent back to the sulphur recovery unit.

**Cansolv** is regenerative technique which uses an aqueous amine solution to achieve selective absorption of sulphur dioxide. The gas to be treated is first saturated in a water prescrubber and is then contacted with the amine solution. The amine solution is regenerated by steam stripping. A slipstream of the amine needs to be purified to prevent the accumulation of salts. The scrubbing by-product is water-saturated SO\textsubscript{2} gas recovered by steam stripping.
**Figure 4.45**  Process overview of Cansolv regenerative scrubbing process

*Labsorb* is a regenerative scrubbing process which utilises an aqueous solution of sodium phosphate as a scrubbing buffer for the absorption of SO₂. It generates a >90% concentrated SO₂ stream that can be used as feed to an SRU or a sulphuric acid plant. The scrubbing solution is regenerated using low-pressure steam, which virtually eliminates the discharge of liquid effluents from the scrubber. Figure 4.46 below shows a simplified flow diagram of the Labsorb process, which consists of a first SO₂ absorption stage, followed by final regeneration stage.

At the absorption stage, the flue-gas is dedusted and quenched in a prescrubber fed with low pH water recirculated from a make-up reservoir, before entering into the absorbing tower itself. The absorbing agent used is a patented solution containing soda (NaOH) and phosphoric acid (H₃PO₄).

The regeneration involves a steam-heated evaporator for the release of the SO₂ absorbed in the reach solvent, followed by a gas/liquid separation, a stripper and a condenser. Concentrated SO₂ saturated in water leaves the condenser as recovered product, while water from the condenser returns to the process after steam stripping. A waste heat boiler before the unit can be used to produce low-pressure steam for buffer generation, further reducing the total operating costs.
$\text{SNQ}_x$ is a regenerative catalytic process which combines a pre-dedusting stage, followed by a WSA (described immediately below) and an SCR stage whose purpose is to abate air pollutants in a combined technique. It reaches a high removal of $\text{SO}_2$, $\text{NO}_x$ and particulates. For more information see Section 4.25.8.

Waste gas sulphuric acid (WSA) is a solid-catalytic process allowing the condensation and the recuperation of concentrated sulphuric acid. It is well adapted to wet gases (no pre-drying stage required) but implies a careful pre-dedusting phase (max. 1 mg/Nm³) in order to keep the specific potassium-vanadium catalyst performances. Gas temperature should be adjusted to 400 – 420 °C. $\text{SO}_2$ reacts with residual $\text{O}_2$ and forms $\text{SO}_3$ which then combines with residual water vapour and is condensed at concentrations of 93 – 98 %. Adjustment of water and air concentrations is eventually requested prior to the catalytic converter.

Achieved environmental benefits

<table>
<thead>
<tr>
<th>General overview</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name of technique</strong></td>
</tr>
</tbody>
</table>

| Efficiency | 90 % (500 mg/Nm³) | 95 – 98 % (250 – 100 mg/Nm³) |

Example: Capacity of the process: 5Mt/yr, 120 000 t/yr liquid refinery fuels, 180 000 t/yr refinery fuel gas. Volume of the flue-gas 1.68 x 10^9 Nm³/yr.
Pollutant: Initial concentration: 5 000 mg/Nm³ (for liquid refinery fuels with 3 % S). Total quantity 8 400 t/yr.

Detailed reported % reduction by technique
Table 4.104: Achieved environmental benefits of various desulphurisation processes

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>SO₂ reduction (%)</th>
<th>Other benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive injection (AI) alone</td>
<td>50 – 70</td>
<td>Like with wet scrubbing, the SD system combines an effective removal of SO₂, SO₃, chlorine and fluorine (&gt;90 % on sulphur compounds, 70 – 90 % on the for halides)</td>
</tr>
<tr>
<td>AI and spray dry absorber (SD)</td>
<td>&gt;92</td>
<td>The acidic effluent from the absorber flows by gravity to a water treatment plant. Here, air is blown into the water to convert the absorbed SO₂ into dissolved sulphate and to saturate the seawater with oxygen (COD treating). The pH is adjusted back to neutral partly by added seawater and partly by aeration. The effluent from the treatment plant is discharged directly back to the sea</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>85 – 98</td>
<td>The acidic effluent from the absorber flows by gravity to a water treatment plant. Here, air is blown into the water to convert the absorbed SO₂ into dissolved sulphate and to saturate the seawater with oxygen (COD treating). The pH is adjusted back to neutral partly by added seawater and partly by aeration. The effluent from the treatment plant is discharged directly back to the sea</td>
</tr>
<tr>
<td>Walther</td>
<td>&gt;88</td>
<td>Product that can be sold as fertiliser. This product has to meet certain criteria (especially heavy-metal content)</td>
</tr>
<tr>
<td>Wet Limestone Scrubber</td>
<td>92 – 98</td>
<td>If the chlorine content is low, this system produces a very low amount of waste water</td>
</tr>
<tr>
<td>Wellman Lord</td>
<td>98 (100 mg/Nm³)</td>
<td>Sulphur can finally be recovered as a product. For the removal of SO₃, ammonia is injected, which leads to the formation of ammonium sulphate. Ammonium sulphate may be used as a fertiliser under certain circumstances (especially heavy-metal content)</td>
</tr>
<tr>
<td>Cansolv</td>
<td>98</td>
<td>Sulphur by-products have a high purity and can be recovered for chemical</td>
</tr>
<tr>
<td>Labsorb</td>
<td>&gt;85</td>
<td>No external flue-gas cooling required upstream of the process. Very low chemical consumption. No residues produced other than limited amounts of sodium sulphate salts, which correspond to less than 1 % of waste mass generated by a wet limestone scrubber. The recovered SO₂ has a high purity (&gt;90 %) and can be recovered as a chemical or treated for sulphur recovery in existing SRUs</td>
</tr>
<tr>
<td>SNOₓ</td>
<td>98</td>
<td>Up to 96 % for nitrogen oxides. Particulates are essentially completely removed</td>
</tr>
<tr>
<td>WSA</td>
<td>99 (¹)</td>
<td>NOₓ are also reduced in a certain extent when used within the SNOₓ process. In combination with an SCR, simultaneous reduction of 95 % NOₓ can be obtained</td>
</tr>
</tbody>
</table>

(¹) Note for TWG: values transferred from the old Section 4.5.10.6 from UBA Austria, to be updated as necessary. No further information available.
Cross-media effects
Specific data on energy consumption for the various desulphurisation techniques (affecting CO₂ emissions) are not detailed. General information, can be found in the LCP BREF [7, EC 2006].

Table 4.105: Cross-media effects of various desulphurisation processes

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>Cross-media effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive injection (AI) and Spray dry absorber (SD)</td>
<td>As the by-product generated by these techniques contains unreacted lime, it requires conditioning before disposal.</td>
</tr>
<tr>
<td>AI process</td>
<td>The disposal of the by-product requires similar care as for SD.</td>
</tr>
<tr>
<td>Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption</td>
<td>These techniques generally produce a lot of waste.</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>Some fly-ash with associated heavy metals and organic substances is transferred to the seawater.</td>
</tr>
<tr>
<td>Walther</td>
<td>The process does not generate solid by-products or liquid waste. If particulates with possible content of metals are present in the flue-gas they appear together with the product.</td>
</tr>
<tr>
<td>Wet limestone scrubber</td>
<td>Waste water generated by the gypsum dewatering process contains suspended solids and trace elements (metals, chlorides) and is to be treated by sedimentation, flocculation and filter pressing. The filter cake is disposed of by landfill and the purified water is drained to sewer.</td>
</tr>
<tr>
<td>Wellman-Lord</td>
<td>Dust: NH₃ is injected to prevent the formation of SO₃. Therefore up to 80 % of the ash consists of (NH₄)₂SO₄, which can be used as a fertiliser or as a basic material for NH₃ production. Waste water from the prescrubber has a sour water quality with a pH of around 2 and must be neutralised and stripped. The purified water may still contain up to 100 mg/l ammonia, but most often, values are in the range of 10 to 50 mg/l.</td>
</tr>
<tr>
<td>Cansolv</td>
<td>No significant side-effect or disadvantage identified so far.</td>
</tr>
<tr>
<td>Labsorb</td>
<td>See Section 4.25.8.</td>
</tr>
<tr>
<td>SNOx</td>
<td>See Section 4.25.8.</td>
</tr>
<tr>
<td>WSA</td>
<td>See Section 4.25.8.</td>
</tr>
</tbody>
</table>
## Operational data

### Table 4.106: Operational data of various desulphurisation processes

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>Operation data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive injection (AI) and Spray dry absorber (SD)</td>
<td>Being a dry process, corrosion conditions are less severe than in the case with WS. Hence, the scrubber is usually made of (uncoated) carbon steel. Calcium chlorides may yet prompt acid corrosion as they precipitate on the absorber walls and attract moisture. Recycling by-product with wet flue-gas to the sorbent make-up tank may suffer from plugging; regular cleaning is required.</td>
</tr>
<tr>
<td>AI process</td>
<td>The system is less effective as regards the removal of HCl, hence the fuel should not have a higher Cl content than approximately 0.3% for corrosion prevention.</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>The process offers simplicity, thus high availability.</td>
</tr>
<tr>
<td>Wet Limestone Scrubber</td>
<td>Chloride aerosols and a visible waste gas plume may occur when fuels are used with a high chlorine content. Aerosol formation can be mitigated by increased liquid to gas ratio in the absorber and the use of multiple tube filters. Deposits of sulphates can be removed by blowing with hot flue-gas or by water washing. NOx has no influence on the FGD process as it does not react with ammonia.</td>
</tr>
<tr>
<td>Wellman-Lord</td>
<td>Operational aspects include problems with respect to fouling, corrosion and erosion. In the prescrubber deposits of ammonium sulphate can occur. The evaporator is susceptible to wear by the abrasive salt slurry, corrosion during shutdowns and mechanical strains related to the high speed centrifuge.</td>
</tr>
<tr>
<td>Cansolv</td>
<td>To be updated</td>
</tr>
<tr>
<td>Labsorb</td>
<td>In the refining sector, this process has been applied so far only to FCC units. See related operational data in Section 4.5.10.6.</td>
</tr>
<tr>
<td>SNOx</td>
<td>See Section 4.25.8</td>
</tr>
<tr>
<td>WSA</td>
<td>To be updated</td>
</tr>
</tbody>
</table>
Chapter 5

Applicability
As a general consideration, it is to be noted that the plot space requirement for scrubbers and ancillary equipment is an important factor for retrofit applications because of their size.

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption</td>
<td>Typically used when the amount of SO₂ to recover are small because they produce waste, for example in small specialised refineries or small natural gas plants</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>Because particulates (may be containing including their heavy metals content) are transferred to the seawater, an efficient particulate abatement technique is necessary previous the seawater scrubbing</td>
</tr>
<tr>
<td>Walther</td>
<td>Not suitable for fuels with an elevated sulphur content, as these result in increased ammonia slip due to the formation of ammonia sulphates. The sulphates are objectionable because of corrosion and aerosol emissions</td>
</tr>
<tr>
<td>Wellman Lord</td>
<td>Despite its excellent emission profile, the process complexity has been an obstruction to discouraged wide-spread application</td>
</tr>
<tr>
<td>Cansolv</td>
<td>In the refining sector, successfully applied to FCC units (see Section 4.5.10.6.)</td>
</tr>
<tr>
<td>Ladsorb</td>
<td>This technique allows significant savings in operating costs compared to non-regenerative wet scrubbing processes, due to the very small consumption of chemicals used in the absorbing buffer make-up, and the intrinsic energy efficiency. See figures for FCC unit applications in Section 4.5.10.6.</td>
</tr>
<tr>
<td>SNOₓ - WSA</td>
<td>See Section 4.25.8.</td>
</tr>
</tbody>
</table>

Economics

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>Economics</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI process</td>
<td>35 – 55 EUR/kWh (unit size: 75 – 300 MWth). Annual operating cost roughly equal capital cost</td>
</tr>
<tr>
<td>Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption</td>
<td>They are typically very cheap compared with other FGD techniques</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>Low capital costs and low operating costs (no bulk chemicals required, although sometimes magnesium hydroxide is used to enhance the alkalinity)</td>
</tr>
<tr>
<td>Wet Limestone Scrubber</td>
<td>75 – 180 EUR/kWh (unit size: 75 – 300 MWth). Annual operating cost roughly equal capital cost. Capital cost: EUR 10 – 20 million. Operating cost EUR 1.6 – 4 million/yr (costs are mainly for caustic soda). Flue-gas flows 200 000 to 650 000 Nm³/h. There are battery limit costs based on 1998 prices and include such items as equipment, licence fees, foundations, construction and commissioning. They are an order of magnitude only. Site-specific factors such as layout, available space and necessary modifications to existing plant could have a significant impact. In some cases these factors might be expected to increase the costs by some 50 %</td>
</tr>
<tr>
<td>Wellman Lord</td>
<td>The investment cost is estimated to be USD 50 million for a unit to handle a flue-gas flow rate of 500 000 Nm³/h and a SO₂ concentration of 0.8 %. The cost includes licensing fees, engineering, equipment delivery, construction, commissioning and start-up services.</td>
</tr>
<tr>
<td>Cansolv</td>
<td>This technique allows significant savings in operating costs compared to non-regenerative wet scrubbing processes, due to the very small consumption of chemicals used in the absorbing buffer make-up, and the intrinsic energy efficiency. See figures for FCC unit applications in Section 4.5.10.6.</td>
</tr>
<tr>
<td>Labsorb</td>
<td>See Section 4.25.8.</td>
</tr>
</tbody>
</table>
Chapter 4

Driving force for implementation

Table 4.109: Overview of the driving forces for the implementation of various desulphurisation processes

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>Driving force for implementation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption</td>
<td>Abatement of small quantities of SO₂</td>
</tr>
<tr>
<td>WellmanLord</td>
<td>The process characteristics can suit the needs of particular industrial sites using high-sulphur fuels (in the US, Japan and Austria the process has been used in refineries)</td>
</tr>
<tr>
<td>Cansolv</td>
<td></td>
</tr>
<tr>
<td>Labsorb</td>
<td>Generates a by-product ready for conversion into liquid SO₂, sulphuric acid or elemental sulphur. Suits the need of industrial processes generating highly sulphurised flue-gases, as SRU tail gases and FCCs, but also fossil-fired boilers and roaster gases from non-ferrous smelters.</td>
</tr>
</tbody>
</table>

Example plants

Table 4.110: Example plants where desulphurisation processes have been implemented

<table>
<thead>
<tr>
<th>Desulphurisation technique</th>
<th>Example plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron chelating, solvent extraction, NaOH adsorption or molecular adsorption</td>
<td>Applied in some small refineries and natural gas plants</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>The process has been applied to some extent (in 1994: 2500 MW/47 units), also used for smelters, refineries and oil-firing (at 3 % S).</td>
</tr>
<tr>
<td>Wet limestone wscrubber</td>
<td>Operational experience with WS is highly satisfactory, demonstrated by high availability. This system is widely applied in power plants. In Germany, e.g. the Mider refinery uses a wet lime desulphurisation process after the three oil-fired heaters of the power plant. The fuels used in this plant are vacuum residues, visbreaker residues and FCC slurry (text from Section 4.10.6.2)</td>
</tr>
<tr>
<td>WellmanLord</td>
<td>More than 40 systems have been applied over the world e.g. on FCCs</td>
</tr>
<tr>
<td>Cansolv</td>
<td>Cansolv units are used on Sulphur plants, FCC and cokers</td>
</tr>
<tr>
<td>SNO₃ - WSA</td>
<td>More than 25 units have been successfully installed worldwide. Applied in particular in AGIP refinery in Gela (Italy, 1997) and in OMV AG refinery in Schwechat (Austria, 2007) in a big oil refinery for power plants burning high sulphur pet coke and residues.</td>
</tr>
</tbody>
</table>

Reference literature
Chapter 5

4.25.6 VOC abatement techniques

When transferring liquids to vessels at atmospheric pressure, the existing mixture of vapour and gas (often air, but also inert) in the receiving vessel is often emitted to atmosphere. Such loading operation is recognised as having an impact on the environment due to the presence of VOC, a precursor of ozone. Directive 94/63/EC (EU Stage 1) requires that Member States prescribe the specific emission reduction measures as laid down in the annexes of the Directive. Also the application of VRUs to prevent escape of these vapours to the atmosphere is specified in the Directive. VRUs aim for recovery of hydrocarbons for reuse. In some cases recovery is not economic, and preference will be given to vapour destruction units (VDU). A more general term covering both options is vapour handling systems (VHS).

4.25.6.1 Establishment of a Programme Techniques for the prevention, detection and control of VOC fugitive emissions

NB: Description of these techniques (in particular LDAR) has been redrafted streamlining with other BREF recent redactions (CWW+LVOC) for improving structure and consistency.

4.25.6.1.1 Techniques to prevent/reduce VOC emissions related to process and plant design

Description
Techniques to reduce diffuse VOC emissions can be considered during both phases of the design:

- process design
- plant design.

Process design
Process design conditions (e.g. temperature, pressure, vapour pressure of the process fluid) can influence the level of diffuse emissions. However, they are not chosen independently, they depend on other parameters (e.g. catalyst activity, availability of utilities such as cooling air, water or steam) as well. In some operations with lower operating temperatures and pressures where the fluid vapour pressures are lower, diffuse emissions are relatively lower [121, ESA 2005].

Techniques to reduce diffuse emissions resulting specifically from refinery process design can be:

- to achieve a balance between feed purity, processing steps, product quality and waste generation
- to treat waste water streams which contain (mixtures of) VOCs by stripping, rectification and extraction or combinations of these techniques in order to remove the substances that could contribute to diffuse emissions (see waste water treatment Section 4.26).

Plant design
The selection of plant components, and the manner in which they are configured, can both greatly influence the extent of diffuse emissions. For new units, there is a significant opportunity during the initial design phase to incorporate a wide range of techniques to reduce the potential for diffuse emissions. For existing plants, efforts can be made to incorporate many of these techniques over time as part of a process of continuous improvement.

Techniques to reduce diffuse emissions through the selection and configuration of refinery components include:
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1. limiting the number of potential emission sources, such as by:
   - designing piping layout appropriately by:
     - minimising pipe run length
     - reducing the number of flanges (connectors) valves and screwed pipe fittings
     - using welded fittings and pipes
   - reducing the number of pumps by using, if possible, other means of fluid transfer e.g. by gravity

2. maximising inherent process containment features, such as by:
   - enclosing (partially or completely) effluent drainage systems and tanks used for effluent storage/treatment
   - minimising emissions during sampling by using closed sampling systems or in-line analysers
   - installing a maintenance drain-out system to eliminate open discharges from drains.

3. selecting high integrity equipment, such as:
   - valves with double packing seals or equally efficient equipment
   - fitting high-integrity gaskets for critical applications
   - pumps/compressors/agitators fitted with mechanical seals instead of packing
   - magnetically driven pumps/compressors/agitators.

4. selecting appropriate materials for equipment, such as:
   - to ensure that all equipment (e.g. gaskets) is selected appropriately for each process application
   - to avoid corrosion by appropriate selection of material of construction,
   - to prevent corrosion by lining or coating of equipment, painting pipes to prevent external corrosion and by using corrosion inhibitors of materials in contact with equipment
   - to apply reactive paints e.g. acid sensitive paints applied on HF alkylation plant flanges.

5. facilitating monitoring and maintenance activities by ensuring good access to components that have the potential to leak

6. collecting and treating emissions, such as conveying potentially collectable leaks (e.g. compressor seals, vents and purge lines) to flares or to flameless oxidizers.

Achieved environmental benefits
Prevention and reduction of diffuse VOC emissions.

Cross-media effects
The collection and containment of diffuse emissions can lead to explosive limits being reached as a consequence of the build up of VOCs e.g. where a cover is installed over a waste water treatment facility. This issue is subject to Explosive Atmospheres Directives 99/92/EC (ATEX 137) and 94/9/EC (ATEX 100).

Environmental performance and operational data
Diffuse emissions can be estimated during process and plant design by using a technique that counts the number of potential emission point sources (flanges, valves, pumps, etc.) and applies standard emissions factors relating to the contained fluid. The reliability of an emission factor in a given application depends on the quality of the factor, the specific pollutants of interest, and the type of source.
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Diffuse emissions from tanks can be estimated using the US EPA ‘TANKS’ software based on algorithms [276, US EPA 2006]. Methods to estimate diffuse emissions for other sources within refineries are provided in [111, CONCAWE 2009].

Technical considerations relevant to applicability
The aforementioned techniques to reduce diffuse emissions related to process and plant design are applicable to all new units that have potential diffuse emissions. For existing units, applicability may be limited by various constraints and efforts should be made to incorporate these techniques over time as part of the process of continuous improvement.

Economics
The cost of techniques to reduce diffuse emissions related to process and plant design depends on the specific installation. The costs are expected to be lower for new plants. In the long run, use of high integrity equipment can reduce maintenance costs and time dedicated to monitoring.

Reduction of diffuse emissions often provides opportunities for saving raw materials, recycling by-products, or avoiding the loss of final products, which all result in economic benefits.

Driving force for implementation
Reduction of VOC emissions
The other driving forces for implementation include:

- reduction in material losses
- safety for employees.

Example plants
All new chemical plants. [Please TWG provide information]

Reference literature
[6, EC 2003] [109, IMPEL Network 2000] [62, CONCAWE, 2008] [110, ESA 2005] [111, CONCAWE 2009]

4.25.6.1.2 Techniques to prevent/reduce VOC emissions related to plant installation and commissioning

Description
The manner in which plant components are installed can greatly affect emissions, and this is an obvious issue prior to the first commissioning of a new plant or a new unit. However, the reinstallation of unit components as part of maintenance or project work on units already in operation can also have a significant impact on emissions.

Techniques to reduce diffuse VOC emissions related to the unit installation can include:

- to have strict and well-defined procedures for construction and assembly
- to ensure that gaskets are installed correctly,
- to have robust commissioning and hand-over procedures to ensure that the unit is installed in line with the design requirements (e.g. the correct gaskets have been installed, the pipe runs do not include additional flanged connections).

Achieved environmental benefits
Prevention and reduction of diffuse emissions particularly diffuse VOC emissions.

Cross-media effects
None.
Operational data
Diffuse VOC emissions from some pre-selected individual plant components or equipment types can be monitored as part of the plant commissioning and hand-over process in order to determine whether the plant has been installed correctly, and in accordance with the design.

Applicability
These techniques are applicable to all new and existing units that have potential diffuse emissions.

Economics
The cost of techniques related to the unit installation to reduce diffuse emissions depends on the specific installation.

Reduction of diffuse emissions often provides opportunities for saving raw materials, recycling by-products, or avoiding the loss of final products, which all result in economic benefits.

Driving force for implementation
Reduction of VOC emissions, reduction in material losses and safety for employees.

Example plants
[Please TWG provide information]

Reference literature
[109, IMPEL Network 2000] [110, ESA 2005].

4.25.6.1.3 Programme for the prevention, detection and control of VOC fugitive emissions

NB: Description of LDAR has been streamlined with other BREF recent redactions (CWW+LVOC) for improving structure and consistency.

Description
Fugitive VOC emissions can be reduced by the detection and subsequent repair or replacement of leaking components. This is achieved by adopting a structured approach, commonly known as a leak detection and repair (LDAR) programme. An LDAR programme includes two fundamental steps:

- identification of the leaking components
- repair of these leaks in order to minimise losses.

Leak detection
Two methods are currently available for the identification of leaks, and each method has its individual strengths and weaknesses. It is therefore necessary to decide upon the purpose behind a measurement exercise when selecting the method. In some circumstances, methods might need to be combined to fully understand the leak levels. Large scale methods (see Section 3.28.1.4) may locate quickly the major emission areas whereas maintenance may be improved using infrared cameras to locate the leaks.

1. Method EN 15446: Sniffing
Leak detection using hand-held analysers is called ‘sniffing’. This method identifies leaking components by measuring the concentration of hydrocarbon vapours (in ppm) in the immediate vicinity of the leak with a flame ionisation detector (FID), a semi-conductive detector or a photoionisation detector (PID). The selection of the most suitable type of detector depends on the nature of the substance to be detected.
To check each potentially leaking component with hand-held analysers is time and cost intensive. Moreover, some leaking points might be difficult to access with the hand-held detectors to obtain a measurement. Sniffing surveys need careful preparation and are usually executed in campaigns that cover a specified portion of the refinery. Some companies have therefore developed a ‘targeted monitoring’ approach in which additional emphasis is put on components with a higher frequency of leaks. For more details see Section 3.28.1.4

2. **Optical gas imaging (OGI) method**

The optical gas imaging method involves the detection of leaks with advanced hand-held infrared cameras that are specially developed for this purpose. Both active and passive systems exist: active systems use an adequately tuned laser beam, while passive systems detect infrared radiation reflected by the equipment. Gas imaging based on passive cameras was introduced in the early 2000s, and enables direct visualisation of both leak and the leaking component and the recording of the images. On these recordings, gas clouds are visible as light or dark plumes.

Direct visualisation of leaks is of great value to improve the efficiency of maintenance on equipment as only the leaking equipment is repaired. Another advantage of the camera is the possibility to detect leaks under insulation and to screen from a distance, so that VOC emissions from components not accessible for sniffing can be located and repaired. However, as no reference protocol of use exists for these OGI instruments, detection limits and representativeness might differ from one user to the next. Furthermore, different commercially available instruments may lead to different sensitivities and detection efficiencies. Moreover, the intensity of the image projected by the camera depends on a number of factors and is not necessarily related to the concentration in the plume.

Infrared cameras therefore need to be employed with full knowledge of their limitations. These cameras can see only a small number of chemicals. For example, unless a BTEX leak is very large the camera will not detect it. In addition to this, they have relatively high detection limits (hundreds of ppm) and do not quantify or speciate the chemicals.

Some refineries are using infrared cameras before start-up to ensure the process is tight. Others are using cameras for safety purposes and for finding large leaks. For more details see Section 3.28.1.4

**Leak repair**

A staged approach is often applied to the repair of leaks.

- an initial intervention such as tightening bolts to eliminate leaks from valve stems or flanges, installing tight caps on open ends. Such an intervention needs to be performed by skilled operators taking due recognition of necessary safety precautions.
- equipment with leaks that cannot be stopped by minor interventions would need to be repaired. This may involve changing gaskets or packing, and may therefore require the equipment to be taken out of service.
- when no effective repair can be performed, replacement of the equipment should be considered.

The LDAR programmes based on sniffing typically do not include tanks and difficult to access plant areas. OGI and whole plant measurements will identify problem areas that are not being monitored and allow them to be addressed. In many instances, they allow for more efficient allocation of maintenance efforts by targeting the highest emitters first.

Control of fugitive emissions involves minimising leaks and spills through equipment changes, procedure changes, and improved monitoring, good housekeeping and maintenance practices. The aim in all refinery processes should be to prevent or minimise the release of VOCs. Because of the size, scope and nature of hydrocarbon processing on refineries, this presents a major challenge, which requires an overall strategy that also devolves down into individual action at a process unit and plant item level. Most VOCs are released through fugitive losses
from sources including valves, flanges, pump seals and equipment vents. Even a small simple refinery may have over 10000 potential sources and the problem is magnified proportionally on the complete complex refineries.

In the case of process component fugitive releases, the only real option is the implementation of a permanent ongoing Leak Detection and Repair (LDAR) programme. This should be developed and tailored to suit the situation concerned, using appropriate techniques, frequencies and priorities. It should provide estimates of fugitive VOC releases for monitoring returns and enable action to be taken to minimise releases. A LDAR contains the following elements:

- type of measurement (e.g. detection limit of 500 ppm for valves and flanges, against the interface of the flange)
- frequency (e.g. twice a year)
- type of components to be checked (e.g. pumps, control valves, heat exchangers, connectors, flanges)
- type of compound lines (e.g. excluding lines that contain liquids with a vapour pressure above 13 kPa)
- an indication of which leaks should be repaired and how fast the action should be taken

The principal areas of fugitive loss are well known and their minimising has been the subject of much investigation and action in refineries worldwide, mainly led by operators subject to extremely tight regulation. Some techniques to consider can be:

- an essential first step of any programme is to establish a fugitive release inventory for the refinery. This normally involves a combination of sampling, measurements, environmental monitoring, dispersion modelling and estimates based on emission factors
- identify all potential sources of VOC releases, by establishing population counts of equipment components in line with up-to-date P&I drawings for processes. This survey should cover gas, vapour and light liquid duties
- quantifying of the VOC releases, initially as 'baseline' estimates, and subsequently to more refined levels. Suitable protocols for this include the '1995 Protocol for Equipment Leak Emission Estimates' (US EPA 453/R-95-017) for process component losses and API methods for tankage losses. Some major companies have developed their own techniques and protocols. US EPA method defines a emission baseline estimate of 10000 ppm and which is more correct appropriate for a plant that, until today, has not implemented any LDAR programme. A recent report shown that from 1000 valves analysed by type, found that the average leakage measured on regulating control valves was over 70000 ppm. Some TWG members question that high emission leakage limit, and propose to set the limit to 500–1000 ppm, and specially with where small chemicals are handled.
- using appropriate dispersion modelling techniques, predicting atmospheric mass flux and concentrations
- employing environmental monitoring techniques, comparing the predicted situation with the measured one
- identification of the processes that have higher fugitive releases
- VOC releases also need to be minimised from refinery utility and ancillary systems and during plant maintenance and cleaning operations. Hydrocarbons should be minimised in cooling water and adequate separation facilities provided to deal with incidents of contamination. After depressurising off-line process vessels to RFG/flare, they normally need to be steamed out to flare and residual liquids returned to oil slops plants, not run to drain before venting to air, when personnel entry is required
- vapour recovery/incineration/use
- a strategy to reduce VOC emissions may include regularly complete inventory and quantification by a DIAL LIDAR (differential absorption light detection and ranging) or a SOF (solar occultation flux) measuring campaign (see Section 3.28.1.4 for more information).
emissions that occur through relief valves are to be routed to flare or dedicated incineration systems, and in exceptional cases vented to a safe location.

- fugitive VOC emissions (sometimes containing H₂S) can be minimised through double dual mechanical seals on pumps, compressors or agitators. For example dual pressurised sealing systems on pumps virtually eliminate leakage of the process fluid into the environment and typically have emissions approaching zero, usually described as ‘not measurable with existing instrument technology’.

- use of low emission valve stem packing (500 ppm) on critical valves, e.g. rising stem gate type control valves in continuous operation, particularly on gas/light liquid high pressure/temperature duties. Valves are the type of equipment that cause most of the leaks (40–65%). Valves with rising stems and in particular control valves are an important source of leaks and may account for as much as 64% of the leaking losses in a plant. It is therefore recommended that a high-integrity low emission packing be installed on these valves that can provide emissions performance below 500 ppm and at the same time is fire safe. To ensure low term leakage performance, valve live loading spring assemblies mounted on the gland bolts will ensure that the low emission packing is constantly loaded even as the material relaxes over time. Control valve solutions with valve live loading exist as maximum achievable control technology (MACT) and emissions performance of 3-5 years is achievable at below 500 ppm. Low emission packing should be specified, and should be certified by an independent test by a reputable testing house. Packing should also be fire safe. Rising stem control valves even with low emission packings can leak excessively after the packing has relaxed in the stuffing box. Studies carried out by a French research institute have shown average leakage concentrations on control valves to be as much high as 70000 ppm. (Power Point Slide Enclosed) In the chemical, petrochemical and refinery industry the use of packed valves incorporating live loading spring assemblies mounted on the gland bolts compensates for normal packing relaxation or the effects of thermal cycling and vibration. Valve Live Loading systems offer considerable improvements in long term sealability on rising stem gate valves, globe valves and regulating control valves. On frequently operated rising stem valves (most problematic) live loading offers a considerable improvement in long term emissions performance (<500 ppm for 3-5 years). Valves have been identified as the greatest source of fugitive emissions in refineries and particularly frequently operated rising stem valves represent the greatest sources of fugitive emissions.

- use of alternative proven types of low release valves where gate valves are not essential, e.g. quarter turn and sleeved plug valves, both of which have two independent seals.

- use of balanced bellows type relief valves to minimise valve leakage outside the design lift range and piping of reliefs to RFG or flare gas, normally via phase separation, without header back pressure.

- minimising the number of flanged connections on pipelines and the use of high specification jointing materials. Flanges should be minimised and high integrity sealing materials should be used and should be fire safe materials. In some critical services, particularly where thermal cycling or possible vibration may exist, flange disc springs can be mounted under the flange bolts to compensate for the effects of thermal cycling and gasket relaxation. Such solutions combined with high performance sealing materials can provide emissions performance of <500 ppm for periods of 3-5 years. Often heat exchangers are not given a separate consideration in the discussion of fugitive emissions. On a typical refinery, there can be several hundred heat exchangers. Due to the size of these flanged connections, the large no. of bolts involved, the non-uniform temperature on the flange and the thermal cycling conditions under which many operate, it is recommended that flange disc-springs are fitted under the nuts of the bolts to maintain a constant gland load on the sealing material. Heat exchangers have a far greater tendency to leak than normal pipe flanges due to their dimensions and in particular in thermal cycling conditions. High-integrity sealing materials are recommended and not the standard typical metal-jacketed gaskets as indicated in the design codes.

- use of canned pumps or double dual seals on conventional pumps. Study the use of non-leaking pumps as diaphragm pumps, bellows pumps, canned rotor pumps, or pumps with magnetic clutches. Magnetic pumps cannot be used for clean liquids at low temperature.
Emissions from centrifugal pumps can be reduced to 33% by replacing packed seals by dual mechanical seals. Turbo compressors can be sealed with labyrinth glands, with rotating rings or floating rings in liquid seals. An escape of the transported medium through the seals should be prevented e.g. by inert gas or liquid sealing medium at elevated pressure. Furthermore, magnetic drive pumps and canned motor pumps have limited applicability and care must be taken when using such pumps in contaminated process streams, process streams containing particulate and higher pressures. It should also be noted that magnetic pumps typically have lower efficiency compared to conventional pumps, drawing more power for the same service. In the end effect, this transfers emissions from the pump (as VOC emissions) to the stack (as CO$_2$, SO$_2$, NO$_2$ emissions).

- piping of compressor seals, vent and purge lines to RFG or flare systems
- use of end caps or plugs on open-ended lines and closed loop flush on liquid sampling points. This is not applicable with circulating fluid (pump discharge) or in tanks. Minimising the releases to air from process hydrocarbon analysers, by optimising sampling volume/frequency and venting to RFG or flare systems.
- install a maintenance drain-out system to eliminate open discharges from drains.
- using totally closed-loop circuits in all routine samplers. To follow product quality, inspection requirements, environmental standards, etc. a sampling schedule is typically set up. With Routine sampling is understood means these that are frequently used or needed. For example, by routine samplers is understood, the samplers of effluent water quality, daily samples of processed crude fuel fired, fuel gas, certain feedstocks (i.e. FCC unit), that are taken to analyse the sulphur concentration. and samplers from intermediates, final products, tanks, etc.

Achieved environmental benefits

Prevention and reduction of fugitive VOC emissions which Fugitive emissions are one of the largest sources of refinery hydrocarbon emissions. A leak detection and repair (LDAR) programme consists of using a portable VOC detecting instrument to detect leaks during regularly scheduled inspections of valves, flanges, and pump seals. Leaks are then repaired immediately or are scheduled for repair as quickly as possible. A LDAR programme could reduce fugitive emissions 40 to 64 percent, depending on the frequency of inspections.

Techniques to reduce VOC emissions are: efficient seals and valves, good maintenance programmes and monitoring of the emissions. Fugitive emissions can be reduced to 0.01% weight when normal fugitive emissions have been calculated as 0.03% weight on throughput. The investment cost for these techniques is negligible and the operating cost is around EUR 0.1 million per year (accounting for 100 EUR per tonne of VOC recovered).

About 93% of the sources of fugitive emission are accessible. The achievable emission reduction depends on the current condition of the components, with typical reduction rates of at least 50 to 75% related to average emission factors. The estimated efficiency for quarterly inspection and maintenance is 80 to 90%. Higher efficiencies may be reached when more intensive inspection and maintenance programmes are implemented.

A good inspection and maintenance programme for valves and flanges is a very cost effective way to reduce NMVOC emissions in a refinery. Savings may reach 0.19 EUR/kg of hydrocarbon reduced.

Environmental performance and operational data

One refinery in the US, which has been using the infrared camera for some years, has compared it with their existing LDAR approach using the sniffing method. They have found that the camera does not detect low level leaks and cannot be used as a substitute. They, however, continue using it for safety and large leak detection purposes.

In Sweden, LDAR is done at all the refineries. Sniffing measurements are done twice a year at every potential leaking point that can be reached. If a start-up of a unit is done, additional
sniffing measurements are carried out. Preem Refinery Lysekil does sniffing measurements on approximately 100 000 potential leaking points twice a year. Leak levels are defined as 100, 500 and 900 ppm (as propane). For medium level leaks (500 ppm) action is taken as soon as possible to reduce the emission. At this refinery, since 1989, the number of leaks in the process area has decreased from 2 % to a level around 0.2 %. OGI is used to complement the sniffing method, although it has not been found that it can replace it. It is especially true for tank roofs which are difficult to monitor with sniffing; OGI has been found to give useful information on emissions.

**Cross-media effects**

None.

**Technical considerations relevant to applicability**

Fully applicable. See descriptions and Section 3.28.1.4 for applicability of each of the detection techniques.

**Economics**

A system for monitoring approximately 3000 refinery components (primarily pumps, seals, valves in high liquid vapour pressure or gas services, and road/rail loading) is estimated to cost about EUR 87500, excluding the modification of poorly performing equipment and cost of labour.

In a typical US refinery with over 200 000 components, the annual cost for an LDAR programme is reported to exceed EUR 750 000 (actual cost USD 1 000 000, average 2010 USD/EUR exchange rate) with the US EPA Method 21 based on sniffing.

It is reported that full monitoring of a complex refinery can take six months or more to complete and in one example costs were 0.6 million EUR (for 2006 in CONCAWE report 2008).

For a reduction efficiency of 50 % by annual inspection for fugitive emissions, OECD estimated no additional costs, but a cost benefit due to hydrocarbon savings. A reduction of 80 % by quarterly inspection and maintenance will cost about EUR 193/ t NMVOC abated. A simple Inspection and Maintenance programme at a small plant may result in an annual cost of EUR 44000, whereas at a large plant with stringent requirements some EUR 875 000 may have to be accounted spent.

The cost of leak detection and repair programme an LDAR for pumps and compressors is EUR 1.75 – 2.5/ t of hydrocarbon emissions reduced.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Refinery Process Units and Equipment (Installed and Retricted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Technology</td>
<td>Leak Detection and Repair Programmes</td>
</tr>
<tr>
<td>Efficiency</td>
<td>50 – 90 %</td>
</tr>
<tr>
<td>Investment Costs</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
| Operating Costs | 0.1 – 0.15 EUR million for 15 Mt/yr refinary$^{(2)}$
| | 0.06 EUR million for 5 Mt/yr refinary$^{(2)}$
| | 0.01 – 0.08 EUR million/yr for a 10 000 ppm programme to
| | 0.8 EUR million/yr for a 100 – 500 ppm programme$^{(2)}$
| Other Impacts: Repair costs | Repair not included in above costs |

Sources:

$^{(1)}$ Industry Propriety Information

$^{(2)}$ IN ECE EC AIR/WG6/1998/E

$^{(3)}$ Hydrocarbon Processing, September 1996, p 121

Table 4.11: VOC control technique applied to refinery

**Driving force for implementation**

Reduction of VOC emissions, reduction in material losses and health and safety for employees.

**Example plants**

LDAR programmes have been used successfully world-wide to reduce VOC releases. Typical survey results show that leaks from glands on valves and pumps are responsible for 90 % or
more of estimated fugitive releases and that a small proportion of valves, virtually on all gas or high temperature light material streams, contribute are responsible for almost all of the total them. See also Preem Refinery Lysekil (SE) under the Environmental performance and operational data paragraph in this section.

Reference literature

Chapter 4

4.25.6.2 Vapour recovery units (VRU)

For consistency, this section includes from section 4.21.16 has been deleted and former text merged with text.

Description

Vapour recovery units (VRUs) are installations designed for the emission reduction of volatile organic compounds (VOC) which are emitted emissions during loading and unloading operations. For a refinery this is particularly relevant to gasoline and other of most volatile products such as naphta, especially crude oil and lighter products. Vapour recovery can also be used to abate emissions from fixed roof tanks storing volatile products which are not fitted with internal floating roofs (see Section 4.21.4). As VOC emission abatement by VRUs is only one aspect of total VOC control in a refinery, this section should be considered in combination with storage, handling and integrated refinery management. Detailed information, in particular for refined product storage, is also provided in the EFS BREF [5, EC 2006]. Additional information is provided in the AEAT report [115, Rudd et al. 2001] on emissions during ship loading and in the ENTEC report on the implementation of Directive 94/63/EC for gasoline emission control [116, ENTEC 2009].

Vapour recovery systems involve two processes:

- separation of the hydrocarbons from air
- liquefaction of the separated hydrocarbon vapours.

The separation processes that may be used to separate hydrocarbon vapours from the air are:

- pressure swing adsorption on activated carbon
- absorption by washing in a low volatility absorbent fluid
- selective membrane separation
- condensation by cooling or compression (separation and liquefaction are combined in a single process).

The liquefaction processes applicable for separated hydrocarbon vapours are: absorption, normally into their own product condensation compression.

The following VRU systems are used for refined products:

- absorption in a cold lean oil stream
- adsorption in twin bed pressure swing operation
- indirect liquid condensation in a refrigerant heat exchanger
- membrane separation by passage through a hydrocarbon selective surface.
Several commercial techniques are available for the recovery of VOC, using one or a combination of the following physical processes:

These techniques can be divided in two large groups according to the type of separation.

One group includes techniques where the separation of the VOC from the air due to pressure swing adsorption on activated carbon, absorption by lean oil washing (kerosene), selective membrane separation or condensation by cooling or compression (this is a special case because separation and re-condensation are both achieved in a single process).

The other group integrates these techniques that the VOC are separated by condensation to liquid state. It includes re-absorption into the gasoline or crude oil, condensation and compression. Follows a short description of these techniques.

- **absorption**: the vapour molecules dissolve in a suitable low volatility (‘lean’) absorption liquid absorbent (water, lyes, glycols or mineral oil fractions such as kerosene or reformate). The absorbent may need to be cooled to reduce its volatility (commonly at -25 to -30 °C for kerosene or reformate). It is then necessary to split the vapour from the absorbent by heating the absorbent/recovered gasoline mix in a heat exchanger and then re-absorbing the rich gasoline vapour in a stream of gasoline. Depending on site-specific conditions, it can be routed to further use in another process. The desorbed gases must either be condensed, further processed or incinerated. Absorption is not commonly used for gasoline vapour recovery in the EU because the technique is considered less efficient than e.g. adsorption.

- **adsorption**: the vapour molecules adhere physically are retained by to activate sites on the surface of adsorbent solid materials, like activated carbon (AC) or zeolite. The adsorbent needs periodical regeneration. Continuous process have two vessels (beds) containing activated carbon which cycle typically every 15 mn between adsorption and regeneration modes. This regeneration of the carbon activity can be done using steam or, more commonly, vacuum pumps. The resulting desorbate is then absorbed (e.g. in a circulating gasoline component stream) in a downstream wash column (wash stage). The residual gas is sent to further treatment. This technique is the one most commonly used for a gasoline VRU. See an example of a typical adsorption unit in Figure 4.47.

![VRU-Activated carbon adsorption process](image)

**Figure 4.47** VRU-Activated carbon adsorption process
membrane gas separation: the vapour molecules dissolve into the membrane, move by diffusion to the other side and desorb into the support material, driven by a pressure difference. The concentration is higher at the desorption side of the membrane, as the vapour molecules are preferentially absorbed into the membrane compared to the gas molecules. They are processed through selective membranes to separate the vapour/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate). The efficiency of the separation process is dependent on the differential pressure across the membrane. For further purification, the membrane process can be combined with other processes. Regeneration is accomplished by depressurisation and vacuum desorption. See an example of a typical membrane separation unit in Figure 4.48.

Figure 4.48 VRU-Membrane separation process

refrigeration/condensation: by cooling of the vapour/gas mixture the vapour molecules condense on the surface of a cold heat exchanger and are separated as a liquid. A second stage (e.g. cryogenic condenser using liquid nitrogen) may be required to meet the emission limit. As the humidity leads to the icing-up of the heat exchanger, a two-stage condensation process providing for alternate operation is required. This method can achieve low exit concentrations if the applied refrigeration temperature is low enough. The vapours are recovered as pure liquids (no waste), which can be returned directly to the storage tank.

hybrid systems: nowadays in practical, combinations of techniques for the VRUs are commercially available on the market which are able to meet very low emissions standards. An example is membrane separation followed by adsorption. Examples are cooling/absorption and compression/absorption/membrane separation.
Achieved environmental benefits

Emissions of the various systems are directly related to the reduction efficiency as reported above and can be as low as 10 mg/Nm³ (without methane). With an efficiency of 99.9% concentrations of 150 mg/Nm³ (without methane) or 2500 mg/Nm³ (with methane) can be achieved, as shown in Table 4.113. The emissions reduction achievable will depend upon the techniques used and the composition and concentration of the VOC in the vapour stream being abated. For example a gasoline vapour stream can have an NMVOC concentration of 1500 g/Nm³. Thus to achieve a vent concentration of 150 mg/Nm³ requires an abatement efficiency of 99.99%

<table>
<thead>
<tr>
<th>VRU technique</th>
<th>NMVOC removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>99–99.95</td>
</tr>
<tr>
<td>Adsorption</td>
<td>99.95–99.99</td>
</tr>
<tr>
<td>Membrane gas separation</td>
<td>99–99.9</td>
</tr>
<tr>
<td>Refrigeration/condensation</td>
<td>99 to 99.5</td>
</tr>
</tbody>
</table>

This method can achieve low exit concentrations if the applied refrigeration temperature is low enough. A great advantage of condensation is that the vapours are recovered as pure liquids (no waste), which can easily be returned directly to the storage tank. Ranges are due to the use of different composition, concentration and flow rates that the VRUs are designed for and whether 1 or 2 stages. Higher removal efficiencies are only reached with high inlet loads.

Table 4.112: Removal efficiency of various VRU techniques

Following text moved from Section 4.21.16 and merged within appropriate paragraphs

It has been estimated that VOC emissions from barge loading can be reduced by 98% by installing a marine vapour loss control system. A vapour recovery unit used in fixed tanks can reduce VOC emissions by 93–99% (down to 102 g/Nm³). A vapour recovery system for the unloading of crude oil vessels can collect about 85% of total VOC, which are condensed and reinjected in the crude feedstock.

Table 4.113 provides some data on the efficiency and environmental performance of vapour recovery units. Non-methanous VOC (NMVOC) and benzene measurements can be performed through FID or GC.
Chapter 4

VOC recovery technique | Emission reduction (%) | down to (g/Nm\(^3\))
--- | --- | ---
Single-stage | 93–99 | 10
Lean oil absorption | 90–95 |
Activated carbon as adsorbent | 95–99 |
Condensation with liquid nitrogen | 90 |
Membrane | 99 |
Double stage | near 100 % | 0.10–0.15

Note for TWG: D1 proposed to delete this Table as it gives more vague data than 4.54 and is actually covered by 4.54 Table 4.113.

Table 4.113: Emissions values for vapour recovery plants during the loading of motor gasolines

<table>
<thead>
<tr>
<th>Plant type</th>
<th>Recovery ((^4)) rates (%)</th>
<th>Half-hourly Mean Average values attainable in continuous operation ((^5)), Total hydrocarbons ((^6))</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NMVOC ((^1)) (g/Nm(^3))</td>
<td>Benzene (mg/Nm(^3))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single-stage condensation plant</td>
<td>80 – 95</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>Single-stage absorption plant</td>
<td>90 – 97</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>Single-stage absorption, adsorption and membrane separation plants</td>
<td>90 – 99.5</td>
<td>(&lt;10^2)</td>
<td>1</td>
</tr>
<tr>
<td>Single-stage adsorption plants with supplementary blower ((^2))</td>
<td>99.98</td>
<td>0.15</td>
<td>1</td>
</tr>
<tr>
<td>Compression, absorption and membrane separation ((^3))</td>
<td>90 – 95</td>
<td>NA</td>
<td>1</td>
</tr>
<tr>
<td>Two-stage plants</td>
<td>99.98</td>
<td>0.15</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^1\) The sum of hydrocarbons and methane ranges from 100 to 2500 mg/Nm\(^3\) or higher. The methane content is not only insignificantly reduced by absorptive or adsorptive processes. Note for TWG: these values are not consistent with other in the Table! Source: Updated TWG 2010 (CONCAWE 4/09)

\(^2\) If single-stage plants are used as a preliminary stage for gas engines, a concentration of approx. 60 g/m\(^3\) is necessary for operation of the gas engine.

\(^3\) These values are given for an HC concentration in the uncleaned gas is of approx. 1000 g/Nm\(^3\).

\(^4\) As an indicator of performance level.

\(^5\) Expressed as an hourly average in continuous operation for consistency with 94/63/EC (Annex II)

\(^6\) Compression followed by a two-stage recovery section: re-absorption of the VOC into a fraction of the condensate being loaded followed by a membrane separation stage.

Source: TWG NO

Cross-media effects

Main effects are related with energy consumption, especially for two stage units, (for cooling, pumping, heating, vacuum), waste (adsorbent/membrane replacement), water effluent (i.e. condensates from steam regeneration of adsorbent, defrost water from condensation units). Two stage units are higher energy consumers: the energy consumption of these plants is (about twice as high) as that of plant with a residual emissions of 5 g/m\(^3\) which correlates with higher CO\(_2\) emissions. Where explosive mixtures can occur, it is important that safeguards be implemented to limit the risk of ignitions and ignition propagation. Need to implement Safeguards should be implemented for the handling of explosive mixtures, especially from mixed chemical vapour streams.

Table 4.114: Cross-media effects associated with the two main VRU techniques

<table>
<thead>
<tr>
<th>VRU technique</th>
<th>Cross-media effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Waste is only relevant in case absorption bed. The adsorbent will require replacement - carbon life is generally greater than 10 years</td>
</tr>
<tr>
<td>Absorption</td>
<td>If water is used, regeneration of the absorption liquid is not necessary, as waste water can be produced and requires can be treated appropriate treatment in a waste water treatment plant. Regeneration more than doubles the investment and energy costs. The only waste generated is the exhausted liquid which needs to be replaced once in many years.</td>
</tr>
</tbody>
</table>
Environmental performance and operational data

In Göteborg harbour (SE), three VRU of adsorption-type (capacities of 1500, 2000 and 2400 m³/h respectively) serving 4 quays are implemented for the treatment of the vapour generated by the loading of around 1.4 million tonnes/year of gasoline. Calculated emissions have been reduced from 300 to 25 tonne/year, and the outlet concentration of total VOC in the released stream is below 10 g/Nm³. The investment cost was around EUR 6.4 million (SEK 65 million) in 2001.

One of the biggest (36 000 Nm³/h) VRU in the world has been in operation since 2008 in the Lysekil Mongstad refinery (NO) for the treatment of vapours generated from the unloading of crude oil ships (two jetties). The installed power reaches 5.7 MW, and the recovery efficiency of the activated carbon bed filter system is estimated at around 85% of total VOC. The investment cost was around EUR 60 million (SEK 630 million) in 2008.

In Germany, recovery rates are reported to enable a minimum VOC emission reduction of 99%.

In France, since the end of 1990s, subsidies to support investment have been provided to companies (15 examples) to reach more ambitious targets than the regulatory framework for recovery of vapours from loading facilities. One process uses adsorption on activated coal and desorption of vapours reducing the pressure. This process allows to reduce the VOC emission level at to 2 g/Nm³, below the regulatory target of 35 g/Nm³.

Technical considerations relevant to applicability

Vapour recovery can be applied to crude loading (with the exception of adsorption unless a pretreatment such as sulphur stripper is not been used, because of adsorbent fouling) dispatch product stations and in ship loading stations having smaller effectiveness being. However, for crude loading, it is less effective than the mentioned above systems for product loading because the higher levels of methane and ethane are collected in the vapour stream in crude oil vapour are recovered with a low efficiency. These systems are not applicable to unloading processes when the receiving tank is equipped with an external floating roof. Vapour recovery units are not considered applicable when the recovery of a small quantity of chemicals is under discussion.

VRUs occupy limited space. Usually they are preassembled and delivered skid-mounted. Commercial VRU capacities range from 500 – 2000 Nm³/h. Adsorption systems are popular due to simplicity, good operability and high performance.

The main technical restrictions, including safety considerations are described in Table 4.115:

<table>
<thead>
<tr>
<th>VRU VOC recovery technique</th>
<th>Restriction in the applicability of the technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption activated carbon</td>
<td>Handling of non-compatible compounds present in the vapour stream may either poison or destroy active carbon e.g. H₂S in crude oil. Due to the heat of adsorption, safety systems are required to ensure that auto-ignition does not occur. Appropriate monitoring to prevent it is also required. At higher inlet concentrations AC is quickly saturated, so regeneration is necessary.</td>
</tr>
<tr>
<td>Membrane separation</td>
<td>Up to 5000 ppm. Technology applicable up to full saturation of HC in the vapour stream. Well suited to systems with large vapour volumes (compressor at the inlet to the membrane unit). For very small or variable vapour volume, e.g. road tanker loading, common practice is to install a variable volume vapour holding tank in the inlet vapour piping to the VRU.</td>
</tr>
<tr>
<td>Condensation with liquid nitrogen</td>
<td>May require double heat exchanger set to enable unit defrosting during continuous operation requirement. SO₂ could result in deposition of elemental sulphur. Flow variance has to be avoided to ensure efficient condensation. Very low temperature equipments require general safety measures.</td>
</tr>
</tbody>
</table>
Vapour recovery units (VRUs) are installations designed for the emission reduction of volatile organic compounds (VOC) which are emitted during loading and unloading operations of light products. For a refinery, this is particularly relevant to gasoline storage and loading as well as for products with equivalent volatility characteristics such as naphtha and BTEX.

<table>
<thead>
<tr>
<th>VRU technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Due to the heat of adsorption, this method cannot handle high inlet concentrations (auto-ignition) requires safety systems to ensure that auto-ignition does not occur. At higher inlet concentrations, the AC is quickly saturated, so regeneration is necessary. Normally, an adsorption VRU applies therefore to two-stage systems: there are two carbon beds which alternate between duties: one is being used for adsorption while the other is being regenerated. The only waste generated is the exhausted activated carbons which need to be replaced only after many years.</td>
</tr>
</tbody>
</table>

Scores of many VRUs at gasoline (un)loading installations for VOC emission reduction have been built in Western Europe following Stage 1 legislation. Hybrid systems are often applied.

**Economics**

For consistency, TWG is invited to check the various costs gathered in this paragraph. Following table proposed to deletion because updated data were made available on costs.

Error! Reference source not found. shows some examples of the cost of vapour recovery units.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Installation cost (EUR million)</th>
<th>Operating cost (EUR million/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour recovery unit for 4 fixed tanks 20 m in diameter (loading volatile products to road, rail or barge, not including equipment for trucks and wagons)</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>Vapour recovery systems for the loading of volatile products to road, rail or barge (not including equipment for trucks and wagons). Cost referred to 4 tanks of 20 m of diameter</td>
<td>Single stage: 1.3</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Double stage: 1.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Vacuum recovery systems. Design flow rate of 14142 m³/h. System will provide overall recovery up to 99.9 % of feedstream with a hydrocarbon concentration of 40%, and a moisture content of 8.7 % v/v (dew point = 38 °C)</td>
<td>0.28 - 1.3</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{\dagger} \) not considering the value of products recovered

Table 4.116: Costs related to vapour recovery units: 3 examples

Based on the AEAT-report [115, Rudd et al. 2001] on abatement of ship loading emissions, Table 4.47 shows capital costs for a VRU plant for the various techniques over a range of vapour flows of up to 2000 m³/h. These costs exclude civil engineering, provision of utility infrastructure and vapour collection systems. The additional corresponding costs are reported to be variable depending on the distance of the VRU to the loading facility. The operating costs of the techniques consist of a component that is independent of throughput, which is in the range EUR 5000 to 40000/yr, plus a variable component which is approximately equal to EUR 0.05/t loaded.
Figure 4.50 Capital costs for some VRU techniques and thermal oxidation (2008)

ENTEC EC 2008 report on the implementation of Directive 94/63/EC provides example cost data for a single-stage adsorption-type unit operating at a recovery rate of 99.7% and an inlet concentration of 1 060 g/Nm³ and therefore at an outlet concentration of 3.5 g/Nm³.

Table 4.117 Example cost data for a single-stage adsorption VRU operating at 3.5 g/Nm³

<table>
<thead>
<tr>
<th>Sites characteristics</th>
<th>VRU n°1</th>
<th>VRU n°2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum loading rate (m³/h)</td>
<td>273</td>
<td>1 090</td>
</tr>
<tr>
<td>Capital cost excluding installation (EUR million)</td>
<td>0.345</td>
<td>0.690</td>
</tr>
<tr>
<td>Annual electricity usage costs (MWh)</td>
<td>20 000</td>
<td>82 000</td>
</tr>
</tbody>
</table>

In France, the investment cost data given in Table 4.118 are available for the process operating at 2 g/Nm³.

Table 4.118 Examples of costs data for some French sites VRU

<table>
<thead>
<tr>
<th>Sites</th>
<th>Loading capacity (tonnes/year)</th>
<th>Instantaneous treatment flow (m³/h)</th>
<th>Year</th>
<th>Investment cost (EUR million)</th>
<th>Avoided tonnes of COV/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>No 1</td>
<td>1 200 000</td>
<td>3 000</td>
<td>2005</td>
<td>0.580</td>
<td>100</td>
</tr>
<tr>
<td>No 2</td>
<td>192 500</td>
<td>800</td>
<td>1999</td>
<td>0.200</td>
<td>106</td>
</tr>
<tr>
<td>No 3</td>
<td>1 000 000</td>
<td>NA</td>
<td>1998</td>
<td>0.980</td>
<td>130</td>
</tr>
</tbody>
</table>

As reported elsewhere, typical VRUs with a capacity of 1000 Nm³/h involve a capital cost of EUR 2 million with an installation factor of 1.5 (as package unit) to 5 (in exceptional cases). Total capital investment strongly depends on site-specific factors, such as the number of loading berths, vessels connected to the system, the distance between berth and the emission control facility (cost of piping and ducting), the need for blowers and safety systems (explosion and flame arresters). The capital costs can range from EUR 4 – 20 million for a VRU of 2000 Nm³/h capacity. The investment costs can range from EUR 2 – 25 million for an efficiency of 99.2% implying an operating cost of EUR 0.02 - 1 million applied to loading operations (slurry, road, rail and internal refinery movements).
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The investment costs corresponding to Göteborg (SE) and Mongstad (NO) refineries (see previous paragraph on Environmental performance and operational data) were the following:

- at Göteborg, three VRU of adsorption-type (capacities of 1500, 2000 and 2400 m³/h respectively) serving four jetties cost around EUR 6.4 million (SEK 65 million) in 2001;
- at Mongstad 36 000 Nm³/h crude oil VRU cost around EUR 60 million (SEK 630 million) in 2008.

Driving force for implementation

European Council Directive 94/63/EC (Stage I) on the control of VOC emissions resulting from the storage of petrol and its distribution prescribes the installation of vapour balancing lines and vapour recovery units (VRUs) or vapour recovery systems (VRS) during gasoline loading/unloading activities at refineries and terminals to reach a limit of 35 g/Nm³.

The Gothenburg Protocol specifies an emission limit of 10 g/Nm³ for total VOC (in a 24-hour period) for new gasoline VRUs.

Example plants

Many examples are found in European refineries. Many VRUs at gasoline (un)loading installations for VOC emission reduction have been built in Europe following Stage-1 legislation or for crude unloading—e.g., at Göteborg harbour (SE), Mongstad refinery (NO), in Germany or in France (see previous paragraphs for environmental performance and operational data).

Reference literature

[107, Janson, 1999], [181, HP, 1998], [211, Ecker, 1999], [45a, Sema and Sofres, 1991], [117, VDI, 2000], [316, TWG, 2000], [247, UBA Austria, 1998], [268, TWG, 2001], [258, Manduzio, 2000], [115, CONCAWE, 1999], [5, EC 2006] [115, Rudd et al. 2001] [117, ENTEC 2009] [77, REF TWG 2010] [111, CONCAWE 2009].

Cross-media effects (text included in the previous paragraph)

Effluent is usually only condensate and is usually negligible.

<table>
<thead>
<tr>
<th>VRU technique</th>
<th>Cross-media effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>If water is used, regeneration of the absorption liquid is not necessary, as water can be treated in a waste water treatment plant. Regeneration more than doubles the investment and energy costs. The only waste generated is the exhausted liquid which needs to be replaced once in many years.</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Waste is only relevant in case absorption bed. The absorbent will require replacement—carbon life is generally greater than 10 years.</td>
</tr>
</tbody>
</table>

Table 4.11b: Cross-media effects associated to the two main VRU techniques

Operational data

The handling of VOC always involves safety measures in view of explosion risks (flame arresters) and the presence of toxic compounds such as benzene. VRUs are compact and require very little energy and process materials to operate. The size and power consumption of VRUs will depend upon the technology, vapour being processed, vapour flow rate and the design emission limit. Usually operating times are longer than two years.

<table>
<thead>
<tr>
<th>VRU technique</th>
<th>If reformate is used recycling to blending tanks is done.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid systems</td>
<td>Due to the complexity of operation it is difficult to maintain the high performance.</td>
</tr>
</tbody>
</table>

Applicability (relevant text merged with previous paragraph)

Vapour recovery units (VRUs) are installations designed for the emission reduction of volatile organic compounds (VOC) which are emitted during loading and unloading operations of light...
products. For a refinery, this is particularly relevant to gasoline storage and loading as well as for products with equivalent volatility characteristics such as naphtha and BTEX.

<table>
<thead>
<tr>
<th>VRE technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Due to the heat of adsorption, this method cannot handle high inlet concentrations (auto-ignition) requires safety systems to ensure that auto-ignition does not occur. At higher inlet concentrations, the AC is quickly saturated, so regeneration is necessary. Normally, an adsorption VRE applies therefore to two-stage systems, therefore has two carbon beds which alternate between duties—one is being used for adsorption whilst the other is being regenerated. The only waste generated is the exhausted activated carbons, which need to be replaced only after many years.</td>
</tr>
</tbody>
</table>

VRUs occupy limited space. Usually, they are preassembled and delivered skid-mounted. Commercial VRU capacities range from 500 to 2000 Nm³/h.

Scores of Many VRUs at gasoline (un)loading installations for VOC emission reduction have been built in Western Europe following Stage 1 legislation. Hybrid systems are popular due to simplicity, good operability and high performance.

Economics (relevant text merged with previous paragraph)
A typical VRU with a capacity of 1000 Nm³/h involves a capital cost of EUR 2 million with an installation factor of 1.5 (as package unit) to 5 (in exceptional cases). Capital investment strongly depends on site-specific factors, such as the number of loading berths connected to the system, the distance between berth and the emission control facility (cost of ducting), the need for blowers and safety systems (explosion and flame arresters) systems. The capital costs can range from EUR 4 to 20 million for a VRU of 2000 Nm³/h capacity. The investment costs can range from EUR 2 to 25 million for an efficiency of 99.2%, implying a operating cost from EUR...
0.02–1 million applied to loading operations (slurry, road, rail and internal refinery movements).

The detailed costs for a VRU unit of 2000 Nm$^3$/h capacity and applying utilities is shown as follows in Table 4.120.

**Driving force for implementation**

In some European countries, some programme applies to storage and loading operations of liquid hydrocarbons with a vapour pressure $>1$ kPa (10 mbar) at ambient temperature. Moreover, the specific requirements on gasoline storage and loading are laid down in the national legislation following the Stage 1 Directive. For refineries the VOC emissions of gasoline and their abatement is by far the most important due to the high vapour pressure ($>27.6$ kPa), the large throughput and the large number of transshipments by truck, rail and barge.

<table>
<thead>
<tr>
<th>Description</th>
<th>EUR</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indirect costs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>210 Detailed Engineering</td>
<td>275</td>
<td>7</td>
</tr>
<tr>
<td>212 Field Supervision</td>
<td>127</td>
<td>4</td>
</tr>
<tr>
<td>213 Inspection</td>
<td>83</td>
<td>2</td>
</tr>
<tr>
<td>260 PMT, NPQC, Owner</td>
<td>124</td>
<td>4</td>
</tr>
<tr>
<td>Subtotal</td>
<td>614</td>
<td>23</td>
</tr>
<tr>
<td>Direct costs—equipment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>311 Heat Exchangers</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>314 Towers</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>315 Deans</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>316 Reactors</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>321 Pumps and Drives</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>326 Tanks and Spheres</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>347 Cooling Towers</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Subtotal</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Direct costs—non equipment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>208 Scaffolding</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>240 Cleanup Construction</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>246 Construction Equipment</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>247 Excavation and Cable Trenches</td>
<td>44</td>
<td>2</td>
</tr>
<tr>
<td>248 Concrete Work and Paving</td>
<td>216</td>
<td>5</td>
</tr>
<tr>
<td>310 Piping</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>315 Pipe</td>
<td>432</td>
<td>26</td>
</tr>
<tr>
<td>316 Structural Steel</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>317 Instrumentation</td>
<td>285</td>
<td>2</td>
</tr>
<tr>
<td>328 Roadside, Walks, Fences</td>
<td>72</td>
<td>1</td>
</tr>
<tr>
<td>327 Electric Power and Lights</td>
<td>403</td>
<td>3</td>
</tr>
<tr>
<td>245 Communication Equipment</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>348 Insulation</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>311 Paint</td>
<td>162</td>
<td>4</td>
</tr>
<tr>
<td>280 Standby Equipment (Cap, Spares)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Subtotal</td>
<td>2273</td>
<td>54</td>
</tr>
<tr>
<td>Total Capital</td>
<td>4148</td>
<td>98</td>
</tr>
<tr>
<td>Expense</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101 Dismantling</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>102 Site Clearance</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>103 Relocation</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>104 Reconditioning</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>105 Temporary Bypasses</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>111 Gas Freeing and Cleaning</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>166 Owner Expense Charges</td>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>Subtotal</td>
<td>341</td>
<td>3</td>
</tr>
<tr>
<td>Final Total</td>
<td>4261</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.120: Total erected cost of a 2000 Nm$^3$/h vapour recovery unit (proposed to delete this detailed table on costs without reference year)

**Example plants**

This technique is used in many refineries.
4.25.6.3 Vapour destruction (VD)

In addition to vapour recovery also vapour destruction can be applied.

Description
Apart from the conventional technique of VOC collection and destruction by routing to a flare system, two specific systems are relevant in this respect.

- **Oxidation**: the vapour molecules are converted to CO$_2$ and H$_2$O either by thermal oxidation at high temperatures or by catalytic oxidation at lower temperatures.
  - **Thermal oxidation** occurs typically in single chamber, refractory-lined oxidizers equipped with gas burner and a stack. If gasoline is present, heat exchanger efficiency is limited and preheat temperatures are maintained below 180 °C to reduce ignition risk. Operating temperatures range from 760 to 870 °C and residence times are typically 1 second or less.
  - **Catalytic oxidation** requires a catalyst to accelerate the rate of oxidation by adsorbing the oxygen and the VOC on its surface. The catalyst enables the oxidation reaction to occur at lower temperature than required by thermal oxidation: typically ranging from 320° to 540 °C. A first preheating step (electrically or with gas) takes place to reach a temperature necessary to initiate the VOCs catalytic oxidation. An oxidation step occurs when the air is passed through a bed of solid catalysts.

Directive 94/63/EC (Stage 1) only allows oxidation in special situations, e.g. when energy is recovered by a gas motor.

- **Biofiltration**: decomposition to CO$_2$ and H$_2$O is achieved at temperatures slightly above ambient by micro organisms located in a solid humidified mass support medium.

Achieved environmental benefits
Respective VOC elimination ratios achievable with such techniques are: thermal oxidation: 99 – 99.9 %, catalytic oxidation 95 – 99 %, and biofilters 95 – 99 %. However, the efficiency of the biofilters is normally controversial: since high removal efficiencies are only reached with high inlet loads, emission concentrations well below 50 mg/Nm$^3$ NMVOC are rarely achieved.

Biotreatment units are rugged, silent, need minimal maintenance and no inputs and do not produce any noise. No fuel or chemicals are required. Biofilters remove or destroy aliphatic and aromatic hydrocarbons, other VOC, H$_2$S and odours in off-gases from process streams, tank vents, relief valves, soil vapour extraction, waste water treatments, etc.

Cross-media effects
Thermal oxidation can give unwanted combustion products such as NO$_x$, requiring extra treatment. Catalytic oxidation requires less energy to arrive at combustion temperatures, and can be competitive with thermal oxidation at low inlet concentrations. Thermal oxidation requires good primary and/or secondary safety measures to prevent explosions, while the efficiency of catalytic oxidation may be reduced by catalyst poisoning and ageing. Incineration of VOCs also generates CO$_2$. Combustion of streams with low concentrations and for the preheating of catalysts additional fuel is consumed.

Waste is only relevant generated in case when biofilters are exhausted. No secondary pollutants or wastes are created.

Operational data
Usually operating times are longer than two years. For biofilters, input air temperature should be 5 – 55 °C and with appropriate moisture level.
Applicability

Any gas that can burn in air will oxidise in biofilters. Installation for the treatment of flows of 17 m³/h up to 135 000 m³/h are found in the literature.

For biooxidation, the method is highly suited for treatment of continuous constant-composition air streams with low concentrations of organic pollutants. The method is not suitable for the direct treatment of the vapour/air mixtures often encountered in transshipments, because such mixtures have mostly higher vapour concentrations (>1 % v/v) and appear as sudden peak flows during the rather infrequent unloading operations. Biotreatment facilities are certainly sensitive to poisoning by presence of unexpected compounds in the incoming vapour stream. Consequently, most of these systems need continuous monitoring to prevent the entrance of undesired compounds.

Biofiltration is only suitable for continuous, constant composition, low concentration vapour streams. These conditions are not not typical of refining applications.

Economics

The economics of a thermal oxidation system with heat recovery will depend on many factors, including the calorific value of the waste stream. In 1998, a substantial payback was already expected based on the heat recovery from a thermal oxidiser furnished with a gas-to-gas heat exchanger that has an efficiency of 60 % and a gas flow of 4720 l/s, the payback for heat recovery will be impressive. Assuming natural gas was used as supplementary fuel, the costs reached around USD 20/million of kcal and USD 0.08/kWh of electric power. For a system running 24 h/day, 350 d/yr, the payback for the USD 0.2 million additional capital investment for a plant-type heat exchanger would be less than five months.

Biofiltration costs significantly less than the other air pollution control techniques. Capital costs vary with flowrate and the destruction/removal efficiency. Capital costs start at about USD 15/m³/h. Operation and maintenance costs are extremely low because no fuel or chemicals are required.

Table 4.121: VOC thermal oxidation control technique applied to refinery

<table>
<thead>
<tr>
<th>Emission source</th>
<th>Refinery process units and equipment (installed and retrofitted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control technology</td>
<td>Collection of atmospheric VOCs and relief valves to flare/incineration system</td>
</tr>
<tr>
<td>Efficiency</td>
<td>Up to 99.5 % destruction efficiency in incineration</td>
</tr>
<tr>
<td>Investment costs</td>
<td>1.3 EUR million for 5 Mt/yr refinery</td>
</tr>
<tr>
<td>Operating costs</td>
<td>3.0 EUR million</td>
</tr>
<tr>
<td>Other impacts</td>
<td>Increase in CO₂ emissions due to combustion</td>
</tr>
</tbody>
</table>

Source: UN-ECE EC AIR/WG6/1998/5

See also Figure 4.50 for costs of thermal oxidation.

Driving force for implementation

Reduction of VOCs.

Example plants

Thermal incineration: more than 107 units are operating worldwide. 76 portables.

Reference literature

[118, VROM, 1999], [181, HP, 1998].
4.25.7 Flares

Description
Flares are used for safety and environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situations, or upsets, unplanned events or unanticipated equipment failure. The flare is usually required to be smokeless for the gas flows that are expected to occur from normal day-to-day operation. This gas flow is usually designed at 15 to 20 10-15 % percent of the maximum design flow, new generation of tip flares might achieve up to 20-25 % of maximum design flow. Flares may become an important a significant SO₂ emitter compared to others when clean fuels are used within the refinery. Flaring is both a source of air emissions and leads to burn potential valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. For routine venting and planned shutdowns, flare gas recovery systems are to be used instead. More information is available in the CWW BREF [6, EC 2003].

Flare systems and designs
Flare systems can normally be divided into two main sections, i.e. the flare collection system with a flare knock-out drum and the flare stack itself. When dealing with large refinery complexes separate knock-out drums may be installed in different process areas with ‘blocking-in’ facilities to allow maintenance during shutdowns of these areas.

In Figure 4.52 a simplified process flow diagram of a flare system is shown.

![Flare system diagram](image)

Figure 4.52: Simplified process flow diagram of a flare system

Many flare systems are available today for various purposes. The chosen flare system depends mainly on:

- The flow, pressure, temperature and composition of the gas that is flared;
- the requirements given for combustion efficiency, radiation, soot and noise;
- the availability and the access to steam, air and gas.
Flares can be categorised by several ways and the following distinctions can be made:

- **the type of flares**: elevated or placed on the ground (elevated are the most common flares and have the greatest capacity);
- **the flare system**: non-assisted flares (low or high pressure) or assisted flares (with steam, air, gas or water)
- **the zone in which the oxidation reaction occurs** and includes the following categories: flame flares (open flame flares) or chamber flares (muffle and screen/shielded flares).

Compared to elevated flares, ground flares lead to poorer dispersion, because of the stack being nearer to the ground and therefore possibly resulting in environmental or health concern (depending on the type of end products).

In chamber flares, combustion occurs inside a cylinder which enables them to operate without smoke formation, noise or radiation. A type of ground flare works as a **premixed surface combustion system** (an enclosed burner), where pre-mixed gas and air burns on a permeable medium. (see [6, EC 2003]).

Table 4.122 shows an overview of the different main groups of flare systems. It also gives a brief description of each flare system, area of application, advantages and disadvantages regarding both environmental and operational consequences.

Extinguished flare systems also exist, where no permanent burning pilot flame is required, but a special mechanism is ignited when the speed of the gas exceeds a defined limit.

**Non-assisted flares system**:
A flare that only burns natural gas without any supply of air or vapour is called a **non-assisted flare**. It is used when non-smoking combustion can be achieved without external assistance. Depending on the pressure in the process equipment, it could lead to a low or high pressure flare. Pressurised gas provides a good mixing of air and waste gases and so reduces the exposure and smoke formation. On the other hand it increases the noise level.

**Assisted flare**
When the pressure in the waste gas to be flared is low an external medium such as steam, air or gas can be used as the driving force. Depending on their respective availability the following can be used:

- high pressure steam for steam-assisted flare;
- high pressure gas, for gas-assisted flare;
- air supply, for air-assisted flare;
- water being injected into the flare when low noise and radiation levels are required.
Table 4.122: Various flare systems applications

<table>
<thead>
<tr>
<th>Flare systems</th>
<th>Description</th>
<th>Application</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-pressure flare</td>
<td>Low-pressure flares are the simplest type of flare. Low-pressure flare tips are designed for a long service life. They are capable of flaring a wide range of waste streams and are primarily used for non-smoking gases.</td>
<td>Low-pressure flares can be used when non-smoking combustion can be achieved without external assistance. Low-pressure flares are used for maintenance and lower gas rates.</td>
<td>Cost-effective; Low maintenance costs Stable, reliable combustion</td>
</tr>
<tr>
<td>High-pressure flare</td>
<td>High pressure flares use the energy in the pressurized gas to create turbulent mixing and induce excess quantities of air for more complete combustion.</td>
<td>High pressure flares are used onland and offshore in order to achieve non-smoking combustion at large flaring rates. Can handle large quantities of flare gas at high pressure and has large capacity.</td>
<td>Cost-effective Clean, efficient and smokeless combustion Lower radiation</td>
</tr>
<tr>
<td>Steam-assisted flare</td>
<td>Steam assisted flares are designed to dispose of heavier waste gases which have a greater tendency to smoke. Steam is injected into the waste stream as external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbons.</td>
<td>Steam assisted flares are employed in low-pressure applications to achieve smokeless flaring where high-pressure steam is available onsite.</td>
<td>Smokeless combustion Low noise; Maximum energy efficiency.</td>
</tr>
<tr>
<td>Air-assisted flare</td>
<td>Air supply is used as external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbon waste gas.</td>
<td>Air assisted flares can be employed for operations that require smokeless, low-pressure flares in areas where steam is not available as smoke suppressant.</td>
<td>Reduce smoke; Lower radiation; Lower noise generation.</td>
</tr>
<tr>
<td>Gas-assisted flare</td>
<td>Gas injection is used as an external momentum force for efficient air/waste gas mixing and turbulence. This promotes smokeless flaring of heavy hydrocarbon waste gas.</td>
<td>Gas-assisted flares can be employed for operations that require smokeless, low-pressure flares in areas where high pressure assisted gas is available. For high-pressure applications that require low noise and radiation, and where water is available.</td>
<td>Maximum combustion; Smokeless performance.</td>
</tr>
<tr>
<td>High-pressure water injection flare</td>
<td>Water is injected into the flare to reduce radiation and flare noise.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sources: [ 86, SFT 2009 ]
Techniques for flaring operations

Techniques to be applied to flares that may reduce emissions are given below:

- Use of pilot burners which give more reliable ignition to the vent gases because they are not affected by the wind
- Steam injection in flaring stacks, which can reduce particulate matter emissions, when design for
- Coke formation in flare tips should be prevented
- Surplus refinery gas should has to be flared, not vented. Knock-out pots to remove liquids should be provided, with appropriate seals and liquid disposal systems to prevent the entrainment of liquids into the combustion zone. Water streams from seal drums should be routed to the sour water system.
- Flare-gas recovery systems have been developed due to environmental and economic considerations, where the flare gas is captured and compressed for other uses. Usually recovered flare gas is treated and routed to the refinery fuel gas system. Depending upon flare gas composition, recovered gas may have other uses. Reductions of flaring to ratios of 0.08 – 0.12 % of production in one natural gas plant in Norway have been reported.
- With the increasingly strict requirements regarding flame visibility, emissions, and noise, enclosed ground flares can offer the advantages of hiding flames, monitoring emissions, and lowering noise. However, the initial cost often makes them undesirable for large releases when compared to elevated systems. A significant disadvantage with a ground flare is the potential accumulation of a vapour cloud in the event of a flare malfunction; special safety dispersion systems are usually included in the ground flare system. For this reason, instrumentation for monitoring and controlling ground flares is typically more stringent than with an elevated system. Moved to environmental benefit + Cross media effects.
- For minimisation of soot formation in the flame, flow measurement with automatic steam control is applied in new installations as well as luminosity measurements with automatic steam control, and remote visual observation using colour TV monitors in plant control rooms allowing manual steam control and detection of permanent availability of the pilot flame. The steam injection serves several purposes. Firstly, it improves the mixing of fuel and air by creating turbulence, and thus enhances combustion efficiency. Secondly, it protects the flare tip by keeping the flame away from the metal. Thirdly, the steam reduces soot emissions as it reacts with solid carbon particles to form CO, which is then further oxidised to CO₂. And lastly, the steam injection probably also reduces thermal NOₓ formation. When hydrogen or very ‘light’ hydrocarbons are flared, steam injection is usually not applied as air-fuel mixing is often good and soot formation is unlikely.

Text moved from former section 3.28.1.3

Flare monitoring

Flare monitoring is needed in order to keep records of each event as part of the monitoring system of the refinery and to report to local authority. Flare systems should be equipped with adequate monitoring and control systems necessary to operate smokelessly and evaluate emissions. Flares should be observed at all times visually monitored under non-emergency conditions. Such systems should be triggered automatically and manually. Monitoring and control systems can be either automatic or manual. They generally include a continuous flow measurement, for which proven non-intrusive systems at the flare base are available, with automatic steam control, a luminosity measurement with automatic steam control, remote visual observation using colour TV monitors in relevant plant control rooms with access to, steam control and pilot flame detection.
Chapter 5

Flare gas flow

Among the various non-intrusive measuring systems that are available and compatible with safety flaring applications, ultrasonic flow measuring has proved to be one of the best options. It has been the preferred choice in most new applications [29, Clearstone 2008]. Ultrasonic flow meters can be used on dry, but also on wet and dirty gas streams, if the liquid content does not exceed ~0.5 percent by volume. If greater amounts of liquids are anticipated, a liquids knockout system should be installed directly upstream of the flow meter. They are applicable to a wide volume range, offer high accuracy, do not require frequent calibration, and have no significant flow restriction. However, they need a sufficient length of straight pipe in order to ensure laminar flow measuring conditions, which can raise difficult constraints in case of retrofitting. They also operate in temperature and pressure ranges which not always correspond to actual process conditions. The approximate cost for such ultrasonic flow meters is estimated at EUR 0.5 million per measuring device [Questionnaire n°27].

Flare gas composition

Flare gas composition can be analysed by periodical sampling and subsequent laboratory analysis, or by continuous measurement devices. When based on online gas chromatography for continuous measurement is highly sensitive to fouling and requires strict (and costly) pretreatment and conditioning of samples in order to remove water and particles before detection measurements.

As an example, two flares gas composition from a Norwegian refinery determined with online gas chromatography are provided in the following below.

Table 4.123: Examples of flares gas composition

<table>
<thead>
<tr>
<th>Components</th>
<th>Main flare (mole %)</th>
<th>Sour gas flare (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>C6+</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>C-Butene</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>CO</td>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td>CO2</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Ethane</td>
<td>12.3</td>
<td>10</td>
</tr>
<tr>
<td>Ethene (ethylene)</td>
<td>2.8</td>
<td>5</td>
</tr>
<tr>
<td>H2</td>
<td>38.9</td>
<td>35</td>
</tr>
<tr>
<td>H2S</td>
<td>0.2</td>
<td>0.2 – 1</td>
</tr>
<tr>
<td>1-butane</td>
<td>2.9</td>
<td>2</td>
</tr>
<tr>
<td>1-butene</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>1-pentane</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Methane</td>
<td>18.4</td>
<td>23</td>
</tr>
<tr>
<td>N2</td>
<td>5.6</td>
<td>16</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.7</td>
<td>1</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Propane</td>
<td>10.9</td>
<td>3</td>
</tr>
<tr>
<td>Propene</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>t-butene</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

NB: the figures provided are based on normal conditions. H2S concentration will vary with the amount of sour gas sent to the flare

Source: [86, SFT 2009]
**Chapter 4**

**Flaring activity and emission records**

On the above basis, flare gas emissions should be estimated and compiled in daily records of the site flaring activity. For each flaring episode, the record should document the measured or estimated flare gas composition, the measured or estimated flare gas quantity, and the episode duration.

The flare gas emissions can be calculated by using estimated or measured flows and concentrations (e.g. H₂S) that have been measured, together with empirical values of emissions factors for NOₓ and CO formation. Available literature gives concentration values around 100 – 400 mg/m³ for NOₓ formed, and around 30 mg/m³ for CO released [28, Tebert et al. 2009]. For estimating VOC emissions, appropriate burnout rates combustion efficiency shall be determined (see [6, EC 2003]). In general, a minimum burnout of 98 % may be assumed under optimised conditions and if guaranteed by the flare provider [6, EC 2003]. Moreover, flares should be regularly checked (notably for unburned VOCs) as part of regular DIAL and/or SOF measuring campaigns undertaken in the refinery (see Section 3.28.1.4).

**Table 4.124:** Example of flare gas NOₓ emissions factors used at a Norwegian refinery

<table>
<thead>
<tr>
<th>Component</th>
<th>Source</th>
<th>Emission factor</th>
<th>Base for emission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>Flare gas</td>
<td>3.13 g/kg</td>
<td>Measurements in 2005</td>
</tr>
<tr>
<td></td>
<td>Flare (purge gas)</td>
<td>3.13 g/kg</td>
<td>Measurements in 2005</td>
</tr>
<tr>
<td></td>
<td>Flare (sour gas)</td>
<td>4.0 g/kg</td>
<td>Emission factor from NOₓ-tax</td>
</tr>
</tbody>
</table>

*Source: [86, SFT 2009]*

**Achieved environmental benefits**

Combustion efficiency, radiation, soot and noise depends on the flare system. Well-operated refinery flares typically obtain a conversion of 98 % to CO₂, 1.5 % are partially combusted products (almost all CO) and 0.5 % are unconverted. Enclosed ground flares have reduced noise and smoke compared to elevated flares. However, the initial cost often makes them undesirable for large releases when compared to elevated systems.

**Environmental performance and operational data**

In order to achieve a combustion that is as complete as possible, the flare should be operated with a minimum flame temperature range of 800 – 850 °C. Flare efficiency is generally maximised through assessment of the heating value of the flared streams and by minimising flame quenching for example by oversteaming. Since air present in the stack can create a potentially explosive mixture with incoming flare gas during low-flare gas loads, a continuous stream of purge gas is required. When using nitrogen, a smaller purging rate is required. In a lot of cases, a molecular water seal is employed which allows for using a lower purging rate.

**Table 4.125:** Example of two flares design conditions in a UK refinery (2007)

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Units</th>
<th>1st flare</th>
<th>2nd flare</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>m</td>
<td>91</td>
<td>137</td>
</tr>
<tr>
<td>Type of system</td>
<td></td>
<td>High pressure</td>
<td>Low pressure</td>
</tr>
<tr>
<td>Maximum capacity</td>
<td>tonnes/h</td>
<td>397</td>
<td>680</td>
</tr>
<tr>
<td>Smokeless capacity</td>
<td>tonnes/h</td>
<td>34</td>
<td>68</td>
</tr>
<tr>
<td>Pilot gas consumption</td>
<td>kg/h</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Purge gas consumption</td>
<td>kg/h</td>
<td>22.7</td>
<td>12.5</td>
</tr>
<tr>
<td>Steam consumption(¹)</td>
<td>tonnes/h</td>
<td>11.8</td>
<td>21.8</td>
</tr>
<tr>
<td>SO₂ emission(²)</td>
<td>kg/h</td>
<td>0.074</td>
<td>0.043</td>
</tr>
</tbody>
</table>

(¹) Steam consumption at maximum smokeless capacity.
(²) From pilot gas and purge gas.
Chapter 5

Cross-media effects
Flare emissions will include, in addition to NOx, CO from combustion, a part of uncombusted flared gas compounds (e.g. VOC, H2S, SO2), thus causing potential health concerns and odour nuisances (mainly for ground flares).

Flare seal water is typically in need of treatment before release. Steam injection for combustion enhancement and soot blowing spends thermal energy.

A significant disadvantage with a ground flare can lead to the potential accumulation of a vapour cloud in the event of a flare malfunction; special safety dispersion systems are therefore usually included in the ground flare system. As a consequence, instrumentation for monitoring and controlling ground flares is typically more stringent than with an elevated system.

In addition, flares, especially steam assisted ones, generate noise and light nuisances.

Technical considerations relevant to applicability
Flaring of toxic gases (never via a ground flare) requires special considerations. To ensure safe operation during periods when the flare may not have a flame present, ground level concentration calculations for hazardous components should be performed assuming the flare as a vent only. Other safeguards may be necessary to mitigate ground-level exposure hazards. Reliable continuous pilot monitoring is considered critical when flaring toxic gases.

There are basically two types of flares, an elevated flare and a ground flare. Ground flares are used when it is necessary to conceal the flare (for various reasons), otherwise the elevated flare is commonly chosen because it can handle larger flow releases more economically. Sometimes a refinery has both a ground flare and an elevated flare. In that case, the ground flare is used to combust small amounts of continuous vents and small relief loads.

The elevated flare is always a vital part of the refinery complex, its primary purpose being safety. This flare system is designed to conduct easily ignitable and toxic vapours from the process area to a remote elevated location. The elevated flare system includes a seal drum to prevent the flame from flashing back into the process units, and an elevated stack with pilot-ignition and steam nozzles at the tip. Due to different burning characteristics of the gases, a separate sour gas flare is usually provided; this flare could be equipped with different burners than the hydrocarbon flare to allow for more efficient combustion of sour gases (H2S).

Economics
Note to TWG: Any data available?

Driving force for implementation
Some local regulations (e.g. South Coast Air Quality Management District-SCAQMD- California – US) require flare minimisation plans. The seven refineries (30 flares) in the SCAQMD area are now required to have continuous flow gas monitors, continuous gas heating value monitors and semi-continuous total sulphur concentrations monitors.

The main other driving force for implementation is health and safety.

The purpose of the flare system is to collect and process vent gases (e.g. pressure relief from the fractionator should pass to the flare) and (large) quantities of fluids during emergency situations or upsets; when safety relief valves are open, during depressurisation operations and purging of process units in case of an emergency situation, during start-up of certain process units or prior to a scheduled shutdown. Provisions are available to separate the liquids from the gases and to incinerate relieved vapours. The liquids are usually returned to the process units or tanks. Pilot burners are normally installed to take care of the constant ignition of released vapours. Moreover, well controlled steam injection systems have been applied to achieve smokeless burning. Flare gas recovery systems are often installed to comply with local regulatory limits on flare operation and, therefore must be sized to conform to any such limits.
Example plants
Flares are common in refineries. Two examples of low flaring ratio refineries in Sweden are provided in Section 3.25.3.

Reference literature
[6, EC 2003] [118, VITO 2009] [86, SFT 2009] Questionnaire number 43, 27.

4.25.8 The SNO\textsubscript{x} combined technique to abate air pollutants

Description
The SNO\textsubscript{x} plant is designed to remove SO\textsubscript{2}, NO\textsubscript{x} and particulate matter from combustion flue-gases, by the coal-fired boilers at the Gela refinery power plant. The SNOX plant is based on a first dust removal stage (by an ESP) followed by catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NO\textsubscript{x} is reduced to N\textsubscript{2}.

The only additional material necessary is the ammonia used for the NO\textsubscript{x} removal. Furthermore, natural gas and water are needed besides small quantities of silicone oil for the acid mist control unit.

The process produces 94 – 95 % pure sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) for sale. The system employs a catalytic converter to oxidise SO\textsubscript{2} to SO\textsubscript{3} at a temperature of 400 – 420 °C. This temperature level allows a deNO\textsubscript{x} operating at 380 °C, to be well fitted in the process. High NO\textsubscript{x} removal at high NH\textsubscript{3} slip is possible with no risk of precipitation of ammonium sulphates, as the reactor temperatures are above the decomposition temperature (350 °C) and any NH\textsubscript{3} slip is destroyed in the SO\textsubscript{2}/SO\textsubscript{3} oxidiser.

The process produces no waste water or waste products, nor does it consume any chemical apart from ammonia for NO\textsubscript{x} control. The high removal of dust is required by the H\textsubscript{2}SO\textsubscript{4} production step. Dedusting with efficiency consistently at 99.9 % is required so as to avoid frequent clean-up of the SO\textsubscript{2}/SO\textsubscript{3} converter and to maintain good product quality.

Sources: [14, DI PISA et al. 2008]

Figure 4.53: SNO\textsubscript{x} process scheme in the Gela refinery
As shown in Figure 4.53, the flue gas train subsequently comprises an air preheater, a high-temperature ESP, the cold side of the regenerative heat exchanger, the deNOx reactor, a heat supply, the SO\textsubscript{2}/SO\textsubscript{3} converter, hot side regeneration heat exchanger, the heat from the acid condenser (operating between 240 – 100 °C, hydrating SO\textsubscript{2} and condensing the resulting acid product) which heat is used as the first step in preheating combustion air. The recovered heat, produced by the conversion process, is substantial and makes up for the power demand when the sulphur content in the fuel (oil or coal) is 2 – 3 %. Areas relating to dust that require attention in operation are the HTEP, the SO\textsubscript{2}/SO\textsubscript{3} converter and the acid falling-film condenser (made of borosilicate glass tubes). Formation of acid mist (aerosol) in the condenser is avoided by a patented heterogeneous nucleation control which is essential for the operation of WSA and SNOx plants.

The SNOx process is divided into four main steps:
- dust removal (ESP). More information in 4.25.4
- selective Catalytic Reduction (SCR) of NO\textsubscript{x}. More information in 4.25.3.3
- catalytic oxidation of SO\textsubscript{2}
- condensation of H\textsubscript{2}SO\textsubscript{4}

**Dust removal (ESP)**
An extensive dust removal from the flue gas is necessary to obtain:
- a long life of the deNOx catalyst
- a long running time between screening of the SO\textsubscript{2} oxidation catalyst
- a high purity of the produced sulphuric acid.

**Catalytic Oxidation of SO\textsubscript{2}**
From the SCR reactor the flue gas is distributed uniformly over the sulphuric acid catalyst in the SO\textsubscript{2} converter. Here the SO\textsubscript{2} initially present in the flue gas is oxidised into SO\textsubscript{3} according to the following reaction scheme:
\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 + 23.6 \text{kcal/gmol SO}_2
\]

**Condensation of H\textsubscript{2}SO\textsubscript{4}**
The SO\textsubscript{3} rich flue gas from the SO\textsubscript{2} converter is cooled from approximately 422°C down to 260°C in the gas/gas exchanger, by heat exchange with the cold unconverted flue gas. Then the SO\textsubscript{3} gas is condensed in the WSA heat exchanger.
When the SO\textsubscript{3} rich gas is cooled, the SO\textsubscript{3} is hydrated to vapours sulphuric acid according to the following reaction scheme:
\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 24.1 \text{kcal/gmol SO}_3
\]
The cleaned gas is discharged into the atmosphere through the stack at 106°C.

**Achieved environmental benefits**
They are summarised as follows:
- removal of up to 98 % of SO\textsubscript{2} and SO\textsubscript{3}, up to 96 % of NO\textsubscript{x}, and essentially all PM
- process qualified for treating high SO\textsubscript{2} concentration flue gas (as in Gela refinery).
- high removal of SO\textsubscript{2}, together with NO\textsubscript{x} and particulate removal (see Table 4.126)
- low additional environmental impacts: no raw material required (only ammonia consumption for NO\textsubscript{x} control), no waste water or waste production
- no cooling water consumption
- production, as by-product of the process, of H\textsubscript{2}SO\textsubscript{4} commercial grade for sale
- high heat recovery.

Particulate removal rate: less than 10 mg/Nm\textsuperscript{3} at ESP outlet
NO\textsubscript{x} removal rate: 90 – 94.7 %
SO\textsubscript{2} removal rate: 91 – 96 % with 5 % v/v O\textsubscript{2} and a temperature of 410°C inlet the SO\textsubscript{2} converter.
Cross-media effects
The electrical consumption corresponds to an installed power of around 10 MW, for a 1 million Nm³/h unit.

Operational data
In Gela, the SNOₓ unit treats the flue-gas from three pet-coke burned boilers (producing 3 x 380 t/h of HP steam) and is designed for 1 million Nm³/h, with an upstream SO₂ concentration ranging from 0.24 to 0.46 % in volume. The ammonia injection rate used to operate the SCR section is about 200 kg/h. The H₂SO₄ production (95 % H₂SO₄ concentration) reaches 13 t/h with a 5.5 % sulphur pet-coke.

Table 4.126: SNOₓ performance from a 72 h-test run after 5 months of operation (Gela)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue-gas flow rate (wet)</td>
<td>Nm³/h</td>
<td>971 000</td>
</tr>
<tr>
<td>Inlet NOₓ (as NO₂)</td>
<td>µg/Nm³</td>
<td>451</td>
</tr>
<tr>
<td>Outlet NOₓ (as NO₂)</td>
<td>µg/Nm³</td>
<td>42</td>
</tr>
<tr>
<td>NOₓ reduction efficiency (¹)</td>
<td>%</td>
<td>90.5</td>
</tr>
<tr>
<td>Inlet SO₂</td>
<td>µg/Nm³</td>
<td>8 243</td>
</tr>
<tr>
<td>Outlet SO₂</td>
<td>µg/Nm³</td>
<td>288</td>
</tr>
<tr>
<td>SO₂ reduction efficiency (¹)</td>
<td>%</td>
<td>96.5</td>
</tr>
<tr>
<td>Outlet SO₃</td>
<td>ppm</td>
<td>3</td>
</tr>
<tr>
<td>Outlet NH₃</td>
<td>ppm</td>
<td>NA</td>
</tr>
<tr>
<td>H₂SO₄ Concentration</td>
<td>% wt</td>
<td>95</td>
</tr>
<tr>
<td>Electricity consumption (Blowers, ESP, pumps)</td>
<td>MWh</td>
<td>132 377</td>
</tr>
<tr>
<td>Ammonia consumption</td>
<td>kg/h</td>
<td>238</td>
</tr>
<tr>
<td>Methane consumption</td>
<td>Nm³/h</td>
<td>456</td>
</tr>
</tbody>
</table>

NB: NA: not available
(¹) Maximum flue-gases available from the boilers during the test run.
(²) After NH₃ grid distribution adjustment efficiency raised to 93 - 95 %
(³) More accurate measurement shows 2 ppm
Source: [14, DI PISA et al. 2008]

In Schwechat, the SNOₓ unit treats the flue-gas from a central CHP power plant fueled with heavy residues from the thermal cracker, together with the tail gases received from the SRU.

Table 4.127: SNOₓ performance (OMV Schwechat)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue-gas flow rate (wet)</td>
<td>Nm³/h</td>
<td>820 000</td>
</tr>
<tr>
<td>Inlet NOₓ (as NO₂)</td>
<td>µg/Nm³</td>
<td>Max 700</td>
</tr>
<tr>
<td>Design outlet NOₓ (as NO₂)</td>
<td>µg/Nm³</td>
<td>&lt;200</td>
</tr>
<tr>
<td>NOₓ reduction efficiency (²)</td>
<td>%</td>
<td>&gt;87 %</td>
</tr>
<tr>
<td>Inlet SO₂</td>
<td>µg/Nm³</td>
<td>Max 8 000</td>
</tr>
<tr>
<td>Design outlet SO₂</td>
<td>µg/Nm³</td>
<td>&lt;200</td>
</tr>
<tr>
<td>SO₂ reduction efficiency (³)</td>
<td>%</td>
<td>&gt;96.6 %</td>
</tr>
<tr>
<td>Outlet SO₃</td>
<td>ppm</td>
<td>NA</td>
</tr>
<tr>
<td>Outlet NH₃</td>
<td>ppm</td>
<td>&lt;1</td>
</tr>
<tr>
<td>H₂SO₄ Concentration</td>
<td>% wt</td>
<td>NA</td>
</tr>
<tr>
<td>Electricity consumption (Blowers, ESP, pumps)</td>
<td>MWₑ</td>
<td>installed</td>
</tr>
<tr>
<td>Ammonia consumption</td>
<td>kg/h</td>
<td>NA</td>
</tr>
<tr>
<td>Methane consumption</td>
<td>Nm³/h</td>
<td>NA</td>
</tr>
</tbody>
</table>

NB: NA: not available
Source: [54, Gallauner et al. 2009]
Chapter 5

Applicability
The Gela Refinery SNOx plant was designed for cleaning the flue gas produced in the boilers at power plant burning a mixture of high sulphur Fuel Oil and high sulphur Petroleum Coke. The Gela Refinery SNOx plant was reported in May 2008 to have been operated with 96% availability on average (including annual planned stops) and no decrease in performance from its start-up in September 1999 (according to measured conversion rates and pressure drops). After a 72500 hour run, the plant had its first general shutdown (1056 hours) for maintenance in June 2006. Only 50% (12 beds out of 24) of the desulphurisation catalyst had been replaced. The SCR catalyst is still the same from the beginning of the plant commissioning.

The Schwechat Refinery SNOx plant started operation in October 2007 and is designed for a turnaround period of a minimum of 6 years.

Economics
A SNOx plant designed for a flue-gas load of 1.0 million Nm³/h at the exit of the existing induced draught fans had a cost of EUR 100 million. For such a unit, reported annual maintenance costs are EUR 4.176 million for a 5-year period between 2003 and 2007, as shown in Table 4.128.

Table 4.128: Maintenance costs (in thousand EUR) of the Gela SNOx plant for 2003-2007

<table>
<thead>
<tr>
<th>Year</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Routine expenses</td>
<td>211.08</td>
<td>423.71</td>
<td>130.04</td>
<td>177.70</td>
<td>124.79</td>
<td>1 067.32</td>
</tr>
<tr>
<td>Extraordinary</td>
<td>112.33</td>
<td>123.21</td>
<td>11.96</td>
<td>128.84</td>
<td>129.79</td>
<td>506.13</td>
</tr>
<tr>
<td>Ordinary outage</td>
<td>14.22</td>
<td>83.03</td>
<td>348.11</td>
<td>1 882.41</td>
<td>274.79</td>
<td>2 602.56</td>
</tr>
<tr>
<td>TOTAL</td>
<td>337.63</td>
<td>629.95</td>
<td>490.11</td>
<td>2 188.95</td>
<td>529.37</td>
<td>4 176.01</td>
</tr>
</tbody>
</table>

Source: [14, DI PISA et al. 2008]

Driving force for implementation
Environmental Italian regulations (D.P.R. 203/88) imposed very severe limit on emissions (particulary on SO₂), so AgipPetroli had to search a way to be able to continue to burn high sulphur pet coke in its power plants in Gela refinery. Reducing air emissions from high sulphur pet coke burning, together with recovering a sulphuric acid by-product at commercial specifications.

Example plants
AGIP Refinery in Gela, Italy (Start-up September 1999), OMV Refinery in Schwechat, Austria (2007), NEFO Power Plant in Nordjyllandsvaerket, Denmark (2005). According to TOPSOE Company, 6 more units were contracted in 2008 for a total of over 5 million Nm³/h of flue-gas.

Reference literature

4.25.9 Odour pollution preventing and control techniques
Note for TWG: After considering the exchange of views through comments received, the entire section on odour monitoring has been moved to Section 3.28.1.5.
4.25.9.1 Use of nitrates for odour control

Description
This technique can be used to reduce the odour generated by any equipment (e.g. storage tanks, sewage systems, oil/water separators) where anoxic conditions can lead to the formation of hydrogen sulphide and other odourous mercaptans in contaminated waters from the biodegradation of sulphur organic compounds by bacteria. This technique consists of adding nitrate-based products in septic water areas, in order to replace bacteria feedstock and to favour the development of denitrificative bacteria which will both reduce added nitrates in nitrogen and existing hydrogen sulphide in sulphates. Nitrate solution can also be injected in bioreactors.

Achieved environmental benefits
In favourable conditions of use, hydrogen sulphide and mercaptans can be significantly reduced and even virtually eliminated. For example:

- an addition of a 400 mg/l nitrate solution in a septic ballast water tank with an appropriate decreasing dosing rate can eliminate a preexisting concentration of 115 mg/l of hydrogen sulphide by >90% after the first 24 hours. After 36 hours, hydrogen sulphide can be almost eliminated, while the nitrate concentration in the treated water remains below 20 mg/l;
- a 250 m³ biofilm reactor has been installed in 1995 for the treatment of ballast waters which have to be stored for long periods (weeks) before being discharged to the waste water treatment plant of a refinery in Norway. The reactor treats up to 600 m³/h of water and removes up to 60 kg H₂S per hour.

The reduction of hydrogen sulphide and mercaptans concentration in the septic pieces of equipment concerned has also major beneficial effects on occupational safety for operators intervening on such equipment.

Cross-media effects
Unappropriate dosing can lead to an excessive contamination of nitrates in the treated waters.

Operational data
The available literature reports:

- a consumption of around 90 – 150 t/year of nitrate-based solution needed for treating the water bottom of a large crude oil tank, avoiding odourous (and dangerous) release of hydrogen sulphide during draining operations;
- a consumption of 100 t/year for the treatment of a ballast water tank kept at a high level as it doubles as a reserved water source for fire fighting. Nitrate-based solution is injected when pumping additional water into the tank, and further additions are made shortly before any discharges.

Applicability
This technique is fully applicable.

Economics
In 2009, the price of the chemical additives used for implementing this technique was around EUR 350 – 550/ton, depending on chemical prices fluctuation, related logistics and number of injection sites at the refinery. In some cases, there could be additional costs for storage tank and pumping system rent.

Driving force for implementation
Elimination of hazardous situations and reduction of odours generated by septic waters

Example plants
This technique is reported to be currently implemented in various refineries operated in UK and Norway.

Reference literature
[ 55, Dixon et al. 2009 ]

4.25.10 Noise prevention and control techniques

Description
Flares, compressors, pumps, turbines and air coolers require particular attention as regards sources of noise. Abatement measures in refineries usually focus on these types of equipment. Note for TWG: this subsection actually contains no operational information and, anyway, has nothing to do in Section 4.25 ‘Waste gas minimisation and treatment’.
4.26 Waste water treatments

This section together with the previous one and the next section are dealing with the end-of-pipe processes that appear in a refinery. Deeper information about the techniques included in this section can be found in the Common waste water and wastegas treatments BREF. The reason why these techniques are appearing here is to give an overall description of the techniques and to avoid repetition. Description of end-of-pipe techniques does not appear in the previous sections. In this Section, general information on environmental benefits, cross-media effects, operational data, applicability is described here. Prevention or minimisation techniques applied to different process activities are found in each of the sections dealing with these production processes. Complementing water management systems that may be found along the document, this section contains the waste water treatments. These techniques are only discussed in this section within this document.

Note for TWG: the intermediate part of this text is translated in Section 4.26.2.

This section only includes the end of pipe processes that appear in treatment of waste water in refinery. Deeper information about the techniques included in chapter can be found in the Common waste water and wastegas treatments BREF.

Note for TWG: this final paragraph is transferred to 4.26.3.

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are or may be implemented for waste waters generated by oil and gas refining.

For a given technique, available data on the way it can be applied and the results it allows for obtaining on particular processes or units have been given in the related sections. The information provided here aims at completing this information on broader aspects, in particular environmental benefits, cross-media effects, operational data, and applicability issues which will not been repeated in other sections.

Moreover, this section also contains a selection of end of pipe processes which concern the whole refinery and have also to be considered in the determination of BAT. Under this category falls the site common waste water treatment plant.

The purpose of the waste water treatment plant is to control the amount of substances in waste water that are emitted to the receiving water body. The configurations of waste water treatment plants may differ from one refinery site to another due to site-specific needs and requirements. The techniques applied at a site may include:

- measures directed at managing waste streams at or near their source
- measures applied downstream of sources to segregate and manage waste streams together that have similar and/or compatible and/or synergistic properties
- end-of-pipe techniques.

When the technique applied includes a biological treatment step, a pretreatment system of sufficient configuration, capacity, coupled with best practices is necessary to assure there is no inhibition of the efficiency of the biological step.
Techniques to consider in the determination of (BAT) include, but are not be limited to:

- techniques that are applied to control routine and non-routine operation and/or maintenance waste water sources that are characterised to have variable flow and/or substance loads that could exceed maximum, including:
  - tank water draws
  - vacuum truck movements
  - equipment clearing activities for maintenance
- waste water source control and efficient operation of the waste water treatment systems
- practices that include utilisation of special procedures and/or temporary equipment to ensure performances are respected when necessary to manage special circumstances such as:
  - spills
  - loss of containment
  - misdirected flows
  - high flow rates
  - high substance load rates from malfunctions
  - incidents
  - routine and/or major maintenance activities.

- practices that assure the cause of deviations in expected treatment performances are identified, immediate corrective action is taken to minimize impact on performance, and corrective actions are implemented to minimize the risk for a repeat occurrence of the deviation.

If needed, further and more in depth information about these techniques, and others that may be applicable to a refinery site, can also be found in the CWW BREF [6, EC 2003].
Chapter 4

Figure 4.54  Process flow diagram of a typical refinery waste water treatment plant

As illustrated in Figure 4.54, a distinction can be made within the global waste water treatment:

- the collection of waste water from units after possible pretreatment
- the removal of insoluble substances: 1st step recovering oil
- the removal of insoluble substances 2nd step recovering suspended solid and dispersed oil
- the removal of soluble substances, including biological treatment (with possible nitrification/denitrification) and clarification
- final treatment systems.

Techniques to consider for these treatment steps are described respectively in sections 4.26.6.1, 4.26.6.2, 4.26.8.1 and 4.26.9.

4.26.1  Management of waste water within a refinery

Note: This section includes reference to techniques described in section 4.15.7

This section try to gives some indication on what can be done in a refinery with in terms of the management of the waste water. In other words, indication will be given as to if it is better to combine waste waters from different processes or if it is better to process them independently in some independent waste water plant. Topics related with to the storage of waste water is also included here. This section deals with process waste water, cooling water and sanitary waste water, ballast water, cleaning water, accidentally oil-contaminated water, continuously oil contaminated water, etc.
Process water integration can be applied at any industrial site, be it a refinery or a combined refinery and petrochemical complex. In this document the concept and practical tools for preparing a process water integration scheme for a refinery is presented. Reference is made to a EU BREF document on waste water treatment.

Description

Some techniques to consider for improving the waste water treatment performance and efficiency in that respect are listed below.

- Apply process water integration (see Section 4.15.7.1).
- Apply water and drainage systems (see Section 4.15.7.2) in order to reuse stripped sour water and sour water can be used to the maximum extent possible as desalter wash water (stripped sour water only) or as wash water in overhead FCC main column to prevent the use of fresh water from natural resources.
- Process water from the dimerisation process should be treated properly because of the high content on phosphate that waste water from this process typically have.
- Use of equalising tanks for the storage of waste water.
- Tanks for the storage of ballast water may cause large VOC emissions. A way to prevent these emissions is to cover the equalising tanks of the waste water treatment systems with floating roofs. Techniques to consider are also included in the Section 4.21.13
- The temperature of the waste water is controlled in order to reduce volatilisation and to secures the performance of the biological treatment.
- Rainwater from polluted plant areas (storm water) should be collected and routed to a treatment plant. For collection a ‘first flush’ scheme may be used. Depending on the initial degree of pollution (mainly oil), the contaminated water should be treated in oil/water/solids-separation systems (API, flotation units, sandfilters) and/or biotreatment units. Non-contaminated water may be discharged directly or reused in order to save costs. It is necessary that the WWTP be able to handle high quantities of rainwater. For this purpose sufficient buffer capacity needs to be installed (storm water tank). Consideration should be made to the implementation of the Water Framework Directive. In locations with low rainfall, segregation of streams is less relevant.
- Control of surfactants in waste water. Surfactants entering the refinery waste water streams will increase the amount of emulsions and sludges generated. They can enter the system from a number of sources including: washing unit pads with detergents; treating gasolines with an end point over 400 °F 200 °C , thereby producing spent caustics; cleaning tank truck tank interiors; and using soaps and cleaners for miscellaneous tasks. In addition, the overuse and mixing of the organic polymers used to separate oil, water and solids in the waste water treatment plant can actually stabilise emulsions. The use of surfactants needs to be minimised by educating operators, routing surfactant sources to a point downstream of the DAF unit and by using dry cleaning, high pressure water or steam to clean oil surfaces of oil and dirt.
- Install a high-pressure power washer. Chlorinated solvent vapour degreasers can be replaced with high pressure power washers which do not generate spent solvent hazardous wastes.
- Use non-hazardous degreasers. Spent conventional degreaser solvents can be reduced or eliminated through substitution with less toxic and/or biodegradable products.

Achieved environmental benefits

Water stream integration and other water management techniques (see Section 4.15.7) aim at reducing the total volume of water used prior to discharge and especially saving high quality potable and demineralised water.

Process effluent volume can be compared to the volumes of process effluent discharged (excluding once through cooling water). Although related, the values are not identical given that there are other sources of water to the effluent system including rainwater on plant surfaces, water separated from crude, ballast water, etc. On the other hand, some water will evaporate, be
used in chemical reactions, etc. The corresponding figures for effluents for 63 European refineries are (all annual averages). Based on Section 3.26 definitions the data of released waste water (2006 to 2008) for 44 European refineries with dedicated waste water treatment plants are the following:

- **Annual average** median (50th percentile) effluent volume: 3.6 million m$^3$/year
- **Range:** 0.07 - 24 million m$^3$/year
- **Specific median (50th percentile)** effluent volume per tonne throughput:
  - 0.53 m$^3$/ tonne throughput
  - 0.44 m$^3$/ tonne throughput
- **Range:** 0.00 to 16.0 m$^3$/ tonne throughput

Other data from an EU+ country with many refineries gives the following ranges depending on the type of refinery:

- 0.1 - 0.3 m$^3$/tonne throughput for pure refineries
- 0.3 - 0.5 m$^3$/tonne throughput for lubricant refineries
- 0.5 - 0.8 m$^3$/tonne throughput for bitumen refineries

Other data from another EU+ country gave a range from 0.18 - 0.21 m$^3$/tonne throughput for three refineries in this country.

Other environmental benefits concern the proper treatment of phosphates, action has been taken in order to reduce the amount of oil to reach the API separators, and the reduction of VOC emissions from waste waters. Reduce the VOC emissions and secure the performance of the biological treatment.

**Driving force for implementation**

To reuse water, reduce the hydrocarbon charge to the waste water treatment and to reduce VOC emissions.

**Reference literature**

[118, VROM, 1999], [197, Hellenic Petroleum, 1999], [107, Janson, 1999], [262, Jansson, 2000], [268, TWG, 2001].

### 4.26.2 Segregation of various waste water streams

Text proposed to delete because addressed elsewhere (in Section 4.15.7).

**Description**

Refinery waste water streams that require monitoring and purification prior to discharge are the following, comprises mainly two streams:

- The first effluent is process water generated in various refinery units as a consequence of steam injection and/or washing hydrocarbon fractions with water. The direct contact with hydrocarbon fractions usually results in a high concentration of dissolved organics. Process water is treated in a sour water stripper (SWS) when it contains hydrogen sulphide and ammonia and is subsequently reused as wash water for the desalter. The resulting effluent is highly contaminated with in oil and solids, has a high chemical oxygen demand (COD > 600 mg/l) and might contain also specific contaminants for which legal limits apply.

- The second significant effluent stream that requires treatment is contaminated rainwater, referred to as surface water run-off, which usually requires only removal of free oil and solids as COD is usually below 100 mg/l.

- Other waste water streams that appear in a refinery are Sanitary water, the cooling water blowdown, tank water bottoms and, eventually, ballast water from ships.
Prior to any effluent treatment, proper segregation and process water integration of main waste water streams should be considered.

4.26.3 Reuse of the treated effluent in refining processes

**Description**

Waste water treatment plants are advanced environmental protection systems for the control of surface water pollution. The purpose of waste water treatment is to remove floating and dispersed oil, suspended solids, dissolved oil, notably BTEX and phenol and other specific compounds such as sulphides, cyanides, heavy metals, phosphate (when polymerisation is present) and nitrogen compounds and other COD. Additionally, the treated effluent can be rendered suitable for reuse in the refinery process. The principle of waste water purification is based on (1) dedicated separation techniques for the dispersed and floating oil and suspended solids from the waste water and (2) removal of dissolved compounds by biological treatment or further treatments.

4.26.4 Sour water stripping (SWS)

Sour water from the various refinery units is, for the main part, stripped in a SWS and can normally be reused together with crude distillation unit overhead wash water as desalter wash water. This is the main process water source in refineries.

**Description**

*One-stage stripping*

Most sour water strippers are single stage, requiring one stripping column. Figure 4.55 shows a typical single-stage sour water stripper. The sour water streams from the process units are collected in a sour water collection vessel. This provides both hold-up for feed and acts as a settler, where oil separation takes place. From this vessel sour water is pumped via a feed/effluent exchanger, to the top of the stripper column. The sour water is counter-currently stripped in the column by steam, either injected live or generated in a reboiler. This column is usually refluxed to reduce the water content in the sour gas. Operating pressure in the column varies from 0.5 to 1.2 barg depending on the destination of the off-gas. Often When necessary pH control is applied to maximise either H2S or NH3 removal.

Sour off-gases from a stripper unit can be routed either to a sulphur recovery unit (SRU), to an incinerator, or to the sour flare. Since off-gases directly routed to an incinerator or a flare can contribute very significantly to the overall refinery release of SO2 (up to 40 %) and NOx, routing to an SRU unit is should be preferred and is now commonly practised. Normally the off-gas from the sour water stripper, leaving the reflux drum contains approximately 30 mol % water.

*Two-stage stripping*

The two-stage sour water stripper differs from the single-stage stripper by operating the first column at a lower pH (6) and, eventually, at a higher pressure (9 barg), removing H2S over the top and NH3/water via the bottom, and the second stage at a higher pH (10), removing the NH3 over the top and a stripped water stream over the bottom. A well designed oil/water separation drum instead of a tank, can also achieve the benefits of reduced hydrocarbon entering the sour water stripper. This results in:

- much lower H2S and NH3 concentrations in the stripped water to be discharged to the effluent treatment plant
- the possibility to send to the SRU only sour off-gases generated at the first stripping stage, which do not contain high NH3 concentrations known as a source of severe perturbation of the Claus reaction due to ammonium deposits.
Figure 4.55: Simplified process flow diagram of a sour water stripping unit (SWS)

Other techniques to consider are:

- Standby stripping facilities or additional storage to be provided for sour water. Duplication of the SWS;
- Sulphide-rich effluents streams should be stripped prior to discharge to effluent treatment. Most commonly SWSs have a surge drum to remove entrained hydrocarbons that can cause upset in the downstream SRU.

**Achieved environmental benefits**

**Single-stage stripping**

The SWS produces sour off-gas and stripped effluent which are routed to down stream units. The table below shows the achievable levels for a single-stage SWS.

<table>
<thead>
<tr>
<th>Source</th>
<th>Flow</th>
<th>Composition min/max</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions: sour gas</td>
<td>SWS off-gas to be routed to SRU</td>
<td>Plant specific</td>
<td>Mainly H₂S and NH₃, content depends on crude quality and refinery configuration</td>
</tr>
<tr>
<td>Effluent: stripped sour water</td>
<td>SWS effluent to be used as desalter wash water or routed to WWTP</td>
<td>20 – 50 m³/h in a 5 Mt/yr refinery</td>
<td>COD: 500mg/l H₂S: 10 mg/ Phenol: 30 – 100 mg/l NH₃: 75 - 150 mg/l</td>
</tr>
</tbody>
</table>

Stripped sour water can be routed to the process units for reuse or to the waste water treatment plant, or preferably, to the process units for reuse, after appropriate cooling if necessary. Normally stripped sour water can be used as desalter wash water, provided its contaminant
levels are adequate (NH$_3$ less than 150 ppm and H$_2$S less than 20 ppm). These limits are required to avoid corrosion in downstream units (i.e. CDU overhead system).

**Two-stage stripping**

Note for TWG (DE): Could you please confirm the reference for this Table (Holborn Refinery) and help clarify the point on NH$_3$ concentration? No extra info made available. 

In the first stage, H$_2$S is separated, whereas in the second one NH$_3$ is removed from water and concentrated to a solution containing 10% NH$_3$ which can be reused to reduce NO$_x$ emissions. Exemplary data of this a typical two-stage stripping are given in Table 4.129.

<table>
<thead>
<tr>
<th>Values parameters</th>
<th>Supply H$_2$S-Stripper Column 1 supply (mg/l)</th>
<th>Efflux NH$_3$-Stripper Column 2 outlet (mg/l)</th>
<th>Final efflux from after treatment by WWTP (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>14 400</td>
<td>599</td>
<td>37</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>98</td>
<td>4</td>
<td>1.1</td>
</tr>
<tr>
<td>N tot. Inorg.</td>
<td>1 373</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>NH$_4^-$N</td>
<td>1 372</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Phenols</td>
<td>182</td>
<td>141</td>
<td>0.1</td>
</tr>
<tr>
<td>Sulphide</td>
<td>1 323</td>
<td>5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The two-stage SWS process can reach an overall H$_2$S and NH$_3$ recovery of respectively 98% and 95% respectively, associated with residual concentrations in the stripped waters in the respective range Hydrogen sulphide: 0.1 – 1.0 mg/l and Ammonia: 1 – 10 mg/l. Sulphide and ammonia loads to be treated in the WWTP are consequently much lower, helping to prevent an additional stage dedicated to treatment (e.g. nitrification/denitrification).

Ammonia generated in the two-stage SWS process can be used within the refinery, in particular to reduce NO$_x$ emissions (SNCR – See in particular Sections 4.5.8.2 and 4.25.3.2). For example, at the Holborn refinery (Germany), the reuse of the NH$_3$-rich effluent from such SWS for a CO boiler achieves a reduction of NO$_x$ of 180 t/yr, NH$_4^-$N of 250 t/yr and solid waste from WWTP of 10% at Holborn refinery.

Other benefits are that the reduction of ammonia and sulphur content in the waste water by SWS. Reduction of ammonia entering the waste water system reduce the need for a nitrification/denitrification process.

**Sour water decantation and equilisation**

The addition of a sour water tank of sufficient capacity homogenises the different water streams, it further removes oil that may cause plugging in the stripper and it helps to produce acid gas of constant composition for the SRU. As less hydrocarbon enters into the SRU, less coking of catalyst results. Catalysts are better protected against coking phenomenon, with favourable effects on SRU efficiency and reliability.

**Cross-media effects**

Routing the off-gases from the stripper unit, especially in the case of a single-stage SWS, can negatively influence the efficiency and the running conditions of the SRU mainly due to the NH$_3$ content in the gas. In the case of a 2-stage SWS, the steam consumption increases significantly with the stripping capacity and pressure.

Combination of 2 stage sour water stripping and reuse of NH$_3$-rich effluent for reduction of NO$_x$ from CO boiler achieves reduction of NO$_x$ by 180 t/yr, NH$_4^-$N by 250 t/yr and solid waste from WWTP by 10% at Holborn refinery.
Most commonly SWSs have a surge drum to remove entrained hydrocarbons, that can cause upsets in the downstream SRU. The SWS feed is normally preheated by feed/effluent exchangers to a tower inlet temperature of 100°C to save stripping steam. A higher feed temperature than 100°C is not advisable since the flashing of the feed upon entry to the stripper tower is to be avoided. For a stripper operating at higher pressure higher temperatures are tolerable. Nevertheless, a feed temperature which results in flashing of the feed in the feed line to the stripper tower is to be avoided.

Decreasing the water content in the off-gas below 30 mol % is not practised as problems with salt deposition from the vapour phase can occur. This salt deposition particularly occurs when CO₂ is present in the sour gas, and the level of corrosive ammonium bisulphide (NH₄HS) in the condensate refluxed to the stripper column increases beyond the level acceptable from a materials and corrosion perspective.

The use of a second stripping column consumes extra chemicals for pH control (acid, caustic) and extra energy.

**Applicability**

Two-stage stripping: in case the SWS bottoms are not reused but are sent to biotreating they may still contain too much NH₃. In order to solve this in the SWS unit, the SWS column can either be equipped with a larger number of stages or a two-stage stripper can be installed (Section enclosed in dotted box in Figure 4.55). In the case of retrofitting for a two-stage stripper, existing SWS can be converted to sour water concentrators to reduce its size. The more or less pure ammonia stream from the second stripper top might be sent to the CO boiler of the FCC unit for deNOxing NOₓ reduction purposes or to the hot flue-gas of a furnace.

**Economics**

The cost for new steam strippers depends on the flow rate and range from about EUR 0.525 – 0.700 million Note for TWG: Very unclear. Is it per capacity unit ? Anybody able to confirm?

The investment costs for expansion of existing sour water stripping in the NH₃ stripper were about EUR 3.3 million. Annual operating costs (steam, energy, cooling water, sulphuric acid, caustic lye, fuel gas) for the entire plant is approximately EUR 0.45 million. In contrast to the annual operating cost for operation of only H₂S strippers (EUR 0.35 million), the annual operating cost are approximately 75000 EUR because the expansion of the NH₃ stripper.

In a French refinery, an existing single-stage low-pressure SWS was upgraded in 2010 by adding a new high-pressure stage (9 barg - 180°C – 30 t/h) dedicated to H₂S removal. Expected investment cost is EUR 24.8 million, obviously much higher than the cost range for a low-pressure stage.

Other data for different sour water strippers are shown in Table 4.130.

### Table 4.130: Economics and performance of sour water strippers

<table>
<thead>
<tr>
<th>Year built</th>
<th>Design NH₃ effluent conc. (mg/l)</th>
<th>Actual performance (mg/l NH₃)</th>
<th>Design flow rate (m³/h)</th>
<th>Capital cost (million EUR)</th>
<th>Operating cost/yr (10^6EUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996</td>
<td>18</td>
<td>22</td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1996</td>
<td>10</td>
<td>30</td>
<td>4.0</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>1992</td>
<td>Max 150</td>
<td>13</td>
<td>20</td>
<td>0.6</td>
<td>97</td>
</tr>
<tr>
<td>1993</td>
<td>50</td>
<td>25</td>
<td>5.4</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>1995</td>
<td>50</td>
<td>32</td>
<td>5.3</td>
<td></td>
<td>175</td>
</tr>
<tr>
<td>1992</td>
<td>100</td>
<td>50</td>
<td>10.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Operational data

<table>
<thead>
<tr>
<th>Electricity (kWh/t)</th>
<th>Steam consumed (kg/t)</th>
<th>Acid and caustic consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 – 3</td>
<td>100 – 200</td>
<td>NA</td>
</tr>
</tbody>
</table>
Driving force for implementation
Nearly all refinery processes have steam injection to enhance the distillation or separation processes. This leads to the production of sour water (containing ammonia and hydrogen sulphide) and/or steam condensate, that will be contaminated with hydrocarbons. Sour water needs stripping prior to further treatment or reuse as wash water. A typical composition of the sour water is 900 mg/l of hydrogen sulphide, 2000 mg/l ammonia, 200 mg/l phenols and 15 mg/l hydrogen cyanide.

Example plants
Two-stage stripping is seldom applied in refineries. In the Holborn refinery in Germany, a two-stage SWS is integrated as an alternative to an effluent denitrification stage in the WWTP. Also in the new Mider refinery a two-stage SWS unit has been installed. The company Total will operate one in Feyzin in 2010 (with a high-pressure single-stage).

Reference literature
[19a, Irish EPA, 1993], [257, Gilbert, 2000], [118, VROM, 1999], [211, Ecker, 1999], [127, UN/ECE, 1998], [302, UBA Germany, 2000], [181, HP, 1998], [316, TWG, 2000], [115, CONCAWE, 1999].

4.26.5 Reduction and recovery of hydrocarbons from waste water at source

Description
Benzene, phenols and hydrocarbons in general in waste water can often be treated more easily and effectively at the point it is where they are generated rather than at the waste water treatment plant after it is mixing with other waste water. Consequently the identification of hydrocarbon sources is the first measure to consider. The techniques described below have been identified by a number which is then used throughout this section. More information is available for each technique in the CWW BREF [6, EC 2003].

1. Nitrogen or air stripping for benzene recovery from waste water. Nitrogen stripping can be used to strip benzene and other low aromatic compounds from waste water. The mixture is treated by activated carbon beds that capture the organic allowing cleaned nitrogen to recycle to the waste water stripper. Periodically, the carbon bed is in situ regenerated with live steam: desorbed organic vapours are carried by the steam to a condenser and are subsequently decanted into organic and water layers. Organics are returned to the refinery as valuable feed.

2. Liquid-liquid extraction from waste waters for phenol extraction from waste water using a countercurrent extraction column. After distillation, the solvent (e.g. butyl acetate) is recycled back to the extraction column.

Reduction of hydrocarbons and aromatic compounds

3. High-pressure wet air oxidation (>20 barg). Water is intensively mixed with air and organic compounds are oxidised in the presence of a catalyst at high temperature and high pressure (250 ºC, 7 MPa). Sulphur-containing substances are oxidised to sulphates; amines and nitriles are converted to molecular nitrogen ammonia that will require a biological or physical treatment step. More information is available in the CWW BREF [6, EC 2003].

4. Low-pressure oxidation (<20 barg). Persistent organic compounds are treated with oxygen and are mineralised in a biological treatment plant (BOC gases).

Addressed in emerging techniques of the CWW BREF [6, EC 2003]:

6. Supercritical water oxidation process. Supercritical water (373 ºC, 221 bar) is used to dissolve organic compounds, which are oxidised in a reactor by injection of oxygen.

7. Energy absorption technology. Sources of contamination with hydrocarbons are desalters (40 %), storage tanks (20 %), slop systems (15 %) and other processes (25 %). It is possible to recognise type and extent of water contamination directly at the source by use of high electromagnetic frequencies (EA – Energy Absorption Technology).
Achieved environmental benefits
1. A refinery has used that system to reduce 1895 l/d of waste water containing 50 ppm of benzene, 100 ppm of toluene/xylenes and 100 ppm of other hydrocarbons liquids. The recovery unit consistently reduced benzene to below 500 ppb. About 35000 kg of hydrocarbon liquid are returned to the refinery feedstock annually. This technique can also be applied to remove MTBE.
2. Recoveries greater than 99 % or raffinate concentrations well below 1 ppm can be achieved. With this technique waste water containing >1 % phenols was treated to get purified water with a phenol content lower than 1 ppm (Efficiencies: higher than 99 %; Koch Process Technology, Inc.). Phenol-containing waste water may also be treated microbiologically.
3. The efficiency of this process is stated to be 99 % for a COD of 30000 mg/l. Sodium sulphide of spent caustic can be reduced from 3 % to <1 mg/l (160°C; 0.9 MPa).
4. No data. Abatement efficiency could be 99 % [6, EC 2003].
5. Efficiency can be higher than in the range 60 – 90 % 99.9 % [6, EC 2003].
6. With this system, emissions of hydrocarbons to water could be reduced (e.g. benzene contamination: minus 80 %).

Operational data
1. Nitrogen stripping has several advantages over air: oxygen does not reduce biological fouling of the stripper and nitrogen reduces the risk of refinery upsets creating explosive mixtures in the recovery unit.
2. Typical utilities consumption typical per m³ water feed are:
   - electricity: 159 kWh
   - steam (20.7 barg): 15.6 kg
   - steam (2.07 barg): 103 kgs
   - water tempered at 45 °C (ΔT = 19 °C): 5.6 m³
   - water cooling at 29 °C (ΔT = 11 °C): 2.5 m³

Applicability
1. This technology is used for the treatment of desalting water and waste water from BTEX-plants (Texaco Development Co; AMCEC, Inc.)
2. They can be designed to handle waste water streams with phenol levels from several hundred ppm to saturation (approx. 7 %) and above.
(2) This method is not applied for high flows.

Economics
1. The design and equipment supply cost of about USD 1 250 000. Annual utility costs are around USD 85 000.
2. Cost effective for levels of phenols higher than 1 %. A base case example for a waste water stream of 27.2 m³/h containing 6 % phenol was treated with 4.3 m³/h solvent in a four-column system. The overall phenol recovery was 99.3 %.
   - Investment, extractor only: USD 1.32/m³
   - complete system: USD 3.43/m³
   - Recovered value: USD 3.96/m³
(3) This method is considered as very expensive.

Driving force for implementation
Reduction and recovery of hydrocarbon
Example plants

1. More than 15 systems ranging from 800 to 120 00 l/min are now operating in various US refineries. Air stripping for the removal of MTBE has been used successfully in at least one European refinery.

2. This system is typically applied when phenol concentrations are high. This type of system treats waste water for a US resin producer.

Reference literature
[181, HP, 1998], [211, Ecker, 1999], [316, TWG, 2000], [321, Helm, Spencer et al., 1998] [2008 data collection questionnaires] [6, EC 2003].

4.26.6 Primary treatments Removal of insoluble substances
Text on 1st step treatment has been moved to 4.26.

Waste water collection
The collection of waste water from the various units after any specific process treatment can be considered part of the global waste water treatment. Actually, a waste water treatment plant (WWTP), especially with a biological step, operates most effectively under constant conditions (pH, hydraulic load or flow rate) and pollutant load or concentrations.

To buffer the WWTP operation against short-term (e.g. daily) and long-term (e.g. weekly) variations, equalisation facilities are in place, either decentralised at the various production installations or centrally in or near the WWTP. The buffering and retention volumes also allow analysis to check compatibility of the waste water influent with the subsequent treatment. Flow and load/concentration balancing are also referred to as equalisation, buffering or homogenisation. More information on this pretreatment step is available in the CWW BREF [6, EC 2003].

Process water coming from the SWS is one of the main process water sources in refineries. Moreover, some incompatible process effluents and drains from off-sites (flares and tanks) add to the total flow of process water. This effluent has to pass first an oil/water separator (CPI, PPI or API) for free oil and solids removal and an equalisation tank where sometimes further oil skimming can be accomplished.

Note to TWG: Former text on preventing odour from this step treatment has been moved to Section 4.26.11.

4.26.6.1 Step 1 – Oil removal

Description
The purpose of this step is the separation and extraction of insoluble hydrocarbon. These techniques rely on the principle of difference in gravity between the phases (liquid – liquid or solid – liquid): the phase with higher density will settle and the one with lower density float to the surface.

Step 1 may generally include:

- API separators (APIs);
- Corrugated plate interceptors (CPIs);
- Parallel plate interceptors (PPIs);
- Tilted plate interceptors (TPIs);
- Buffer and/or equalisation tanks.
Internal corrugated plates used in CPIs, PPIs, and TPIs reduce the residence time required to achieve separation of the insoluble hydrocarbons targeted for removal and, therefore, reduces the required separation system compared to APIs.

These techniques aim at achieving separation and extraction of free oil droplets generally greater than or equal in size to 150 µm.

The water phase exiting these separation systems will generally contain insoluble dispersed oil droplets, emulsified oil droplets, suspended solids, soluble oil not in the form of droplets, soluble inorganic substances, soluble organic substances, and trace amounts of insoluble free phased hydrocarbon and settleable solids.

Accumulations of viscous and/or semi-solid hydrocarbon materials with little fluid characteristics may not be effectively removed by gravity flow using a fixed position overflow skimming pipe. Close operator monitoring and intervention on demand may be necessary to extract viscous and/or semi-solid hydrocarbon material accumulation on the surface using manual measures.
Achieved environmental benefits
Performance of CPIs and APIs as regards oil removal suggests 50 – 100 ppm oil in the outlet. Text moved to 4.26.11.

Cross-media effects
Separators operating with internal corrugated plates are susceptible to solids fouling.

These systems may not be equipped with internal mechanical solids extraction systems or internal mechanical oil extraction systems. Systems not equipped with internal mechanical solids extraction systems may be at risk for solids accumulation and eventual plate pack fouling from the bottom up if accumulated solids cannot be effectively removed through either the gravity drain and/or pump-out techniques.

Systems not equipped with internal mechanical oil extraction systems may be at risk for hydrocarbon accumulation on the surface of the water phase.

When separators are not covered they can lead to VOC emissions.

Operational data
Covers can present problems for the skimming of free oil.
Data?

Applicability
These systems are fully applicable. CPIs are easier to cover than APIs. Retrofitting to existing separators may be complicated depending on structural design, type of mechanical oil skimmers and solid scraper systems used, and position of electrical drivers. Significant modifications may be needed.

Economics
Costs are estimated with at about 460 EUR per kt of HC emissions reduction by provision of floating covers for waste water separator bays. For covering, the investment for the installation of two 200 m$^3$ floating slab covers is about EUR 75,000 and the total annual operating costs about EUR 42,800 per year. Moved to 4.26.11
Table 4.131 Examples of costs for API units

<table>
<thead>
<tr>
<th>Year built</th>
<th>Type</th>
<th>Capacity (m³/h)</th>
<th>Capital cost (EUR x 10^6)</th>
<th>Operating cost/yr (EUR x 10^3)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>API</td>
<td>750</td>
<td>8.825</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1962</td>
<td></td>
<td>600</td>
<td></td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>1966</td>
<td></td>
<td>187</td>
<td></td>
<td>148</td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td></td>
<td>300</td>
<td>0.694</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td></td>
<td>1100</td>
<td>8.500</td>
<td>Estimation for a new API unit</td>
<td></td>
</tr>
</tbody>
</table>

Source: [120, CONCAWE 2012]

Driving force for implementation

Reduction of VOC emissions and odours. Maximising the collection of oil. It has been estimated that between 0.5 and 4% of the crude oil processed in a refinery can be found in the waste water before any treatment, depending on the complexity of a refinery. Consequently, oil is always recovered from the drainage system before the waste water is passed for final treatment.

Example plants

Well proven technologies. In some European refineries, the API and PPI. From 44 refinery sites from the TWG sample data collection with dedicated WWTPs, 42 reported having one separator and among them 11 were covered. See detailed figures in Table 4.135. Separators have been progressively covered in a growing number of European refineries.

Reference literature

[107, Janson, 1999], [115, CONCAWE, 1999], [258, Manduzio, 2000], [127, UN/ECE, 1998], [247, UBA Austria, 1998], [48, TOTAL 2010], [119, CONCAWE 2011].

4.26.6.2 Step 2 - Further oil/water/solid separation

Description

This further step requires the use of chemicals to improve the solid/liquid or liquid/liquid separation of the remaining hydrocarbons and suspended solids in the waste water stream after the first step treatment. An injection of coagulant or flocculant is necessary to trap the oil droplets and the suspended solids that passed the first treatment. In order to improve the flocculation, a pH adjustment may be required prior to it.

Techniques for this treatment step may include:

- Dissolved gas flotation (DGF);
- Induced gas lotation (IGF);
- Sand filtration.

DGF and IGF are the same techniques as respectively DAF and IAF used in other industrial sectors where air bubbles will permit to float the flocculated. But where particles potentially explosive vapors may accumulate, the pressurization system uses gases instead of air to reduce risks.

DGF and IGF techniques aim at achieving separation and extraction of free oil droplets generally less than 150 µm in size, emulsified oils and suspended solids. The formed sludge is brought to the water surface by air flotation whereby tiny air bubbles are also captured by the sludge flocs. The sludge is skimmed off and the water is routed to a biotreater the next treatment step. Sand filtration (or dual-media) is an alternative process to the flotation. Clarifiers may also be an alternative.

For all these separation techniques, the size of the flocs entering the separation step is crucial. Only flocs over several µm will be stopped. If the flocculation is not efficient, oil and particles...
will pass through the process. The water phase exiting this step will generally contain soluble oil not in the form of droplets, soluble inorganic substances, soluble organic substances, and trace amounts of free oil droplets, dispersed oil droplets, settleable and suspended solids.

### 4.26.7 Secondary treatments

The next step after the primary treatments is that waste water is processed for the removal of dispersed oil and solids by air flotation where with the aid of polyelectrolytes flocs are formed which capture oil and suspended solids (sometimes a sand filter is used for this duty).

Text on odour has been moved to Section 4.26.11

Another technique to consider for this step is:
- the treatment of the DAF float separately, rather than sending it to the slop oil system;
- Use continuous slip stream filtration to remove amine degradation products.

#### Achieved environmental benefits

Flotation units achieve 10 – 20 ppm of oil and prepare the waste water to benefit for a good biological treatment.

#### Cross-media effects

These techniques may lead to VOC and HC emissions. See section 4.26.11 for odour reduction.

#### Operational data

Chemicals utilisation includes acid and/or alkali for pH correction, polyelectrolyte or FeSO₄ or FeCl₃ flocculant coagulant requirements or polyelectrolyte for of the flocculation units. In practice, pH correction and polymer dosing to the flocculation flotation unit need daily attention and fine tuning if needed. The energy requirement for the WWTP is relatively low, the aeration compressor being the largest consumer.

#### Applicability

Fully applicable.

#### Economics

<table>
<thead>
<tr>
<th>Year built</th>
<th>Type</th>
<th>Design flow rate (m³/h)</th>
<th>Capital cost (EUR x 10⁶)</th>
<th>Operating cost/yr (EUR x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>DAF</td>
<td>80</td>
<td>0.2</td>
<td>18</td>
</tr>
<tr>
<td>1994</td>
<td>DAF</td>
<td>300</td>
<td>1.4</td>
<td>20</td>
</tr>
<tr>
<td>1989</td>
<td>IAF</td>
<td>400</td>
<td>2.4</td>
<td>47</td>
</tr>
<tr>
<td>1993</td>
<td>DAF</td>
<td>350</td>
<td>8.0</td>
<td>683</td>
</tr>
<tr>
<td>1996</td>
<td>IAF</td>
<td>818</td>
<td>0.4</td>
<td>112</td>
</tr>
<tr>
<td>1996</td>
<td>DAF</td>
<td>50</td>
<td>3.1</td>
<td>–</td>
</tr>
<tr>
<td>1996</td>
<td>DAF</td>
<td>800</td>
<td>1.5</td>
<td>–</td>
</tr>
</tbody>
</table>

#### Driving force for implementation

To reduce the hydrocarbon and solids content from waste water Reduce VOC and odours.

#### Example plants

Well proven technologies. From 44 refinery sites from the TWG sample data collection with dedicated WWTP, 40 reported having one flocculation step (mainly DAF type) and two reported the use of a sand filter. See detailed figures in Table 4.135.
4.26.8 Tertiary treatments
4.26.8.1 Step 3 – Biological treatment

Description
Step 3 aims at biological assimilation of the soluble hydrocarbons, inorganic substances and organic substances that are contained in the water phase after previous treatment steps. Insoluble substances contained in the water phase that exits Step 2 may also be subject to biological assimilation.

Biological treatment techniques may include:

- fixed bed systems
- suspended bed systems.

One of the most commonly used suspended bed systems in refinery WWTPs is the activated sludge process. Fixed bed systems may be, for example the biofilter or trickling filter.

By using these techniques, soluble substances are removed from the waste water through the process of adsorptive contact with the biomass, followed by absorption into the biomass and assimilation of the soluble substances. This assimilation results primarily into new biomass growth and carbon dioxide from the biomass respiration process.

The biomass maintained in the bioreactor is typically a mixture of naturally occurring microorganisms that are acclimated to assimilating the soluble substances in the waste water.

A clarification step may be necessary to separate the biomass solids from the biologically contacted waste water prior to discharge to the environment.

Suspended bed biological treatment systems can be configured for biological nitrification/denitrification.

VOC emissions during aeration can be minimised by replacing shallow aeration turbines with air (or oxygen) dosing devices at the bottom of the aeration basin.

After the sludge is skimmed off in the flotation process, the water is routed to a biotreater, usually an activated sludge unit or to a trickling filter. By means of bacteria nearly all dissolved hydrocarbons and other organics are removed.

Nitrification/denitrification

In case deep nitrogen removal is required, denitrification in a biotreater is an option. Oxygen using (aerobic) bacteria is able to convert ammonia into nitrate and in a so called anoxic stage (without aeration) in the biotreater other bacteria are able to convert nitrate into atmospheric nitrogen, which escapes as bubbles. The generated biomass or biosludge is allowed to settle in a clarifier and for the main part recycled to the biotreater. Primary sludge from the flocculation unit and excess biosludge are usually sent to a thickener prior to dewatering and disposal (Figure 4.59). Air Flocculation Flotation processes can be operated with Dissolved or Induced Air (DAF or IAF resp.).

Through this system, biological nitrification occurs with oxygen where ammonia-nitrogen is oxydised to nitrite (with Nitrosomonas bacteria) and then to nitrate (Nitrobacter). Subsequent biological denitrification of nitrate to nitrogen gas takes place under anoxic conditions and in presence of a carbon source (heterotrophic bacteria).
Chapter 5

Other techniques to consider follow:

- Heterotrophic denitrification combined with autotrophic sulphide oxidation (the reductive potential of sulphide is used to eliminate nitrogen via denitrification. Simultaneously, sulphide is oxidised, so that sulphide precipitation in subsequent biological treatment unit is unnecessary).
- use of granular activated carbon (GAC). Pollutants are adsorbed and biologically treated in an oxygen rich atmosphere. (attainable COD: <100 mg/l)
- use of powdered activated carbon (PAC, similar to GAC)
- the Macro-porous polymer extraction (MPPE) which can be placed upstream of the biological treatment plant. It uses porous polymer beads containing an immobilised extraction liquid. Based on high affinity of the hydrocarbon components for this liquid, phenols, BTEX, PAH, etc. can be removed.
- covering of the waste water treatment plant. Fixed covers are to be avoided have to be designed taking into account loss prevention purposes (building up of explosive vapours)
- emissions to air of VOC (including benzene) and odorous components (hydrogen sulphides and mercaptans), are not uncommon and cannot always be controlled fully by up-stream measures. Therefore sometimes the aeration basins of biotreaters can be provided with covers as an emission reduction measure, sometimes with off-gas treatment (use of a biofilter or reinjection into the aeration basin).
- safety aspects (i.e. the explosiveness of VOC-air mixtures) are to be attended, however they are less dangerous than in up-stream units.

**Achieved environmental benefits**

A biotreater can remove 80 – 90 % of dissolved oil and COD as well as 90 – 98 % of BOD under normal operating conditions. Natural nitrogen removal is normally about 10 % in an activated sludge unit (ASU), 70 – 80 % in a nitrification/denitrification biotreater (DNB) and up to 90 % in a tertiary (add-on) denitrification unit. For MAH/phenol >95 % removal can be achieved based on a well-adapted biological system. Oxygen aeration in activated sludge plants can be up to 50 % more efficient than air aeration techniques.

**Cross-media effects**

Energy consumption, activated carbon wastes when GAC or PAC are applied and methanol consumption (for heterotroph bacteria) when denitrification is applied. Waste water treatment generates sludge. If waste water treatment is not properly operated the amount of sludge can be increased.

**Operational data**

If a denitrification biotreater is applied pumping energy is relatively high. If a tertiary treatment unit is used for ammonia removal by biological nitrification, methanol can be used as in a subsequent denitrification stage as an oxygen receptor for denitrifying bacteria. In some refinery biotreaters powdered activated carbon is dosed for meeting discharge specs. The sensitivity of a biotreater against shock loads (peak discharges) of toxic compounds (e.g. sulfolane, MTBE, phenol, cyanide, sulphide) is relatively large and should be avoided. Methods to consider include spill prevention measures, appropriate procedures good housekeeping and equalisation in a buffer tank.

**Applicability**

Fully applicable, bearing in mind that toxic or inhibitory streams should not enter a biotreater.

For additional information, the CWW BREF [6. EC 2003] provides input concentration thresholds for a list of substances that are toxic to a biological activated sludge process (Table 3.9 p 139) and substances that are likely to inhibit a biological nitrification/denitrification process (Table 3.11 p 148). Furthermore, other inhibitors to nitrification than these referred to in the CWW BREF should be considered: ammonium and nitrite, sulphides, benzene and phenols.
Ammonium and nitrite
Ammonium and nitrite can slow down nitrification, mainly in non-dissociated form (NH₃ and HNO₂). The effects of ammonium and of nitrite on Nitrosomonas and Nitrobacter bacteria species, that are mostly involved in the biological nitrification activity, are a function of the concentrations and pH values as shown in the Figure 4.58.

*Nitrosomonas*, responsible for the degradation of ammonium into nitrite, are inhibited at concentrations of free ammonia between 10 – 150 mg/l. *Nitrobacter*, in turn, degrade nitrite in nitrate but are inhibited at concentrations of free ammonia between 0.1 – 1 mg/l.

When *Nitrobacter* are inhibited, non-dissociated nitrite can have a retro-effect on *Nitrosomonas* at concentrations between 0.2 and 2.8 mg/l, which causes nitrification to stop almost entirely.

When the active sludge is acclimated, nitrification will take place even if the concentration of ammonia or nitrous acid is higher than the limit values listed above. Concentrations of 10 mg/l NO₂-N are not expected to cause problems during nitrification.

---

**Figure 4.58:** Nitrification tolerance of *Nitrosomonas* and *Nitrobacter* species

*Legenda:*
*Zone A:* inhibition of *Nitrosomonas* and *Nitrobacter* by ammonia
*Zone B:* inhibition of *Nitrobacter* by ammonia
*Zone C:* full nitrification
*Zone D:* inhibition of *Nitrobacter* by nitrous acid.

Sulphides
The biological nitrification processes need very low concentrations of heavy metals in complexated forms. However, sulphurous compounds are strong inhibitors to nitrification, as they have a chelating effect which limits the availability of these heavy metals. Sulphide itself can already inhibit the nitrification at concentrations as low as 0.5 mg/l, leading to a strong reduction of the activity of nitrifying bacteria.

Benzene and phenol
In favourable conditions, an aerobic WWTP is able to cope with concentrations of phenols up to 400 mg/l without any effect on the active sludge. However, high phenol concentrations and phenol peaks are toxic for nitrifying bacteria. Benzene is less toxic for nitrifying bacteria than phenol. However, *Nitrosomonas* have an enzyme which can oxidise benzene into phenol, and consequently increase the substrate toxicity. In Table 4.133 are reported some concentration levels associated with their inhibition effects.
Table 4.133: Inhibition effects of phenol and benzene on the biological nitrification

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Degree of inhibition (1)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 mg/l</td>
<td>IC50 Nitrosomonas</td>
<td>Blum en Speece (1991)</td>
</tr>
<tr>
<td>5 – 6 mg/l</td>
<td>IC75 in active sludge</td>
<td>Dyreborg (1995)</td>
</tr>
<tr>
<td>4 – 10 mg/l</td>
<td>Minimum inhibition limit value</td>
<td>Eysenbach (1994)</td>
</tr>
<tr>
<td>3 mg/l</td>
<td>IC50 Complete inhibition</td>
<td>Juliastuti (2003)</td>
</tr>
<tr>
<td>50 mg/l</td>
<td>Acclimatisation of sludge by gradually highering the concentration</td>
<td>Stafford (1974)</td>
</tr>
<tr>
<td>100 mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>IC50 Nitrosomonas</td>
<td>Blum en Speece (1991)</td>
</tr>
</tbody>
</table>

NB: IC = the concentration of an inhibitor that is required for 50 % inhibition of its target.

According to many sources, mainly peak concentrations are really problematic for nitrification, which can be partially solved by installing enough up-stream buffering capacity.

Economics
A complete API, equalisation tank, DAF, DNB biotreater, clarifier train for 125 m$^3$/h requires an investment cost of about EUR 15 million provided the up-stream drainage infrastructure is available. Operating costs are in the order of EUR 1.5/m$^3$.

A floating cover (assuming a 800 m$^3$ h process capacity of oily water, with VOC emission up to 1000 t/yr) will result in a 90 % VOC recovery efficiency for the following costs:

- Investment cost EUR 0.6 million
- Operating cost: EUR 0.03 million per year

Examples of recent costs data for biotreatment

In France, a recently (2009-2010) installed 5 000 m$^3$ aeration tank biotreater, treating 450 m$^3$/h, was built for EUR 18 million (costs including only building and installation of the basin).

Two other examples of re-engeenered WWTP are provided in Table 4.134.

Table 4.134: Example of cost for waste water treatment plant at a refinery site

<table>
<thead>
<tr>
<th>Site reference and description</th>
<th>Units</th>
<th>Capacity</th>
<th>Capital cost (million EUR)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONCAWE 1 Re-engeneering of WWTP system 2003 to 2005</td>
<td>DAF (2 units)</td>
<td>750 m$^3$/h</td>
<td>8.860</td>
<td>4.430 per unit</td>
</tr>
<tr>
<td></td>
<td>Bioreactor (Biox design)</td>
<td>1 000 m$^3$/h</td>
<td>5.565</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sludge management system</td>
<td>-</td>
<td>2.970</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DAF VOC recovery system</td>
<td>-</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total units costs</td>
<td>-</td>
<td>17.479</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total project costs</strong></td>
<td></td>
<td><strong>40.000</strong></td>
<td>including API covering + non process stream separations</td>
</tr>
<tr>
<td>CONCAWE 2 Re-engeneering of WWTP system 2005</td>
<td>Existing DAF upgrading</td>
<td>NA</td>
<td>2.000</td>
<td>2 units</td>
</tr>
<tr>
<td></td>
<td>Bioreactor (Biox) upgrading</td>
<td>NA</td>
<td>2.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stormwater collection tank</td>
<td></td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total units costs</td>
<td></td>
<td>5.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Total project costs</strong></td>
<td></td>
<td><strong>NA</strong></td>
<td></td>
</tr>
</tbody>
</table>

Source: CONCAWE 2011
Driving force for implementation
Removal of dissolve organic compounds by biological treatements.
Denitrification biotreaters are usually applied in environments sensitive to nitrates.

Example plants
Well proven technologies. From 44 refineries TWG data collection, 30 reported an activated sludges technique, 8 reported a biofilter or a trickling filter technique. In addition, 12 refineries reported a nitrification or denitrification step technique. See detailed figures in Table 4.135.
Nitrification/denitrification biotreater installations are operational at least at Harburg and Rheinland (DE) Gother and Gothenburg (SE) refineries, and an anoxic reactor at Antwerp (BE).
An MPPE-unit (Macro Porous Polymer Extraction) is installed at the Kollsnes and Ormen Lange gas plant (NO) for reducing organic components in the process water.
Anqing refinery (China) is to operate in 2012 a 1 000 m3/h powdered activated carbon treatment unit combined with biological treatment in order to reuse 500m3/h of water from this site.

Current use of waste water techniques in refineries has been investigated in 2008 through a CONCAWE survey whose results are the following.

Table 4.135: Type of waste water treatment reported by refineries (CONCAWE survey 2008)

<table>
<thead>
<tr>
<th>Treatment type</th>
<th>Number of sites</th>
<th>Type of biological treatment</th>
<th>Number of sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three stage biological</td>
<td>103</td>
<td>Activated sludge</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trickling filter</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerated lagoon</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Non-aerated lagoon</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fixed bed biofilm reactor</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerated tank</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Other</td>
<td>1</td>
</tr>
<tr>
<td>Mechanical</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Physical</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>API separator</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>External WWTP</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>125</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A study made, by a Norwegian refinery, in 2005 to compare the MPPE and the Activated Carbon (AC) adsorption processes showed the following cost (see Table 4.136).

Table 4.136: Examples of costs of two waste water treatment processes at a gas plant in Norway

<table>
<thead>
<tr>
<th>Process</th>
<th>Capital cost (million EUR)</th>
<th>Operating cost/yr (10^3 EUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro Porous Polymer Extraction</td>
<td>0.5 – 0.6</td>
<td>130</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>0.26 – 0.39</td>
<td>39</td>
</tr>
</tbody>
</table>

NB: Cost estimated from conversion ratio (2005) of 1 NOK = EUR 0.1289

Reference literature
[181, HP, 1998], [45a, Sema and Sofres, 1991] [16, Polders 2009] [112, CONCAWE 2011]
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4.26.9 Additional treatments

In countries where water is a scarce resource it is sometimes economically attractive to further improve the quality of the effluent in order to reuse the water as wash cooling water or even as a source for the preparation of boiler feed water (BFW). In that case sand filtration (SF), followed by a combination of ultrafiltration (UF) or activated carbon filtration (AC) and reverse osmosis (RO) for salt removal generates sufficiently pure water for entering the demineralisation unit of the BFW preparation unit. Other techniques are ozonation/oxidation, ion exchange and incineration.

Description
Techniques for the reduction of salt contents of the waste water includes: ion exchange, membrane processes or osmosis. Metals may be separated by precipitation, flotation, extraction, ion exchange or vacuum distillation.

Achieved environmental benefits
See Section 4.26.10

Cross-media effects
Energy consumption, wastes and concentrates from exhausted activated carbon, membranes and metal sludges.

Operational data
Activated carbon is needed if AC filtration appears in the system.

Economics
When the WWTP is extended with SF and AC, the operating costs of the resulting WWTP is doubled compared with a WWTP without these systems (base case). With UF and RO both the investment costs and the operating costs will approximately triple the base case.

Driving force for implementation
These systems have been installed at some locations only in BFW preparation. Applied in refineries where shortages of water supply may occur.

Example plants
Sandfilters, ultrafiltration, activated carbon and reverse osmosis are proven technologies in many industrial sectors. From the 2010 TWG data collection, within the 44 refineries sample the following breakdown treatment steps were reported.
### Table 4.137: Techniques reported for WWTP within 2010 TWG data collection

<table>
<thead>
<tr>
<th>Treatment type</th>
<th>Number of sites reporting</th>
<th>Techniques reported as used at this step</th>
<th>Number of sites(*)</th>
<th>% use of the technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>First step</td>
<td>44</td>
<td>API</td>
<td>37</td>
<td>84 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CPI</td>
<td>7</td>
<td>16 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Buffering-Equalisation</td>
<td>21</td>
<td>48 %</td>
</tr>
<tr>
<td>Second step</td>
<td>44</td>
<td>DAF</td>
<td>30</td>
<td>68 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IAF</td>
<td>4</td>
<td>9 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Flocculation/Flotation</td>
<td>5</td>
<td>11 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sand filtration</td>
<td>4</td>
<td>9 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>None or not identified</td>
<td>3</td>
<td>7 %</td>
</tr>
<tr>
<td>Third step (biological)</td>
<td>44</td>
<td>Activated sludge</td>
<td>27</td>
<td>61 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trickling filter</td>
<td>1</td>
<td>2 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Biofilter</td>
<td>11</td>
<td>25 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>None or not identified</td>
<td>4</td>
<td>9 %</td>
</tr>
<tr>
<td>Additional step</td>
<td>44</td>
<td>Sand filtration</td>
<td>9</td>
<td>20 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lagoon</td>
<td>4</td>
<td>9 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Miscellaneous (**)</td>
<td>9</td>
<td>20 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No final treatment</td>
<td>22</td>
<td>50 %</td>
</tr>
</tbody>
</table>

(*) Various techniques may be reported for same site
(“”) For additional step, miscellaneous includes e.g. oxidation pond, clarification, decantation and DAF or IAF

### Reference literature

[181, HP, 1998]. [2008 data collection questionnaires].

### 4.26.10 Global refinery waste water treatments performance

#### Description

This section contains what deals with emission values that can be achieved, individually or in combination, by an overall today’s waste water treatment of in refineries. The waste water system considered contains primary, secondary and tertiary treatment, the various treatment steps including optional final one as shown in Figure 4.54.
Figure 4.50 Simplified process flow diagram of a typical refinery waste water treatment plant, including a denitrification/nitrification biotreater. (replaced by new one at the beginning of chapter 4.26)

**Achieved environmental benefits and environmental performance**

Ranges of release levels expressed in concentration on a yearly average basis displayed in Table 4.138 are considered to be achievable for key water parameters typically used to characterise a refinery release to water using a good combination of techniques described in this section. Specific load values are shown here as indicative parameters as they can be strongly dependent on the complexity or the type of refinery. These ranges suppose, in particular, that the treatment capacity of each treatment step is well adapted to the actual effluent load (average and peak regimes) received at the WWTP. Depending on the nitrogen intake, lowest range limits for nitrogen compounds would require the use of a specific denitrification/nitrification stage.
Table 4.138: Emissions to water reported concentrations and loads found in appropriately operated WWTP

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reported concentration (mg/l) (yearly average)</th>
<th>Indicative corresponding load (g/tonne crude oil or feedstocks processed) (yearly average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum temperature</td>
<td>30 – 35 ºC</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.5 - 8.5</td>
<td></td>
</tr>
<tr>
<td>Total suspended solids (TSS) (dried @ 105 ºC)</td>
<td>≤5 – 15</td>
<td>1 – 5</td>
</tr>
<tr>
<td>Total organic carbon (TOC)</td>
<td>5 – 15</td>
<td>1 – 5</td>
</tr>
<tr>
<td>Total hydrocarbon oil content THC (EN 9977-1 or EN 9977-2)</td>
<td>&lt;0.1 – 1</td>
<td>&lt;0.1 – 0.5</td>
</tr>
<tr>
<td>Biological oxygen demand BOD (5 day ATU @ 20 ºC)</td>
<td>2 – 10</td>
<td>0.5 – 3</td>
</tr>
<tr>
<td>Chemical oxygen demand COD (2 hour)</td>
<td>&lt;30 – 60</td>
<td>&lt;10 – 25</td>
</tr>
<tr>
<td>Ammoniacal nitrogen (as N)</td>
<td>0.25 – 2.5</td>
<td>0.1 – 1</td>
</tr>
<tr>
<td>Nitrites (as N)</td>
<td>&lt;0.05 – 0.2</td>
<td>0.05 – 0.1</td>
</tr>
<tr>
<td>Nitrates (as N)</td>
<td>&lt;0.5 – 2</td>
<td>0.2 – 1</td>
</tr>
<tr>
<td>Kjeldahl nitrogen (as N)</td>
<td>≤2 – 5</td>
<td>1 – 2.5</td>
</tr>
<tr>
<td>Total nitrogen (as N)</td>
<td>2 – 10</td>
<td>0.5 – 3</td>
</tr>
<tr>
<td>Cyanides</td>
<td>0.003 – 0.01</td>
<td>0.001 – 0.005</td>
</tr>
<tr>
<td>Fluor (refineries using HF alkylation)</td>
<td>&lt;0.2 – 2</td>
<td>&lt;0.25 – 1</td>
</tr>
<tr>
<td>Phosphates (as P)</td>
<td>0.1 – 0.5</td>
<td>0.05 – 0.15</td>
</tr>
<tr>
<td>Total P (as P)</td>
<td>0.05 – 0.5</td>
<td>0.05 – 0.15</td>
</tr>
<tr>
<td>Sulphides</td>
<td>0.005 – 0.05</td>
<td>0.002 – 0.02</td>
</tr>
<tr>
<td>Sulphite</td>
<td>&lt;2</td>
<td></td>
</tr>
<tr>
<td>AOX (as Cl)</td>
<td>&lt;0.1 – 0.2</td>
<td>&lt;0.01 – 0.06</td>
</tr>
<tr>
<td>Benzene</td>
<td>&lt;0.001 – 0.005</td>
<td>&lt;0.001 – 0.002</td>
</tr>
<tr>
<td>Benz(a)pyrene Polycyclic aromatic hydrocarbons (PAH-16)</td>
<td>&lt;0.0001 – 0.001</td>
<td>&lt;0.0001 – 0.0003</td>
</tr>
<tr>
<td>BTEX</td>
<td>&lt;0.001 – 0.005</td>
<td>0.001 – 0.005</td>
</tr>
<tr>
<td>MTBE (lower levels for refineries not producing MTBE)</td>
<td>&lt;0.001 – 0.01</td>
<td>0.001 – 0.005</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.01 – 0.1</td>
<td>0.001 – 0.02</td>
</tr>
<tr>
<td>Tensioactives (ionic and anionic)</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td>Heavy metals (Cd+ Cr+ Cu+ Hg+ Mn+ Ni+ Pb+ Se+ Sn+ V+ Zn)</td>
<td>0.05 – 0.2</td>
<td>0.02 – 0.1</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.001 – 0.003</td>
<td>&lt;0.0001 – 0.001</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.001 – 0.005</td>
<td>&lt;0.0001 – 0.001</td>
</tr>
<tr>
<td>Total Cr</td>
<td>&lt;0.001 – 0.003</td>
<td>&lt;0.0001 – 0.001</td>
</tr>
<tr>
<td>Cr (VI) as Cr</td>
<td>&lt;0.001 – 0.002</td>
<td>&lt;0.0001 – 0.001</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.001 – 0.003</td>
<td>&lt;0.0001 – 0.001</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.005 – 0.05</td>
<td>&lt;0.001 – 0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.0001 – 0.001</td>
<td>&lt;0.0001 – 0.005</td>
</tr>
<tr>
<td>Fe</td>
<td>0.15 – 0.5</td>
<td>0.01 – 0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.003 – 0.05</td>
<td>&lt;0.001 – 0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>0.002 – 0.05</td>
<td>&lt;0.001 – 0.02</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.0001 – 0.0005</td>
<td>&lt;0.0001 – 0.001</td>
</tr>
<tr>
<td>V</td>
<td>&lt;0.005 – 0.02</td>
<td>&lt;0.001 – 0.005</td>
</tr>
</tbody>
</table>

Levels given within this table are ranges of achievable levels from the effluent treatment plant. Some of the concentration values have been reported for different average periods. No distinction have been done in here. They are given on the basis of 95% of values not exceeding the relevant level. The water flow is calculated for process water and purging water of the closed loop cooling system.

References: [101, World Bank, 1998], [181, HP, 1998], [262, Jansson, 2000], [257, Gilbert, 2000], [118, VROM, 1999], HELCOM and OSPAR recommendation, [268, TWG, 2001] [Updated TWG 2008 data collection questionnaires]

From several recent measurements campaigns (2005 to 2010), CONCAWE reported the following concentration ranges for some pollutants in a sample of 60 to 80 European refineries (see Table 4.139).
Table 4.139: Reported emissions from on-site waste water treatment refineries (CONCAWE)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration(¹) range (µg/l)</th>
<th>5 percentile (µg/l)</th>
<th>Median (µg/l)</th>
<th>95 percentile (µg/l)</th>
<th>Number of valid reports(²)</th>
<th>Practical limit of quantification (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.0007 – 160</td>
<td>0.013</td>
<td>0.50</td>
<td>115.3</td>
<td>52</td>
<td>0.1</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.094 – 979</td>
<td>0.58</td>
<td>20.74</td>
<td>366.7</td>
<td>76</td>
<td>100</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.0013 – 9.9</td>
<td>0.012</td>
<td>0.50</td>
<td>7.59</td>
<td>57</td>
<td>0.8</td>
</tr>
<tr>
<td>Lead</td>
<td>0.0002 – 50</td>
<td>0.050</td>
<td>3.34</td>
<td>39.67</td>
<td>61</td>
<td>5</td>
</tr>
<tr>
<td>Mercury</td>
<td>17.9 10⁻⁶ – 8</td>
<td>0.0045</td>
<td>0.18</td>
<td>1.54</td>
<td>56</td>
<td>0.1</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.9 10⁻⁶ – 162</td>
<td>0.86</td>
<td>7.08</td>
<td>86.63</td>
<td>62</td>
<td>5</td>
</tr>
</tbody>
</table>

(¹) Yearly weighted average based on various frequency sampling  
(²) Number of real detects and the results reported as ½ of LoQ for below LoQ observations  
Source: Multi data set from [121, CONCAWE 2012]

Another data set on water emissions has been made available by CONCAWE (Report 10/3) for a spot sample campaign measurements including 105 refineries in Europe. From direct discharging sites (90% of the entire refineries sample), the following ranges are reported for a number of parameters (Table 4.140.).

Table 4.140: Reported emissions from grab sample campaign measurements (CONCAWE)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration range (mg/l)</th>
<th>5 percentile (mg/l)</th>
<th>Median (mg/l)(²)</th>
<th>Average (mg/l)(³)</th>
<th>95 percentile (mg/l)</th>
<th>Number of valid measurement(⁴)</th>
<th>Limit of quantification (LoQ) mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total hydrocarbon content (Oil in Water)(¹)</td>
<td>0.05 – 55</td>
<td>0.05</td>
<td>0.18</td>
<td>1.55</td>
<td>6.7</td>
<td>101</td>
<td>0.05</td>
</tr>
<tr>
<td>COD</td>
<td>16 – 391</td>
<td>23</td>
<td>48</td>
<td>61</td>
<td>135</td>
<td>94</td>
<td>10</td>
</tr>
<tr>
<td>BOD</td>
<td>1 – 130</td>
<td>1</td>
<td>4</td>
<td>8</td>
<td>23</td>
<td>87</td>
<td>3</td>
</tr>
<tr>
<td>Kjeldahl-N</td>
<td>1 – 83</td>
<td>1</td>
<td>3.4</td>
<td>7</td>
<td>23</td>
<td>82</td>
<td>1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.003 – 1.7</td>
<td>0.003</td>
<td>0.0013</td>
<td>0.059</td>
<td>0.103</td>
<td>96</td>
<td>0.005</td>
</tr>
</tbody>
</table>

(¹) Oil in Water: measurements made by GC-FID method compatible with EN9377-2 – LoQ 0.05 mg/l  
(²) For average calculation, <LoQ has been replaced by LoQ  
(³) For average calculation, <LoQ has been replaced by LoQ  
(⁴) May include several streams for a same site  
Source: [122, CONCAWE 2010]

Operational data
Effluent treatment units are designed so that the most important key parameters (suspended solids, TOC, COD and BOD) of the final discharge stream can be appropriately monitored in order to ensure efficient treatment. automatically leading allowing in some extent to limited operator attention, and even less, if sufficient up stream water management measures are being taken to ensure a constant quality and flow of water and adequate buffering. The specific constrains of each parameter analysis are to be taken into account e.g. TOC and COD can be monitored continuously whereas BOD need several days for the analysis.
Examples of two data sets based on short term averaging period (daily or monthly) for COD emissions for one entire year appear in Figure 4.60 and Figure 4.61. From these data it is possible to estimate the variation around the reported yearly average.
Table 4.141: Examples of emissions to water values variation

<table>
<thead>
<tr>
<th>Site</th>
<th>Parameter (Unit)</th>
<th>Yearly average</th>
<th>Daily average variation</th>
<th>Monthly average variation</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR-01</td>
<td>COD (mg/l)</td>
<td>Avg. = 82</td>
<td><a href="1"> 56 % – 156 %</a></td>
<td><a href="1"> 66 % – 123 %</a></td>
<td>Based on daily data</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Med. = 84)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FR-02</td>
<td>COD (mg/l)</td>
<td>Avg. = 49</td>
<td><a href="2"> 50 % – 200 %</a></td>
<td><a href="2"> 80 % – 140 %</a></td>
<td>Based on monthly aggregated data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FR-01</td>
<td>TSS (mg/l)</td>
<td>Avg = 8</td>
<td><a href="3"> 25 % – 215 %</a></td>
<td><a href="3"> 51 % – 190 %</a></td>
<td>Based on daily data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FR-02</td>
<td>TSS (mg/l)</td>
<td>Avg = 11</td>
<td><a href="3"> 17 % – 235 %</a></td>
<td><a href="3"> 52 % – 87 %</a></td>
<td>Based on monthly aggregated data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Expressed as a range: [Percentile 5 %/Yearly Average -Percentile 95 %/yearly average]  
(2) Expressed as a range: [Minimum data/Yearly Average -Maximum data/yearly average]  
(3) Expressed as a range: [Min. monthly average/Yearly Average-Max. monthly average/yearly average]

Figure 4.60 Daily COD concentration variations from one refinery site (FR-01)
Figure 4.61 Monthly COD concentration variations from one refinery site (FR-02)

Table 4.142: Emissions to water values possible daily variations from seven European refinery sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Chemical oxygen demand COD (mg/l)</th>
<th>Total suspended solids TSS (mg/l)</th>
<th>Total petroleum hydrocarbons TPH (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yearly average</td>
<td>Max/Min ratio</td>
<td>P5/Avg ratio</td>
</tr>
<tr>
<td>Site 1</td>
<td>2010</td>
<td>84.40</td>
<td>7.33</td>
<td>0.54</td>
</tr>
<tr>
<td>Site 2</td>
<td>2010</td>
<td>49.60</td>
<td>4.86</td>
<td>0.71</td>
</tr>
<tr>
<td>Site 3</td>
<td>2009</td>
<td>67.75</td>
<td>2.50</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>78.40</td>
<td>74.00</td>
<td>0.25</td>
</tr>
<tr>
<td>Site 4</td>
<td>2009</td>
<td>67.92</td>
<td>12.32</td>
<td>0.37</td>
</tr>
<tr>
<td>Site 5</td>
<td>2010</td>
<td>44.52</td>
<td>24.60</td>
<td>0.45</td>
</tr>
<tr>
<td>Site 6</td>
<td>2009</td>
<td>47.03</td>
<td>10.72</td>
<td>0.53</td>
</tr>
<tr>
<td>Site 7</td>
<td>2010</td>
<td>52.57</td>
<td>35.20</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>2011</td>
<td>78.72</td>
<td>10.72</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Source: CONCAWE, 2012
Table 4.143  Summary of daily variations from seven European refinery sites

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Daily variations max/min ratio range</th>
<th>Daily variations P95 %/yearly average range</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>2.5 – 224</td>
<td>1.43 – 2.51</td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>20–120</td>
<td>1.82 – 2.82</td>
<td></td>
</tr>
<tr>
<td>TPH</td>
<td>9.8 – 522</td>
<td>1 – 2.83</td>
<td>Linked to limit of detection and type of analytical method</td>
</tr>
</tbody>
</table>

Source: CONCAWE-2012

Note for TWG:
As shown in the previous examples provided for a very limited number of sites and parameters, it can be possible to derive variations ranges around average values for some short term data.
The possible short term variations are assessed based on analysis of the 95th for COD, TSS and THC. Expressed as a % yearly average. The TWG is asked to provide feedback on these data and their possible use.

Applicability
WWTP usually occupy significant space at refineries, particularly the biotreater due to the relatively slow biodegradation process. In order to save space, it is advisable to integrate water management principles into the for a more compact design leading to a compact. A full train WWTP occupies a space of 1 ha, not including an observation basin which many refineries have installed as a last line of defence. The amount of rainwater depends of course on the local climatic conditions and the size and layout of the refinery.
The WWTP system as described previously is applicable at all refineries. It may be advisable to install an observation basin between the final treatment step and the discharge to prevent any waste water that is not treated adequately to be directly discharged. In this case the collected water can be re-routed for additional treatment. Such basin do require the addional space to be available.

Reference literature
[ 77, REF TWG 2010 ] [ 121, CONCAWE 2012 ] [ 122, CONCAWE 2010 ].

4.26.11 Reduction of odours

Description
Text moved from previous sections
For both various steps of WWT, emissions to air of VOC (including benzene) and odorous components (hydrogen sulphides and mercaptans) are directly related to the surface area of the open separation and collection compartments. The release of dissolved gases in the dissolved air flotation (DAF) or dissolved gas (DGF) flotation unit increases the effective water area exchanging with air and produced a continuous gas flow through the water column into the gas space above the liquid surface. The substances volatilised by diffusion into the gas bubbles and above the water column are then subject to ambient air convection. The generation of VOC and odours, however, are not uncommon and cannot always be controlled fully by up-stream measures. Therefore can be further reduced by covering dissolved air flotation (DAF) these units with closed and tightly sealed covers. However, due to eventual fluctuations of the internal pressure, such covers cannot be 100 % tight and have to be mechanically protected by an atmospheric vent. For being considered acceptable in order to protect covers together with minimising convective losses, usual dimensions of such vents are around 0.90 m minimum height and 10.2 cm maximum diameter. An additional pressure relief/vacuum breaker valve can also be installed in order to accommodate an exceptional gas exchange rate beyond the vent capacity.
Cover vents can be collected and treated. can be provided with covers as an emission reduction measure, sometimes with an appropriate off-gas treatment system (e.g. biofilter, activated carbon absorber, incinerator, thermal oxidizer - see Section 4.25.6.3) or reinjected into the aeration basin. Safety aspects (explosiveness of VOC air mixtures) are to be attended.

Achieved environmental benefits
VOC emissions from oil separators can be reduced to 3 g/m³ by covering the CPI and API. The HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of [117, VDI, 2000]:

- 20 g/m² per hour for open oil separator
- 2 g/m² per hour for covered oil separator

Cross-media effects
When API or PPI separators are covered, the flammability/explosion limits and the toxicity concentration thresholds for some gaseous sulphur compounds may easily be reached. Consequently, occupational safety and environmental protection should be carefully considered at equipment design stage, and appropriate procedures should be set up for ensuring safe operating conditions. Safety should be addressed in case of fixed roof tank at any step of WWT.

Applicability
Significant modifications may be needed before accepting a cover. Retrofitting to existing units may be complicated depending on structural design, type of mechanical float skimmers and solid scrapper systems used, and position of electrical drivers.

Economics
For covering the 1st step separator units, the investment for the installation of two 200 m³ floating slab-covers is about EUR 75 000 and the total annual operating costs about EUR 42 800 per year. Note to TWG: Could you check this data and provide a reference?

Table 4.144: VOC controls in oily water operations (installed and retrofitted)

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Oily water sewers/sumps/separations and drainage operations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control technique</td>
<td>Automatic drainage facilities</td>
</tr>
<tr>
<td>Efficiency</td>
<td>80 %</td>
</tr>
<tr>
<td>Investment costs</td>
<td>0.002 – 0.03 EUR million/tank (1)</td>
</tr>
<tr>
<td>Operating costs</td>
<td>Small</td>
</tr>
<tr>
<td>Other impacts comments</td>
<td>May not be suitable for all tank stocks</td>
</tr>
</tbody>
</table>

(1) Source: Industry propriety information

A floating cover (assuming a 800 m³/h process capacity of oily water, with VOC emission up to 1000 t/yr) will result in a 90 % VOC recovery efficiency for the following costs:

- Investment cost EUR 0.6 million
- Operating cost: EUR 0.03 million per year
Example plants
Separators have been progressively covered in a growing number of European refineries.

As described previously (see Sections 4.26.6 and 4.26.7) main step for smell limitation from WWTPs is the covering of most emitting pieces of equipment (e.g. separators, DAF/DGF) by a closed and tightly sealed cover, and the appropriate recycling or treatment of vented odorous gases. This section will present other possible techniques to be used within refinery WWTPs for odor reduction.

4.26.11.1 Water buffer tanks

Description
Water buffer tanks are used upstream and/or downstream of API/CPI/PPI separation systems to receive variable rate transfers of waste water containing insoluble floating oils, insoluble suspended oils and solids, and soluble substances. This section also includes process area storm water surge tanks.

As for any other treatment step, the generation of odours from open top water buffer tanks will be directly related to the surface area of oil and water that will come in contact with air. Substances will be volatilised by diffusion into the air and be subjected to the convective forces of air flow. The generation of odours can be minimised reduced by maintaining the smallest possible surface area of oil and water in contact with air. For such purpose, the tank should be routinely checked and maintained free of oil by the operator, and the following actions can be taken:

- Operate the water buffer tank with a fixed roof equipped with a pressure relief/vacuum breaker valve to prevent convective losses when the tank level is static;
- Use an internal floating roof or an external floating roof equipped with at least a primary seal or, more efficiently, a primary and secondary seal between the floating roof and the tank shell, for further reducing the diffusive and convective losses;
- Instead of gravity draining to an open collection system, install an internal oil skimming system to extract oil from the tank through closed piping using a pump station or vacuum truck to minimize the possible loss of volatile substances.

Achieved environmental benefits
By using a fixed roof tank or a floating roof tank, the emission of VOC and other odorous compounds can be reduced by 80 – 90 % compared to an open system. This ratio can be even higher and reach 99 – 99.9 % if vented emissions from the fixed roof tank are collected and routed to an appropriate off-gas treatment system (e.g. biofilter, activated carbon absorber, incinerator, thermal oxidizer - see Section 4.25.6.3).

Cross-media effects
None in particular to be mentioned

Safety should be addressed in case of fixed roof tank (same as for DAF or CPI unit)

Applicability
All new installations can be originally constructed with dual-sealing floating roofs or other systems with equivalent efficiency. Many existing water buffer tanks can be retrofitted with floating roofs, and existing floating roof tanks originally designed for crude or fuel storage can also be reused as water buffer tanks.
Chapter 5

Economics
Note for TWG: please provide data, in particular for the revamping and reuse of existing crude tanks as water buffer tanks. No extra information provided

Driving force for implementation
Reduce VOC emissions and odour pollution.

Example plants
Several examples in Europe.

Reference literature
[48, TOTAL 2010]
4.27 Waste management

This section together with the two previous ones are dealing with the end of pipe processes that appear in a refinery. The reason why these techniques are appearing here is to give an overall description of the techniques and to avoid repetition. Description of end of pipe techniques does not appear in the previous sections. In this Section, general information on environmental benefits, cross-media effects, operational data, applicability is described here. Prevention or minimisation techniques applied to different process activities are found in each of the sections dealing with these production processes. Complementing waste minimisation and prevention of generation of waste that may be found along this chapter, this section contains the waste management systems that may be found within refineries. These techniques are only discussed in this section within this document.

This section is complementary to previous sections of Chapter 4 related to individual production processes or units. It gives sector-specific information on key management, reduction and abatement techniques that are, or may be implemented for waste generated by oil and gas refining. European legislation for waste is fully applicable to refinery sector and especially the waste hierarchy which is described in 2009/98/EC directive, as a priority order in waste prevention and management:

- prevention;
- preparing for reuse;
- recycling;
- other recovery, e.g. energy recovery;
- disposal.

For a given technique, available data on the way it can be applied and the results it allows to obtain on particular processes or units have been given in the related sections. The information provided here aims at completing this information on broader aspects, in particular environmental benefits, cross-media effects, operational data, and applicability issues which will not been repeated in other sections.

Residual refinery wastes are typically in the form of sludges, spent process catalysts, filter clay, and incinerator ash. Other waste fractions are waste from flue-gas desulphurisation, fly ash, bottom ash, spent activated carbon, filter dust, inorganic salts as ammonium sulphate and lime from water pretreatment, oil-contaminated soil, bitumen, sweepings, spent acid and caustic solutions, and chemicals, among others. The treatment of these wastes includes incineration, land treating off-site, landfilling onsite, landfilling off-site, chemical fixation, neutralisation, and other treatment methods.

4.27.1 Establishment of a waste management programme

Description

The establishment of an Environmental Management System (Section 4.15.1) should contain elements to prevent waste generation and some pollution prevention techniques that help to prevent pollution of soil and groundwater. Some techniques that may be included are:

- implementation of a sludge master plan with the aim to reduce the sludge generated.
- provide enclosed sampling loops
- cleaning and assembly only in specially constructed and dedicated areas
- providing dedicated drainage systems
- physical barriers such as clay walls or plastic membranes can be installed around the site boundary. To be effective at containing oil pollution, these have to extend below the water table. Monitoring wells will also be required to ensure that if oil does build up behind the barrier, it can be removed before it has a chance to escape under the barrier. A
second form of barrier is a ditch also extending to below the groundwater table. Any oil leaving the site can be observed floating on the water in the ditch and recovered. The outer face of the ditch can be sealed with an impervious layer such as concrete, plastic, clay, steel piling etc.

- Groundwater, like surface water basically flows downhill. Therefore, groundwater can be prevented from leaving a site by lowering the level inside the site by pumping so that it is lower than the level outside. Water will then flow into the site rather than outwards. The pumped water has obviously to be disposed of. It may be possible to use this water for supply purposes on site. If it is to be discharged, then monitoring will be required to ensure that it is not contaminated. If it is, then it will have to be treated in which case, this method will be limited by the capacity of the effluent treatment system.

- Minimisation of underground piping. Underground piping can be a source of undetected releases to the soil and groundwater. Inspecting, repairing or replacing underground piping with surface piping can reduce or eliminate these potential sources. Retrofitting can be very expensive.

- Perform a risk analysis to rank in order of significance cases where accidental leak may occur (elements to consider are the product in the tanks/pipes, the age of the equipment, the nature of the soil and groundwater that would be affected). Prioritise areas where impermeable floors are needed most. Produce a multi-year master plan to program necessary steps.

- Periodically screening of leaks in sewers and pipes.
  - Correct conditioning of a catalyst during a run extends catalytic life.
  - Control of sodium content in visbreaker feedstock reduces coke formation.
  - Process optimisation leads to less off-specification product and hence less recycling.
  - Recycling caustic sufficiently can ensure it is completely spent.
  - Sorting waste mixes e.g. concrete and scrap metal, could be a cost-attractive effective option (cheaper disposal routes for some components) and eliminates risk of unwanted components.
  - Asbestos lagging: special equipment for compaction and packing.
  - Where still relevant, tetraethyl lead and tetramethyl lead (TEL/TML) scale and sludge: permanganate treatment eliminates TEL/TML traces.
  - Oiled solids (soil): de-oiling in an oil extractor.
  - Neutralisation: mixing polymerisation catalyst ($H_3PO_4$) with lime.
  - Process treatment by steaming, flushing or regeneration prior to disposal: clay and sand filters; catalysts.
  - Solids released to the waste water sewer system can account for a large portion of a refinery’s oily slurges. Solids entering the sewer system (primarily soil particles) become coated with oil and are deposited as oily slurges in the API oil/water separator. Because a typical sludge has a solids content of 5 to 30 percent by weight, preventing one kg of solids from entering the sewer system can eliminate 3 to 20 kg of oily sludge. The Amoco/US EPA study estimated that at the Yorktown facility, 1000 tonnes of solids per year enter the refinery sewer system. Methods used to control solids include: using a street sweeper on paved areas, paving unpaved areas, planting ground cover on unpaved areas, re-lining sewers, cleaning solids from ditches and catch basins, and reducing heat exchanger bundle cleaning solids by using antifoulants in cooling water.
  - A significant portion of refinery waste arises from oily slurges found in combined process/storm sewers. Segregation of the relatively clean rainwater runoff from the process streams can reduce the quantity of oily slurges generated. Furthermore, there is a much higher potential for the recovery of oil from smaller, more concentrated process streams.

**Achieved environmental benefits**

The aim of such a waste management programme is to prevent the generation of waste contaminates of the soil and the groundwater as well as to reduce its final amount of waste generated.
4.27.2 Sludge management and treatment

Description
Sludges are defined as semi-liquid residue from industrial processes and waste water treatment. Emulsions of oil-in-water, stabilised by the presence of solids. In refineries, a number of different types of sludges are generated at the following sources: crude and product tanks (bottoms), API separation units, flocculation and flotation units, DAF, contaminated soil. Biological sludges represent an important category of sludges in terms of oil content and dewaterability. According to CONCAWE, in 1993, 41% of the European refinery sludges were incinerated, 9% was land farmed and 30% land filled. It is foreseen that land filling and land farming of sludges will be severely restricted increasingly prohibited by forthcoming EU legislation, which promote the increase of means that the scope for sludge prevention reduction but also for incineration at third parties will increase in the future.

Pretreatment and treatment of sludge
The purpose of sludge treatment by dewatering, drying and/or incineration is to reduce the volume and the residual hydrocarbon content in order to save costs in subsequent processing or disposal costs. The principle of mechanical dewatering by decanters is based on centrifugal forces and on the density difference between water, oil and solids. The principle of the thermal treatment steps is based on a combination of evaporation by indirect heating and/or the destruction of the organic constituents by thermal oxidation (incineration).

Decanter centrifuges are the most widely used for dewatering both oily and biosludges. Steam dryers are almost exclusively applied for biosludge and function as a pretreatment step for incineration. Landfarming of sludge cakes is still being practised but is increasingly restricted in view of emissions and soil contamination risks.

Decanter centrifuges are widely used in sludge dewatering and deoiling applications throughout the (refining) industry, either as fixed facilities or as a mobile service rendered by contractors. Dewatered biological and oily sludges can be further processed using drying and/or incineration techniques resulting in virtually oil-free residues for which useful applications are available.

Oily sludge dewatering is only applied at refineries that dispose of sludge cakes outside their premises in order to reduce the volume and associated disposal cost. Disposal to cement kilns, coal-fired power plants, dedicated sludge incinerators, municipal and hazardous waste incinerators are all practised used. Drying is currently hardly employed by refineries due to safety risks. De-oiling/dewatering of sludges gives a small volume of solid, low solvent waste, (centrifuging or filtration). De-oiling/dewatering of sludges gives small volume of solid, low solvent waste, (centrifuging or filtration).

An option for refineries with cokers is to reuse oily sludges in the coking process as already mentioned in section 4.7.5

In Figure 4.62 a simplified process flow diagram is shown of a decanter combined with a fluidised-bed incinerator (FBI) being considered BAT the most appropriate technique for sludge incineration in the WI BREF [82, COM 2006]. The feeding of sludge cake into the sand bed of the FBI can be accomplished with a positive displacement pump. It should be mentioned that the emissions of SO2, NOx, CO, organic compound, PAH and heavy metals generated by these systems should be properly controlled by suitable abatement techniques as addressed in the WI BREF.

Text on condition of incineration of sludge replaced par cross reference to WI

The oxygen for incineration is provided by air injection into the bed via a wind box and a perforated floor. An air ventilator enables the sand in the bed to fluidise. The burned out ash particulates leave the bed and are removed by flue gas treatment. This can consist of a waste heat boiler (WHRB), an electrostatic precipitator (ESP), a scrubber section, a flue gas heater (to avoid a visible steam plume), a flue gas ventilator and a stack. The ash is transported by a
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Chain/bucket conveyor combination or pneumatically to a hopper, and it usually requires dedusting by water spray and agglomeration in a double paddle mixer. At smaller incinerators, a water quench is used to cool the flue gas from 850°C to about 150 °C prior to fabric (bag) filtration.

Operating temperatures of the bed can be controlled at respectively 800 – 850 °C and or 850 – 950 °C. The WHB operates between 250 and 450 °C, the ESP at 220 °C and the scrubber between 200 and 50 °C. In a FBI, all ash is carried over the top with the flue gas, which provides a large dust loading (typically 50000 mg/Nm³) to the WHB and ESP. Some 50 % of the dust is collected in the WHB, which can be regarded as a settling chamber. The entrainment efficiency of an ESP is typically 99 %, leaving the (venturi) scrubber system to eliminate ± 500 mg/Nm³ to the stringent CEC limit of 5 mg/Nm³. The ash might find a useful outlet in concrete or asphalt depending on the quality.

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Achieved environmental benefits
Generation of sludges can be reduced minimised and can be maintained to values between 0.1 to 0.5 kg per tonne of feedstock processed within the refinery.

Cross-media effects
The cross media effects of sludge incineration are addressed in the WI BREF. Scrubbing might require caustic if acidic (SO₂ and NOx) components are present in the flue gas in concentrations which need to be removed to legal limits. The FBI with flue gas treatment and ash handling is a closed system with fully automated control. The system is kept under slight negative pressure. The described system is regarded state-of-the-art for sludge incineration and is able to fulfil all legal stack emission requirements. Dioxins (PCDD/F) could be an issue at high chlorine loading combined with sub-optimum operation conditions. Flue gas treatment systems for domestic sludge incinerators uses impregnated activated carbon filters (ACF) or zeolites are installed for
mercury/dioxin control. Effluent from the scrubber system can be substantial. Recirculation of scrubber water is only a cost-effective proposition if treatment is required prior to discharge.

Operational data
Safety issues are associated with start-up and (planned or emergency) shutdown, for which a flame control interlock and a nitrogen purging system is required. Anaerobic and pyrophoric sludges (tank bottoms) can cause safety problems during storage and drying. The energy requirements of sludge drying and incineration depend strongly on the sludge cake characteristics (water and residual oil contents). Energy integration with FBI is two fold: air preheating of the primary fluidisation air is standard, and steam generation can be economically accomplished with systems able to generate >8 tonnes of MP steam/hour. An intrinsic disadvantage of FBI is the relatively large excess of air utilised in order to keep the bed fluidised.

Applicability
Reuse of oily sludges in coking process is dependent of the availability of this unit and specifications of final product. Dewatering units are fully applicable are mainly used for Because of its high cost, options as reduction/recycling of waste are more typical waste minimisation options to be applied before waste incineration. Fluidised-bed incinerators may be an option for third-party is a proven technology already fully applicable in waste industry receiving waste streams.

Operational data and economics
For an FBI with a capacity of 4 t/h sludge cake (20 % dry solids) a footprint of about 50x100 m is required including tankage and complete flue-gas and ash handling. The installation is normally 12 - 15 m high (tanks, incinerator, WHB, ESP, ash hopper) and the stack height is usually at least 40 m, depending on ancillary installations. The above-described system would be suitable for a large 20 Mt/yr refinery and requires a capital investment of about EUR 37.5 million (including installation). The operational costs could amount to EUR 500 - 700/tonne dry solids. If large scale domestic sludge incinerators are available, which are entitled to take industrial sludges, the installation of a dedicated sludge incineration system is not economically justifiable. This certainly would be the case for smaller refineries, indicating that contract dewatering, drying and incineration are competitive to own processing. A combination of decanters with an advanced drying system for oily sludge occupies only 10 - 15 % of the above indicated space, and would involve a capital investment of EUR 5 million due to the fact that since expensive flue-gas treatment is avoided.

Driving force for implementation
Oil recovery. Operating cost reduction. Waste legislation At some locations it has become common in the last 5 – 10 years to minimise sludges, collect them in tanks or basins and recover the oil and water phases after gravity settling as much as possible.

Example plants
Decanter centrifuges are reliable, advanced and proven techniques with minimum emissions. At refinery locations permanent decanter centrifuges have for example been installed at refineries in Godorf, Gothenburg and Stanlow. A few times per year, contractors are hired in either for on-site sludge processing or for collection and off-site processing (decanting, drying, incineration in cement kilns, power plants or in industrial/domestic waste or dedicated sludge incinerators).

Sludge incineration plants using the fluidised-bed system are considered state-of-the-art but require advanced design and process control. At several refineries such as Mobil, Wilhelmshafen, Shell Pernis and Godorf, Esso Botlek these systems were already built in the 1970s. Some of them have been dismantled due to the current availability of more economic options compared with necessary investment and operation in additional flue-gas cleaning equipment. For oily sludges, mixing with other wastes and use as secondary fuel in cement kilns and/or power plants represents are an attractive disposal route if these plants use appropriate abatement techniques. International sludge contractors employ either mobile decanter and
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drying systems for oil recovery (Impex, EPMS, Soil Recovery A/S) or fixed oily sludge treatment systems (ATM).

4.27.3 Spent solid catalyst management

A BREF on Non-Ferrous metals has been already published. In that BREF the techniques used for the recovery of metals from secondary materials such as refinery catalysts used in the oil and gas refining industry are described in the NFM BREF [123, EC 2001] is extensivelly treated.

The use of catalytic processes in refineries has increased significantly in the last 20 years. This increase is mainly due to the introduction of catalytic residue conversion processes such as heavy oil residue cracking, hydrocracking and residue hydroconversion, hydrodemetallisation and hydrofinishing and also Hydrogen production. Since 1980 a significant expansion has taken place of the hydrotreating and hydrodesulphurisation capacity as well as of sulphur recovery units and associated tail gas treatment, whose processes also utilise catalysts. Traditional catalytic processes such as fluid catalytic cracking, catalytic reforming and isomerisation are also generators of spent catalysts.

The purpose of spent catalyst management is to minimise environmental and health impacts. To achieve this goal spent catalysts are carefully handled, safely removed, carefully packed and sent for reactivation or metal reclamation. Metal recovery aims at the conversion of spent catalysts into useful products, which can be recycled and reused with minimum impact on the environment.

The principle of spent catalyst management is a scheduled, strictly regulated and safe handling of the materials involved, usually executed by specialised contractors during plant turn-arounds. Arrangements with the supplier of fresh catalyst can sometimes be made for them to take back the spent catalyst.

Regeneration of hydroprocessing catalysts is usually possible 3 or 4 times. The ultimate spent catalysts are almost exclusively reworked by third parties into commercial metal oxides or metal salt solutions. Although a regeneration process has been developed for spent FCC catalysts, this process is hardly used due to the availability of cheaper alternatives. The catalyst carrier (alumina and/or silica) can sometimes be converted into products or otherwise disposed of. Some refineries practice storage of store spent catalysts at the refinery site in appropriate environmental conditions with permission of the authorities. Spent catalysts are distinguished by type, process, composition and recyclability. A summary is given in Table 3.106.

- **Co/Mo catalysts** from hydrodesulphurisation, hydrocracking, hydrotreating. Extensive regeneration and reclamation options are available.
- **Ni/Mo catalysts** are typically used in hydrotreaters and hydrocracking units. Regeneration and reclamation capacity is available.
- **Ni/W catalysts** are used in lube oil hydrofinishing. This category experiences limitations to dispose off in view of the high Tungsten content (24 % w/w).
- **FCC spent catalysts**, also including heavy oil and residue cracking spent catalysts (RCC), are the largest catalyst waste category in refineries. Outlets in road building are becoming available.
- **Reformer and Isomerisation catalysts** are exclusively reprocessed by the suppliers of the fresh catalysts. Replacement contracts have been concluded since the introduction of these processes due to the very expensive noble Pt metal involved.
- **Hydrodemetallisation catalysts** typically have high vanadium contents (10 - 20 %) and are currently alumina based (used to be silica). Direct disposal to the steel industry is possibly the most cost-effective option.
- **Zn containing beds** from H₂ plants are typically recycled to the Zn-industry where ZnS ores are processed. Amounts are some 50 t/yr.
The applied regeneration processes are based on pyrometallurgical techniques (roasting, calcination, smelting, sintering and reduction furnaces) for the thermal destruction of the inorganic matrix and on hydrometallurgical methods (aqueous/acid extraction, crystallisation, precipitation, separation and drying) for recovery/purification of metal salts either in dry form or as liquid metal concentrates.

The reclamation plants (more information in NFM BREF) are typically operated in batch mode and contain many different unit operations. From the total spent catalysts, only some 5% pure products are produced. The remainder is either ferro-alloy feed or ceramic raw material. The plant usually processes relatively small batches. Spent hydroprocessing catalysts can vary considerably in composition. Hence the plants have limited process automation.

Text moved from Section 4.5.9.4

4.27.3.1 Control and reuse of the catalyst fines

Description
Significant quantities of catalyst fines are often present around the catalyst hoppers, reactors and regeneration vessels of the FCC unit as well as these collected by the abatement techniques mentioned above. The fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. These techniques may be considered housekeeping measures, included in Section 4.15. Some techniques to consider are:

- dry sweeping the catalyst fines and sending the solids to be recycled or disposed of as non-hazardous waste;
- use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse for collection;
- recycling of the fines (cement production).

Achieved environmental benefits
Reduced the emission of particulates.

Cross-media effects
None worth to be mentioned.

Note for the TWG: could you confirm that dry sweeping does not raise issues related to catalyst purity?

Operational data
No data available. Note for TWG: please provide any useful information available

Applicability
Fully applicable especially during catalyst loading/unloading processes.

Economics
No data available. Note for TWG: please provide any useful information available

Driving force for implementation
Reduction of soil contamination by particulates.

Example plants
Techniques already in use in US refineries.

Reference literature
[80, March Consulting Group, 1991].
4.27.3.2 Removal of catalyst from slurry decant oil

Description

Two types of techniques have been applied to improve the separation of catalysts from slurry decant oil used in cat crackers. One system incorporates high-voltage electric fields to polarize and capture catalyst particles from decant oil; catalyst fines suspended in the separator underflow are recycled back to the reactor. In another system, the amount of catalyst fines reaching the decant oil can be minimized by installing high-efficiency cyclones in the reactor to shift catalyst fines losses of the decant oil to the regenerator, where they can be collected by any particulate abatement technique. A third method is to use a mechanical filter with backwash.

Achieved environmental benefits
Decant oil sludge from an FCC can contain significant concentrations of catalyst fines. These fines often do not allow the use of decant oil as a feedstock and require treatment which generates an oily catalyst sludge. Catalysts in the decant oil can be minimized by using a decant oil catalyst removal system.

Cross-media effects
These techniques have their own energy consumption.

Operational data
No data available. Note for TWG: please provide any useful information available

Economics
No data available. Note for TWG: please provide any useful information available

Applicability
Hydrocyclones are applied in many FCC units.

Driving force for implementation
Reduction of consumption of catalyst and reduction of the decant oil sludge.

Example plants
Hydrocyclones, for removal of catalyst fines, are successfully applied in many FCCs.

Reference literature
[316, TWG, 2000]

Description

Achieved environmental benefits
Recovery of metals from catalyst

Cross-media effects
The management of spent catalysts is an area of environmental concern because prolonged uncontrolled storage may lead to soil and groundwater contamination with heavy metals.

If the refinery has taken proper catalyst management measures, the environmental concerns focus usually on the spent-catalyst regeneration facilities. Most of these plants currently operate with proper flue gas and effluent treatment facilities and comply with present day emission standards. This is an important requirement for being acceptable for oil companies to make use of these spent-catalyst reclamation contractors. Covering spent-catalyst reception facilities is operational or being considered.

Operational data
Safe handling of chemicals is an important issue for spent catalyst metal reclaimers as toxic and pyrophoric materials are being handled. For the refinery, utilisation of energy and process materials during spent catalyst handling are not particularly relevant.

Economics
Cost for processing and metal recovery depend strongly on the composition of the spent catalyst concerned. For high metal waste, even a recovery fee will be paid to the waste generator. Current processing costs for an average HDS catalyst could be in the order of EUR 500/tonne. Recent stringent internationally accepted legal procedures, amongst which special packaging (for rent 2 m³ containers at EUR 5/day), labelling and acceptance requirements as well as transportation costs could add considerably to these costs. On-site processing of spent catalysts is not economic for a refinery.

Spent FCC catalysts with limited V/Ni concentrations are accepted with consent of authorities by raw material suppliers to the road building industry. The material is sometimes used in cement and as asphalt filler.

Example plants
The regeneration of spent catalysts started in the early 1980s. All processors use pyrometallurgical and hydrometallurgical processes with varying degrees of sophistication, recovery capabilities and environmental performance. These processes currently applied are considered acceptable and proven technology.

Reference literature
[118, VROM, 1990; 122, REPSOL, 2001]

4.27.4 Recycling and re-using waste
Recycling and reuse of wastes unintended by-products in different refinery processes reduces the quantity of waste for disposal.

4.27.4.1 Treatment of heavy residues
Heavy residues generated by refineries are the heaviest fractions from the different units (distillation, conversion). They may not have application for products and are typically reused within the refinery. These residues have a where their calorific value can be exploited. Below is a list of treatments that may be applied to reduce the amount of these residues. All these techniques are already analysed in other sections but are put together here to help the reader to understand what refineries may do with their heavy residues.

1. Methods to increase the hydrogen content (hydrogenation)
   - Catalytic hydrogenation (included within Section 4.13) such as Resid Fining, RCD UNIBON, Unicracking, HYVAHL-ASVAHL hydrotreatment, AUROBAN, H-Oil, LC-Fining, HYCON;
   - Non catalytic hydrogenation (included within Section 4.22) as Hydrovisbreaking, Dynacracking, Donor Solvent Visbreaking.

2. Methods to increase the C-content
   - Catalytic cracking (included within Section 4.5) such as Reduced crude resid catalytic cracking (RCC), Heavy oil Cracking, VEBA combi cracking (VCC), Deep catalytic cracking (DCC);
Non catalytic cracking (included within Section 4.7 and 4.22) as delayed coking, fluid coking, flexicoking, LR-Coking, deasphalting: DEMEX, Rose-Technology, visbreaking, thermal cracking, and partial oxidation.

4.27.4.2 Improving the recovery of oils from oily sludges

Because oily sludges make up a large portion of refinery solid wastes, any improvement in the recovery of oil from the sludges can significantly reduce the volume of waste. There are a number of technologies currently in use to mechanically separate oil, water and solids, including: belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll centrifuges, disc centrifuges, shakers, thermal dryers and centrifuge-dryer combinations.

4.27.4.3 Regenerate or eliminate filtration clay

Clay from refinery filters must periodically be replaced. Spent clay often contains significant amounts of entrained hydrocarbons and, therefore, must be designated as hazardous waste. Techniques that may be applied are:

- Back washing spent clay with water or steam can reduce the hydrocarbon content to levels so that it can be reused or handled as a non-hazardous waste.
- Another method used to regenerate clay is to wash the clay with naphtha, dry it by steam heating and then feed it to a burning kiln for regeneration.
- In some cases clay filtration can be replaced entirely with hydrotreating (See Section 4.20.4).

4.27.4.4 Reprocessing off-specification products

It is customary in refineries to have dedicated tankage (so-called or ‘slops’) for the collection of hydrocarbon streams/intermediate products that cannot be blended into final products for the market. These slops are generally reprocessed, often by injection into the crude oil feedstock to the crude distilling unit or to the coker. Often segregation is practised between wet and dry slops. The wet slops tank is equipped with facilities to separate (drain) water from oil (to prevent slugs of water from coming into the crude distiller). In some refineries separate slops processing(distillation) facilities are installed [259, Dekkers, 2000].

Streams from water treatment units (e.g. oil/water mixtures from interceptors) can be routed to the wet slops tank. Oil from sludge thickeners (centrifuges/decanters) can be routed to the slops tanks. In that way also The oil in sludges from DAF units can be recovered that way also [259, Dekkers, 2000].
4.27.4.5 Recycle/Reuse outside the installation

Some options to reduce the waste generation is the recycle or reuse of them. Follows some examples that can be considered as good environmental practices:

- Treat catalysts for metal recovery (reforming, desulphurisation) (See 4.20.2)
- waste lubes: re-refining (See 4.27.4.6)
- drums/containers: reconditioning
- spent caustic can be used: (See 4.20.2)
- alkylation process: CaF₂
  - for HF production
  - as a fluxing agent (steel industry)
- resale of polymerisation plant catalyst as a fertiliser (See 4.18.2)
- sale of gypsum or sulphuric acid from flue-gas desulphurisation units
- for dust: in the regenerative flue-gas desulphurisation process according to Welmann Lord NH₃ is injected to prevent the formation of SO₃. Therefore up to 80 % of the ash consists of (NH₄)₂SO₄, which can be used as a fertiliser or as a basic material for NH₃ production [250, Winter, 2000].
- paper, wood, glass, scrap metal according to selective collection and recycling schemes and circuits which may be implemented at national or regional levels.
- construction/demolition debris:
  - concrete to a crusher, for use in road building etc.
  - asphalt scrapings reused, e.g. in road building

It has to be mentioned that reuse of waste fractions/residues outside the company is only an option, if these waste fractions meet certain criteria (such as concentration of pollutants in a fertiliser) and do not alter the original product characteristics (e.g. when using gypsum in the cement industry).

4.27.4.6 Reuse of waste lubes

Note for the TWG: this Section should be updated and transferred in appropriate section, depending on the new information announced at the KOM (in particular from CZ and SK) No data provided

Description
Waste lubes can be reused within the refinery as fuel component or as feedstock for re-refining. Controlled incineration of waste lube oils is another alternative.

Achieved environmental benefits
Reduction in the amount of waste lubes produced within the refinery and act as a receiver of waste lubes.

Cross-media effects
Waste lubricating oils are generally undefined and may contain all kind of additives that need to be disposed of properly, and contaminants (even PCB’s). Inclusion of contaminated waste lubes into commercial fuel oil would expose the customer to high risks. Inclusion of this waste in refinery fuel poses a safety risk.
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Applicability
Some applicability problems have been detected. For example, waste lubricating oil from garages may contain organic chlorides used as degreasers; in hydrotreaters they will be converted into HCl and cause severe corrosion in this high pressure unit filled with hydrogen. Only by application of well-controlled pretreatment techniques, the treated waste oil can be upgraded to a fuel component. Such a pretreatment activity is normally not compatible with refinery operations and is done outside the refinery by specialised companies, which also do the collection of the waste oils. The only exception to the use of waste lubes as fuel component is for waste lube oil that is generated in the refinery itself and of which its composition is beyond any doubt.

Driving force for implementation
Reduce the amount of waste lubes

Reference literature
[259, Dekkers, 2000].

4.27.4.7 Recycle lab samples
Lab samples can be recycled to the oil recovery system.

4.27.5 Biodegradation of wastes
KOM conclusion 2.4: TWG to confirm that oily sludge land farming is still used, and to provide key updated info on this technique (surface, yield, residues, monitoring…)

Note to TWG: From chapter 3: only 7% of sludge were landfarmed. Propose to delete this section and clearly state that this technique is not BAT

This section contains methods for the biodegradation of refinery wastes that may be used specifically within refineries on site. This section does not contain methods for the remediation of contaminated soils. As it was stated in the scope of this document, soil remediation techniques are considered out of the scope of this document.

Description
Many hazardous chemicals present in refinery waste can be converted by microbiological methods to harmless compounds such as water and carbon dioxide. In general, the microbiological degradation of contaminants in soil is very slow in nature, because process conditions for such degradation are seldom favourable. To accelerate degradation a number of conditions have to be fulfilled.

Current techniques for biological decontamination are based on optimisation of the process conditions for microbiological degradation. The appropriate micro-organisms for microbiological degradation may already be present in the waste to be treated or may have to be added. The latter is necessary if special micro-organisms are required. These special micro-organisms can be obtained by selection and adaptation.

Operational data
The most important factors are the availability of temperature control, sufficient oxygen, nutrients, and the appropriate micro-organisms. Also important are the concentration level of the contaminants and the variation in concentration. The presence of toxic compounds can disturb the degradation process. Sometimes the presence of natural organic compounds has a positive influence on the biodegradation process.

In summary the following conditions have to be met in order to optimise the degradation rate of a waste generated by a refinery:
sufficient number of microorganisms of the right strains
- non-toxic concentrations of contaminants or other compounds
- adjustment of an accurate water content
- presence of sufficient nutrients (mainly P and N in ratio 1:10)
- presence of sufficient oxygen for aerobic processes and a full depletion of oxygen for anaerobic processes
- favourable temperature (20–30°C)
- pH 6–8
- temperature control
- measures have to be applied to prevent emissions into air by volatile contaminants or degradation products (by covering the area and by treating the exhaust air) and to prevent emissions into water and soil (by sealing the floor and reuse of excess water).
- sufficient availability of contaminants (preferably without high peak concentrations) to the microorganisms including good mixing of nutrients, waste, inert (e.g. soil) and contaminants.

Reference literature
[115, CONCAWE, 1999]

4.27.6 Stabilisation/solidification of waste
This issue is addressed in Waste treatment WT BREF [87, EC 2006]

Description
The processes described below are commonly used:

Solidification
A process in which materials are added to the waste to produce a solid. It may involve a solidifying agent that physically surrounds the contaminant (i.e. cement or lime), or it may utilize a chemical fixation process (i.e. sorbents). The resulting waste is usually an easily handled solid with low leachability. Several processes exist:

- Cement-based processes. In this process the slurried waste is mixed with cement and during the hardening process is incorporated in the rigid concrete matrix. In the same line, spent catalytic cracker unit (FCC unit) catalyst may be used as an additive in cement manufacturing. When the cement is used, the catalyst component forms insoluble hydrates with the chalk present in the cement mixture, which also gives beneficial fixation of heavy metals.
- Thermoplastic techniques. In general the use of thermoplastic solidification techniques is restricted to dry solid materials.
- Mixing with bitumen. The processing of waste with bitumen is applied in the oil manufacturing industry as a disposal method. This process allows treatment of soils with high levels (up to 10%) of high boiling range hydrocarbons.
- Stabilisation - The conversion of a waste to a chemically stable form that resists leaching. This may be accomplished by a pH adjustment. Stabilisation also generally results in a solidification of some sort (monolith or dry granular solid).
- Chemical Stabilisation. These processes are based on the reaction of lime with waste materials and water to form a chemically stable product. When compacted, the porosity to water is very low. This reduces the risk of leaching.

Encapsulation
Complete coating or enclosure of a waste with a new, non-permeable substance. Two types of encapsulation techniques exist: micro-encapsulation and macro-encapsulation.

The micro-encapsulation techniques are based on the reduction of the surface to volume ratio of the waste by formation of a monolithic, hard mass with a very low permeability. Macro-encapsulation is the enclosing of a relatively large quantity of waste, such as an entire waste
container. Wastes are macro-encapsulated by surrounding them with a stiff, weight-supporting matrix, and a seam-free jacket.

Achieved environmental benefits
Stabilisation and solidification are treatment processes designed to improve waste handling and physical characteristics, decrease surface area across which pollutants can leach, or limit the solubility of hazardous constituents.

Applicability
Cement-based processes
The process is especially effective when the waste contains metals because at the high pH of the cement mixture most metal compounds are converted into insoluble metal hydroxides. In the case of spent catalyst, most metal compounds are present as hydroxides which as such may also increase the strength and stability of the waste containing concrete. On the other hand, the presence of organic impurities may act as interfering agents to the curing of the concrete and this limits the application of this disposal route.

Thermoplastic techniques
In general the use of thermoplastic solidification techniques is restricted to dry solid materials. This technique is not suitable to be used for wastes containing:

- organic chemicals (these may act as solvents)
- oxidising salts (these can react with the organic material causing deterioration to the matrix material; at elevated temperatures these mixtures are extremely flammable)
- dehydrated salts (e.g. sodium sulphate easily dehydrates at temperatures required to plasticise bitumen; when the bitumen matrix is soaked in water, rehydration of the sodium sulphate can occur, and this can cause the bitumen to swell and split apart).

Mixing with bitumen
It is applied as a disposal method for spent FCC catalyst and used for the production of a filler component in road asphalt where the catalyst is present as a minor component. The catalyst particles are completely encapsulated which makes aqueous extraction unlikely. This process allows treatment of soils with high levels (up to 10%) of high boiling range hydrocarbons. The soil is mixed with bitumen to produce a stable end-product suitable for use in road construction.

Chemical Stabilisation
This technique is suitable to immobilise watery sludges to yield a powdery hydrophobic product which can be compacted. The immobilised product, is water-repellent and hardens with time and often has very good properties for civil engineering applications like foundations, tank bases, bundwall and road-making.

Encapsulation
This technique is suitable for on-site treatment of disposal sites of accumulated spent acid tars and oily sludges which are difficult to transport and to dispose of by other means. A disadvantage is that the treated product occupies a larger volume than the original sludge. Because it can be applied on-site, the encapsulation process may be considered for single applications like rehabilitating refinery sites after decommissioning or cleaning up an oil-polluted site after a spill. The decision to apply the process depends on the future use of the site and local legislation. The process is less attractive for the treatment of regularly produced sludges because of the increased mass generated for disposal.

Reference literature
[115, CONCAWE, 1999]
4.27.7 Waste storage

Wastes awaiting disposal should be stored in an environmentally acceptable manner, as approved by the local control authority. Storage should not give rise to secondary environmental problems such as odour or pollution of groundwater due to rainwater percolation through or run-off from the site. Storage should be in closed vessels, containers or bags, on a site surrounded by a bund wall or toe wall, with drainage to a prepared system. Special precautions are of course required for pyrophoric materials to eliminate the risk of fires; they must be kept wet, sealed or blanketed with inert gas.
Chapter 5

5 BEST AVAILABLE TECHNIQUES (BAT)

SCOPE

These BAT conclusions concern the following industrial activities specified in Section 1.2 of Annex I to Directive 2010/75/EU, namely:

- 1.2 Energy industries: Refining of mineral oil and gas.

This document addresses the activities and processes set out in the following table.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Subactivities or processes included in each category of activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylation</td>
<td>All alkylation processes: HF, H$_2$SO$_4$ and solid-acid</td>
</tr>
<tr>
<td>Base oil production</td>
<td>Deasphalting, aromatic extraction, wax processing, … and lubricant oil hydrofinishing</td>
</tr>
<tr>
<td>Bitumen production</td>
<td>All techniques from storage to final product additives</td>
</tr>
<tr>
<td>Catalytic cracking</td>
<td>All types of catalytic cracking units such as fluid catalytic cracking</td>
</tr>
<tr>
<td>Catalytic reforming</td>
<td>Continuous, cyclic and semi-regenerative catalytic reformer</td>
</tr>
<tr>
<td>Coking processes</td>
<td>Delayed and fluid coking process. Coke calcination</td>
</tr>
<tr>
<td>Cooling systems</td>
<td>Cooling techniques applied in refineries</td>
</tr>
<tr>
<td>Desalting</td>
<td>Desalting of crude oil</td>
</tr>
<tr>
<td>Combustion for energy production</td>
<td>Refinery power plants including all types of technologies applied within EU refineries and burning refinery fuels. Energy production techniques using only conventional or commercial fuels are not covered.</td>
</tr>
<tr>
<td>Etherification</td>
<td>MTBE, ETBE and TAME production</td>
</tr>
<tr>
<td>Gas separation processes</td>
<td>Separation of light fractions of the crude oil e.g. refinery fuel gas (RFG), liquefied petroleum gas (LPG)</td>
</tr>
<tr>
<td>Hydrogen consuming processes</td>
<td>Hydrocracking, hydrotreating, hydrocracking, hydroconversion, hydroprocessing and hydrogenation processes</td>
</tr>
<tr>
<td>Hydrogen production</td>
<td>Gasification (coke and heavy oils), steam reforming and hydrogen purification</td>
</tr>
<tr>
<td>Integrated refinery management</td>
<td>Environmental activities, utility and overall refinery management</td>
</tr>
<tr>
<td>Isomerisation</td>
<td>Isomerisation of hydrocarbons compounds C$_4$, C$_5$ and C$_6$</td>
</tr>
<tr>
<td>Natural gas plants</td>
<td>Natural gas (NG) processing including liquefaction of NG</td>
</tr>
<tr>
<td>Polymerisation</td>
<td>Polymerisation, dimerisation and condensation</td>
</tr>
<tr>
<td>Primary distillation units</td>
<td>Atmospheric and vacuum distillation units</td>
</tr>
<tr>
<td>Product treatments</td>
<td>Sweetening and final product treatments</td>
</tr>
<tr>
<td>Storage and handling of refinery materials</td>
<td>Storage, blending, loading and unloading of refinery materials</td>
</tr>
<tr>
<td>Visbreaking and other thermal conversions</td>
<td>Thermal treatment such as visbreaking or thermal gasoil</td>
</tr>
<tr>
<td>Waste gas treatment</td>
<td>All techniques to reduce or abate emissions to air</td>
</tr>
<tr>
<td>Waste water treatments</td>
<td>Techniques to reduce or treat waste water prior to release</td>
</tr>
<tr>
<td>Waste management</td>
<td>Techniques to prevent and reduce generation of waste</td>
</tr>
</tbody>
</table>

These BAT conclusions do not address the following activities:

- the exploration and production of crude oil and natural gas
- the transportation of crude oil and natural gas
- the marketing and distribution of products.
Other reference documents which may be of relevance for the activities covered by these BAT conclusions are the following.

<table>
<thead>
<tr>
<th>Reference document</th>
<th>Subject</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Waste Water and Waste Gas Treatment (CWW)</td>
<td>Waste water management and treatment techniques</td>
</tr>
<tr>
<td>Industrial Cooling Systems (ICS)</td>
<td>Cooling processes</td>
</tr>
<tr>
<td>Economics and Cross-media Effects (ECM)</td>
<td>Economics and cross-media effects of techniques</td>
</tr>
<tr>
<td>Emissions from Storage (EFS)</td>
<td>Storage, blending, loading and unloading of refinery materials</td>
</tr>
<tr>
<td>Energy Efficiency (ENE)</td>
<td>Energy efficiency and integrated refinery management</td>
</tr>
<tr>
<td>Large Combustion Plants (LCP)</td>
<td>Combustion of commercial fuels</td>
</tr>
<tr>
<td>Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (LVIC-AAF)</td>
<td>Steam reforming and hydrogen purification</td>
</tr>
<tr>
<td>Large Volume Organic Chemical Industry (LVOC)</td>
<td>Etherification process (MTBE, ETBE and TAME production)</td>
</tr>
<tr>
<td>General Principles of Monitoring (MON)</td>
<td>Monitoring of emissions to air and water</td>
</tr>
<tr>
<td>Waste Incineration (WI)</td>
<td>Waste and waste water management</td>
</tr>
<tr>
<td>Waste Treatments Industries (WT)</td>
<td>Waste and waste water management</td>
</tr>
</tbody>
</table>

The techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive. Other techniques may be used that ensure at least an equivalent level of environmental protection.
General considerations

Averaging periods and reference conditions for air emissions

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for air emissions given in these BAT conclusions refer to daily average values under the following standard conditions: dry gas, temperature 273.15 K, pressure 101.3 kPa.

<table>
<thead>
<tr>
<th>For periodic measurements</th>
<th>BAT-AELs refer to the average value of three spot samples of at least 30 minutes each</th>
</tr>
</thead>
<tbody>
<tr>
<td>For continuous measurements(*)</td>
<td>Unless stated otherwise, BAT-AELs refer to daily average values</td>
</tr>
<tr>
<td>(*) Continuous measurement means, according to CEN standard definition measurement using an 'automated measuring system' (AMS) or a 'continuous emission monitoring system' (CEMS).</td>
<td></td>
</tr>
</tbody>
</table>

From combustion and catalytic processes, reference conditions for oxygen are shown in Table 5.1.

<table>
<thead>
<tr>
<th>Table 5.1: Reference conditions for BAT-AELs concerning air emissions from combustion and catalytic cracking processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activities</td>
</tr>
<tr>
<td>--------------</td>
</tr>
<tr>
<td>Combustion process using liquid or gaseous fuels with the exception of gas turbines and engines</td>
</tr>
<tr>
<td>Catalytic cracking (regeneration of catalyst)</td>
</tr>
<tr>
<td>Gas turbines and engines</td>
</tr>
</tbody>
</table>

Conversion to reference oxygen concentration

The formula for calculating the emissions concentration at a reference oxygen level (see Table 5.1) is shown below.

\[
E_R = \frac{21 - O_R}{21 - O_M} \times E_M
\]

Where:

- \(E_R (mg/Nm^3)\): emissions concentration corrected to the reference oxygen level \(O_R\)
- \(O_R\) (vol %): reference oxygen level
- \(E_M (mg/Nm^3)\): emissions concentration referred to the measured oxygen level \(O_M\)
- \(O_M\) (vol %): measured oxygen level.

Averaging periods for waste water discharges

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for waste water emissions given in these BAT conclusions refer to the average value of a flow proportional sample taken over a period of 24 hours.
Definitions

For the purpose of these BAT conclusions, the following definitions apply:

<table>
<thead>
<tr>
<th>Term used</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>A segment/subpart of the installation in which a specific processing operation is conducted</td>
</tr>
<tr>
<td>New unit</td>
<td>A unit first operated on the site of the installation following the publication of these BAT conclusions or a complete replacement of a unit on the existing foundations of the installation following the publication of these BAT conclusions</td>
</tr>
<tr>
<td>Existing unit</td>
<td>A unit which is not a new unit</td>
</tr>
<tr>
<td>Process off-gas</td>
<td>The collected gas generated by a process which must be treated e.g. in an acid gas removal unit and SRU</td>
</tr>
<tr>
<td>Flue-gas</td>
<td>The exhaust gas exiting a unit after an oxidation step, generally combustion (e.g. regenerator, Claus unit)</td>
</tr>
<tr>
<td>Tail gas</td>
<td>Common name of the exhaust gas from an SRU (generally Claus process)</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds as defined under Directive 2010/75/EU</td>
</tr>
<tr>
<td>Diffuse VOC emission</td>
<td>Non-channelled VOC emissions that are not released via specific emission points such as stacks. They can result from 'area' sources (e.g. tanks) or 'point' sources (e.g. pipe flanges).</td>
</tr>
<tr>
<td>Fugitive VOC emission</td>
<td>Diffuse VOC emissions from 'point' sources.</td>
</tr>
<tr>
<td>NOx expressed as NO2</td>
<td>The sum of nitrogen oxide (NO) and nitrogen dioxide (NO2) expressed as NO2</td>
</tr>
<tr>
<td>SOx expressed as SO2</td>
<td>The sum of sulphur dioxide (SO2) and sulphur trioxide (SO3) expressed as SO2</td>
</tr>
<tr>
<td>H2S</td>
<td>Hydrogen sulphides. Carbonyl sulphide and mercaptan are not included</td>
</tr>
<tr>
<td>Hydrogen chloride expressed as HCl</td>
<td>All gaseous chlorides expressed as HCl</td>
</tr>
<tr>
<td>Hydrogen fluoride expressed as HF</td>
<td>All gaseous fluorides expressed as HF</td>
</tr>
<tr>
<td>FCC unit</td>
<td>Fluid catalytic cracking (FCC) is the common process name. The catalytic cracking is a conversion process for upgrading heavy hydrocarbons. It uses heat and a catalyst to break larger hydrocarbon molecules into lighter molecules.</td>
</tr>
<tr>
<td>SR Unit</td>
<td>Sulphur recovery unit—see technique definition in Glossary Section 5.21.3</td>
</tr>
</tbody>
</table>
| Combustion unit | Liquid, gas or multi-fuel fired unit burning refinery fuels (distillation and conversion residues from the refining of crude-oil) alone or with other fuels for the production of energy at the refinery site.  
NB: Combustion plant running exclusively on commercial fuels are covered by the LCP BREF  
**Note to TWG:** TWG is asked to provide feedback on this definition in order to clarify the scope of combustion addressed in this document |

NOTE: Whilst cross-references are provided to other parts of this BREF in this draft document in order to aid the work of the TWG, they will not be included in the final BAT conclusions themselves. Such cross-references are consequently displayed in [square brackets and italics].
Chapter 5

5.1 General BAT conclusions for the Refining of mineral oil and gas

Unless otherwise stated, the BAT conclusions presented in this section are generally applicable.

The process specific BAT conclusions included in Sections 5.2 to 5.20 apply in addition to the general BAT conclusions mentioned in this section.

5.1.1 Environmental management systems

1. BAT is to implement and adhere to an environmental management system (EMS) that incorporates all of the following features:

   i. commitment of the management, including senior management;
   ii. definition of an environmental policy that includes the continuous improvement for the installation by the management;
   iii. planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
   iv. implementation of the procedures paying particular attention to:
      (a) structure and responsibility
      (b) training, awareness and competence
      (c) communication
      (d) employee involvement
      (e) documentation
      (f) efficient process control
      (g) maintenance programmes
      (h) emergency preparedness and response
      (i) safeguarding compliance with environmental legislation.
   v. checking performance and taking corrective action, paying particular attention to:
      (a) monitoring and measurement (see also the reference document on the General Principles of Monitoring)
      (b) corrective and preventive action
      (c) maintenance of records
      (d) independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;
   vi. review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
   vii. following the development of cleaner technologies;
   viii. consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;
   ix. application of sectoral benchmarking on a regular basis.

Applicability
The scope (e.g. level of details) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.
Chapter 5

5.1.2 Energy efficiency

2. In order to use energy efficiently, BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Design techniques</td>
<td>Methodology based on a systematic calculation of thermodynamic targets for minimising energy consumption of processes. Used as a tool for the evaluation of total systems designs</td>
</tr>
<tr>
<td>a. Pinch analysis</td>
<td>Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled.</td>
</tr>
<tr>
<td>b. Heat integration</td>
<td>Heat integration of process systems ensures that a substantial proportion of the heat required in various processes is provided by exchanging heat between streams to be heated and streams to be cooled.</td>
</tr>
<tr>
<td>ii. Process control and maintenance techniques</td>
<td>Use of energy recovery devices e.g.: waste heat boilers, expanders / power recovery in the FCC unit</td>
</tr>
<tr>
<td>a. Heat and power recovery</td>
<td>Automated controlled combustion in order to lower fuel consumption per tonne of feed processed often combined with heat integration for improving furnace efficiency</td>
</tr>
<tr>
<td>b. Process optimisation</td>
<td>Systematic mapping of drain valve systems in order to reduce steam consumption and optimise its use</td>
</tr>
<tr>
<td>c. Management and reduction of steam consumption</td>
<td>Systematic mapping of drain valve systems in order to reduce steam consumption and optimise its use</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.10.1]

5.1.3 Solid materials storage and handling

3. In order to prevent, or where that is not practicable, to reduce dust emissions from the storage and handling of dusty materials BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. store bulk powder materials in enclosed silos equipped with a dust abatement system (e.g. fabric filter)</td>
<td></td>
</tr>
<tr>
<td>ii. store fine materials in enclosed containers or sealed bags</td>
<td></td>
</tr>
<tr>
<td>iii. store under cover stockpiles of coarse dusty materials</td>
<td></td>
</tr>
<tr>
<td>iv. use road cleaning vehicles.</td>
<td></td>
</tr>
</tbody>
</table>

5.1.4 Monitoring of emissions to air and key process parameters

4. BAT is to monitor emissions to air and key process parameters at the units mentioned in the following table and to use the indicated monitoring techniques with at least the minimum frequency given and in accordance with EN or ISO standards. If EN or ISO standards are not available, BAT is to use national or other international standards that ensure the provision of data of an equivalent scientific quality.
### Chapter 5

#### 5.1.5 Operation of waste gas treatment systems

5. In order to prevent or reduce emissions to air, BAT is to operate the acid gas removal units, sulphur recovery units and all other waste gas treatment systems with a high availability and at optimal capacity.

**Applicability**
Special procedures can be defined for specific operating conditions, in particular:

i. during start-up and shutdown operations

ii. during other special operations which could affect the proper functioning of the systems (e.g. regular and extraordinary maintenance work and cleaning operations of the units and/or of the waste gas treatment system)

iii. in case of insufficient waste gas flow or temperature which prevents the use of the system at full capacity.

---

<table>
<thead>
<tr>
<th>Description</th>
<th>Process unit</th>
<th>Minimum frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. Monitoring of emissions to air</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i. Monitoring of SO\textsubscript{2}, NO\textsubscript{x}, and dust associated with the control of surrogate parameters</td>
<td>Catalytic cracking and combustion units</td>
<td>Continuous(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>Sulphur recovery units (SRU)</td>
<td>Continuous(^{(2)}) for SO\textsubscript{2}</td>
</tr>
<tr>
<td>ii. Monitoring of NH\textsubscript{3} emissions, in particular when selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) techniques are applied</td>
<td>All units equipped with SCR or SNCR</td>
<td>Continuous</td>
</tr>
<tr>
<td>iii. Monitoring of CO emissions when partial combustion occurs, especially for FCC units or where primary techniques are applied for NO\textsubscript{x} emissions reductions</td>
<td>Catalytic cracking and combustion units</td>
<td>Continuous</td>
</tr>
<tr>
<td>iv. Monitoring of emissions of metals (Ni, Sb, V),</td>
<td>Catalytic cracking and combustion units</td>
<td>Monthly</td>
</tr>
<tr>
<td>v. Monitoring of dioxins and furans</td>
<td>Catalytic reformer</td>
<td>Yearly</td>
</tr>
<tr>
<td><strong>II. Monitoring of key process parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i. Monitoring of parameters to prevent/reduce pollution, e.g. O\textsubscript{2} content in flue-gas, N and S content in fuel or feed</td>
<td>Catalytic cracking and combustion units</td>
<td>Continuous for O\textsubscript{2} content Periodic at a frequency based on fuel/feed changes</td>
</tr>
<tr>
<td>ii. Monitoring of key parameters to ensure process stability, e.g. temperature, air flow</td>
<td>Catalytic cracking, combustion units and sulphur recovery units (SRU)</td>
<td>Continuous or periodic at a frequency based on process stability</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Monitoring based on SO\textsubscript{2} emissions measurements may be replaced by calculations associated with measurements of sulphur content of the fuel or the feed when it can be demonstrated that this alternative leads to a lower level of uncertainty

\(^{(2)}\) Continuous SO\textsubscript{2} emissions from SRU may be replaced by a material balance provided appropriate measurements of SRU efficiency are based on regular plant performance tests.
6. In order to prevent and reduce ammonia (NH₃) emissions to air when applying selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) techniques BAT is to maintain suitable operating conditions of the SCR or SNCR waste gas treatment systems, with the aim of limiting emissions of unreacted NH₃. BAT associated emission levels. See Table 5.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL&lt;sup&gt;(1)&lt;/sup&gt;</th>
<th>mg/Nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia expressed as NH₃</td>
<td>≤5 - 15 mg/Nm³</td>
<td></td>
</tr>
</tbody>
</table>

<sup>(1)</sup>The higher levels are associated with higher inlet NOx concentrations, higher NOx reduction rates and the ageing of the catalyst.

[This BAT conclusion is based on information given in Section 4.25.3.2]

7. In order to prevent and reduce emissions to air when using a sour water stripping unit, BAT is to route the acid off-gases from this unit to an SRU or any equivalent gas treatment process. It is not BAT to directly incinerate the sour water stripping and incondensable untreated gases.

[This BAT conclusion is based on information given in Section 4.26.4]

### 5.1.6 Monitoring of emissions to water

8. BAT is to monitor emissions to water for the pollutants mentioned in Table 5.3 by using the monitoring techniques with at least the frequency given in Table 5.3. and in accordance with EN or ISO standards. If EN or ISO standards are not available, BAT is to use national or other international standards that ensure the provision of data of an equivalent scientific level.

### 5.1.7 Emissions to water

9. In order to reduce water consumption and the volume of contaminated water, BAT is to use a combination of the techniques given below:
Chapter 5

Technique Description Applicability

i. Water stream integration Reduction of process water produced at unit level prior to discharge by internal reuse of water stream from e.g. cooling, condensates, especially for use in crude desalting Generally applicable for new units. For existing units applicability may require a complete rebuild of the unit

ii. Water and drainage system for segregation of contaminated water streams Design of an industrial site aiming at an optimised water management where each stream is treated as appropriate, by e.g. routing generated sour water (from distillation, cracking, coking units, etc.) to appropriate pretreatment such as a stripping unit Generally applicable for new units. For existing units applicability may require a complete rebuild of the unit

iii. Segregation of non-contaminated water streams (e.g. once-through cooling, rain water) Design of a site in order to avoid sending non-contaminated water to general waste water treatment and to have a separate release after possible reuse for this type of stream. Generally applicable

iv. Prevention of spillages and leaks Practices that include utilisation of special procedures and/or temporary equipment to ensure performances are respected when necessary to manage special circumstances such as spills, loss of containment, etc. Generally applicable

[This BAT conclusion is based on information given in Sections 4.15.7.1, 4.15.7.2, and 4.26]

10. In order to reduce the emission load of pollutants in the waste water discharge to the receiving water body, BAT is to remove insoluble and soluble polluting substances by using a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Removal of insoluble substances by recovering oil (e.g. with separators or corrugated plate interceptor)</td>
<td>See Section 5.22.2</td>
<td>The technique is generally applicable</td>
</tr>
<tr>
<td>ii. Removal of insoluble substances by recovering suspended solid and dispersed oil (e.g. by flotation)</td>
<td>See Section 5.22.2</td>
<td>The technique is generally applicable</td>
</tr>
<tr>
<td>iii. Removal of soluble substances including biological treatment (e.g. activated sludge or biofiltration) and clarification</td>
<td>See Section 5.22.2</td>
<td>The technique is generally applicable</td>
</tr>
<tr>
<td>iv. Additional final step treatment (e.g. nitrification denitrification process)</td>
<td>See Section 5.22.2</td>
<td>The techniques is generally applicable</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Sections 4.26.]

BAT associated emission levels. See Table 5.3.
### Table 5.3: BAT-associated emission levels for direct waste water discharges from the refining of mineral oil and gas and monitoring frequencies associated with BAT

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>BAT-AEL long term (yearly average)</th>
<th>BAT-AEL short term*</th>
<th>Note to TWG [LoQ= limit of quantification mg/l]</th>
<th>Monitoring type/ measurement frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total hydrocarbon content (THC)</td>
<td>mg/l</td>
<td>0.1 – 1.5</td>
<td>To be determined(*)</td>
<td>Require method (**) compatible with EN 9377-2 (gas chromatography) [LoQ: 0.1]</td>
<td>Flow proportional sample (/)daily</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>mg/l</td>
<td>2 – 25</td>
<td>To be determined</td>
<td>[LoQ: 2]</td>
<td>Flow proportional sample (/)daily</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)(2)</td>
<td>mg/l</td>
<td>30 – 125</td>
<td>To be determined</td>
<td>[LoQ: 30]</td>
<td>Flow proportional sample (/)daily</td>
</tr>
<tr>
<td>BOD5</td>
<td>mg/l</td>
<td>2 – 20</td>
<td>To be determined</td>
<td>[LoQ: 2]</td>
<td>Flow proportional sample (/)daily</td>
</tr>
<tr>
<td>Ammoniacal nitrogen (expressed as N)</td>
<td>mg/l</td>
<td>0.1 – 10</td>
<td>To be determined</td>
<td>[LoQ: 0.05]</td>
<td>Flow proportional sample (/)daily</td>
</tr>
<tr>
<td>Total nitrogen(3) (expressed as N)</td>
<td>mg/l</td>
<td>1 – 20</td>
<td>To be determined</td>
<td>[LoQ: 0.05]</td>
<td>Flow proportional sample (/)daily</td>
</tr>
<tr>
<td>Lead, expressed as Pb</td>
<td>mg/l</td>
<td>0.005 – 0.030</td>
<td>To be determined</td>
<td>Priority substance [LoQ: 0.005]</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
<tr>
<td>Cadmium, expressed as Cd</td>
<td>mg/l</td>
<td>0.002 – 0.008</td>
<td>To be determined</td>
<td>NB: priority hazardous substance [LoQ: 0.002]</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
<tr>
<td>Nickel, expressed as Ni</td>
<td>mg/l</td>
<td>0.005 – 0.100</td>
<td>To be determined</td>
<td>Priority substance [LoQ: 0.005]</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
<tr>
<td>Mercury expressed as Hg</td>
<td>mg/l</td>
<td>0.000 1 – 0.001</td>
<td>To be determined</td>
<td>NB: priority hazardous substance [LoQ: 0.000 1]</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
<tr>
<td>Vanadium</td>
<td>mg/l</td>
<td>No AEL proposed for Vanadium reporting only</td>
<td>To be determined</td>
<td>Assessment of environmental concern to be done; V is proposed to be monitored and reported</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/l</td>
<td>Phenol index &lt; 0.100</td>
<td>To be determined</td>
<td>(*** )</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
<tr>
<td>Benzene, toluene, Ethyl benzene, Ethylene (BTEX )</td>
<td>mg/l</td>
<td>Benzene: 0.001 – 0.050 No AEL for T.E.X reporting only</td>
<td>To be determined</td>
<td>[Benzene LoQ: 0.0001]</td>
<td>Flow proportional sample (/)monthly</td>
</tr>
</tbody>
</table>

(*) Refers to a composite flow proportional sample taken over a period of 24 hours.
(1) Where on-site correlation is available, COD may be replaced by TOC. The correlation between COD and TOC should be elaborated case by case.
(2) Where TotalN = TKN + Nitrates + Nitrites
(3) Where TotalN = TKN + Nitrates + Nitrites

**Note to TWG:** No short term data available from initial data collection. Proposed BAT-AELs are based on 2008 TWG data collection using yearly averages and some individual refineries sites long period daily data. TWG is asked to provide daily average emission level values for a long time span (data and graphs under Excel format) at refinery sites. A recently provided dataset for 7 refineries (daily values), is available in Section 4.26.10 of the BREF. The possible short term variations are assessed based on analysis of the 95th for COD, TSS and THC. Expressed as a % yearly average. The TWG is asked to provide feedback on these data and their possible use in the BAT conclusions.

**Note to TWG:** Based on TWG data collection, various methods were reported for THC measurements – Clarification of reference method is therefore proposed

**(*** ) Note to TWG:** Phenol analytical method to clarify, e.g compatible with ISO 6439:1990 Maxi mum LoQ (Index): 0.005
5.1.8 Waste generation and management

11. In order to prevent, or where it is not practicable, to reduce waste generation, BAT is to adopt and implement a waste management plan that, in order of priority, ensures that waste is prepared for reuse, recycling, recovery or disposal.

[This BAT conclusion is based on information given in Section 4.27.1]

12. In order to reduce the amount of sludge to be treated or disposed of, BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Sludge pre-treatment</td>
<td>Prior to final treatment (e.g. in a fluidized bed incinerator), the sludges are dewatered and/or de-oiled (by e.g. centrifugal decanters or steam dryers) to reduce their volume</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Re-use of sludge in process units</td>
<td>Certain types of sludge (e.g. oily sludge) can be processed in units (e.g. coking) as part of the feed due to their oil content</td>
<td>Applicability is restricted to sludges that can fulfil the requirements to be be processed in units with appropriate treatment</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.27.2]

13. In order to prevent pollution of the soil, it is not BAT to use biodegradation of oily sludge by spreading on land (land farming.)

[This BAT conclusion is based on information given in Section 4.27.5]

14. In order to reduce the generation of spent solid catalyst waste, BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Spent solid catalyst management</td>
<td>See Section 5.23</td>
</tr>
<tr>
<td>ii. Removal of catalyst from slurry decant oil</td>
<td>See Section 5.23</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.27.3]
5.1.9 Noise

15. In order to prevent or reduce noise BAT is to use one or a combination of the techniques given below:

i. Make an environmental noise assessment and formulate a noise management plan as appropriate to the local environment
ii. Enclose noisy equipment/operation in a separate structure/unit
iii. Use embankments to screen the source of noise
iv. Use noise protection walls.

[Note: No specific information for noise reduction management from REF BREF ]

5.1.10 BAT conclusions for integrated refinery management

16. In order to prevent or reduce diffuse VOC emissions, BAT is to apply a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
</table>
| I. Techniques related to plant design | i. limiting the number of potential emission sources  
ii. maximising inherent process containment features  
iii. selecting high integrity equipment  
iv. facilitating monitoring and maintenance activities by ensuring access to potentially leaking components | Applicability of the techniques may be limited for existing units |
| II. Techniques related to plant installation and commissioning | i. Well-defined procedures for construction and assembly  
ii. Robust commissioning and hand-over procedures to ensure that the plant is installed in line with the design requirements. | Applicability of the techniques may be limited for existing units |
| III. Techniques related to plant operation | Risk-based leak detection and repair (LDAR) programme in order to identify leaking components, and to repair these leaks. See Section 5.21.6 | Generally applicable |

[This BAT conclusion is based on information given in Section 4.23.6. and 3.28.1.4]

Note to TWG: If needed, a possible BAT statement referring to the use of management techniques at the refinery level, in order to reduce overall SO\textsubscript{X} and NO\textsubscript{X} emissions to air, according to the guideline described in Annex 9.9 of the BREF may be proposed, provided a sufficiently detailed BAT-AEL can be defined.

[This BAT conclusion is based on information given in Section 4.15.9.3].
5.2 BAT conclusions for alkylation process

5.2.1 Hydrofluoric acid alkylation process

17. In order to prevent hydrofluoric acid (HF) emissions to air from the hydrofluoric acid alkylation process, BAT is to use a wet scrubbing technique (with alkaline solution to treat incondensable gas streams prior to venting to flare.

Description
See Section 5.21.3

Applicability:
The technique is generally applicable. Safety requirements due to the hazardous nature of hydrofluoric acid are to be considered.

18. In order to reduce emissions to water from the hydrofluoric acid alkylation process, BAT is to use a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Precipitation/Neutralisation step</td>
<td>Precipitation (with, e.g. calcium or aluminium-based additives) or system neutralisation (where the effluent is indirectly neutralised with KOH)</td>
<td>Generally applicable. Safety requirements due to the hazardous nature of HF are to be considered</td>
</tr>
<tr>
<td>ii. Separation step</td>
<td>The insoluble compounds produced at the first step (e.g. CaF$_2$ or AlF$_3$) are separated in, e.g. a settlement basin</td>
<td>Generally applicable.</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.2.1]

5.2.2 Sulphuric acid alkylation process

19. In order to reduce the emissions to water from the sulphuric acid alkylation process, BAT is to reduce the use of sulphuric acid by regenerating the spent acid and to neutralise waste water generated by this process before routing to waste water treatment.

[This BAT conclusion is based on information given in Section 4.2.2]

5.2.3 Solid acid alkylation process

[From information given in Section 4.2.3 it has not been possible to derive BAT conclusions]
5.3 BAT conclusions for base oil production process

20. In order to prevent and reduce the emissions of hazardous substances to air from base oil production processes, BAT is to select less hazardous substances to use as solvent.

Description
In aromatic extraction units, phenol, cresol and sulphur dioxide can be substituted by less hazardous substances such as furfural or n-methylpyrrolidone (NMP).

In dewaxing units, toluene and chlorinated hydrocarbons can be substituted by less hazardous substances such as propane and mixtures based on methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK).

[This BAT conclusion is based on information given in Sections 4.3.2, 4.3.3]

21. In order to prevent and reduce emissions to air from the base oil production process, BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Multi-effect extraction</td>
<td>Solvent extraction process including several stages of evaporation: double or triple effect</td>
<td>The use of a triple effect process may be restricted to non-fouling feed stocks.</td>
</tr>
<tr>
<td>ii. Common hot oil system</td>
<td>System where a fluid (hot oil), specific to a temperature/pressure application is circulated through an oil-or gas-fired or an electric heater, to provide the required heating medium temperature to the desired application and is then returned to the tank after appropriate filtering to keep its performance</td>
<td>Generally applicable.</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Sections 4.3.1 and 4.3.10]

5.4 BAT conclusions for the bitumen production process

22. In order to prevent and reduce emissions to air from bitumen production process, BAT is to treat the gaseous overhead by using one of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Thermal oxidation of gaseous overhead over 800 °C</td>
<td>See Section in 5.21.6</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Wet scrubbing for gaseous overhead</td>
<td>See Section 5.21.3</td>
<td>Generally applicable for bitumen blowing unit</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Sections 4.4.1, 4.4.2, 4.4.3 and 4.4.4]
5.5 **BAT conclusions for the catalytic cracking process**

23. In order to prevent or reduce NO\textsubscript{x} emissions to air from the regeneration of the catalyst, BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Use of promoters or additives</td>
<td>Use of a substance which selectively promotes the combustion of CO only and prevents the oxidation of the nitrogen which contains intermediates to NO\textsubscript{x}: e.g. non-platinum promoters</td>
<td>Applicable only in full combustion mode. Appropriate distribution of air in the regenerator may be required to obtain the maximum benefit</td>
</tr>
<tr>
<td>(a) Low NO\textsubscript{x} CO oxidation promoters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Specific additives for NO\textsubscript{x} reduction</td>
<td>Use of specific catalytic additives for enhancing the reduction of NO by CO</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Hydrotreatment of feed</td>
<td>Based on hydrogenation reactions, hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed when upgrading the refinery fractions for compliance with products specifications. See Section 5.21.3</td>
<td>Applicability is limited by availability of hydrogen production and hydrogen sulphide (H\textsubscript{2}S) treatment capacity (e.g. amine and Claus units)</td>
</tr>
</tbody>
</table>

II. Secondary or end of pipe techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Selective catalytic reduction (SCR)</td>
<td>See Section 5.21.2</td>
<td>To avoid potential fouling downstream, additional filtering might be required upstream the SCR. Applying the technique in existing units may require significant space availability</td>
</tr>
<tr>
<td>ii. Selective non-catalytic reduction (SNCR)</td>
<td>See Section 5.21.2</td>
<td>Generally applicable for partial combustion FCCs with CO boilers. For full combustion FCC without auxiliary boilers, additional fuel injection (e.g. hydrogen) may be required to match a lower temperature window</td>
</tr>
<tr>
<td>iii. Low temperature oxidation</td>
<td>See Section 5.21.2</td>
<td>Need for additional scrubbing capacity. Ozone generation and risk management associated to be properly addressed</td>
</tr>
</tbody>
</table>
Chapter 5

BAT associated emission levels. See Table 5.4.

Table 5.4: BAT-AELs for NO\textsubscript{X} emissions from catalytic cracking process (regenerator)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{X} expressed as NO\textsubscript{2}</td>
<td>&lt;30 – 200 For full combustion mode units</td>
</tr>
<tr>
<td></td>
<td>&lt;30 – 300 For partial combustion mode units</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.5.8.]

24. In order to reduce dust and metals emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Use of an attrition-resistant catalyst</td>
<td>Selection of catalyst substance which is able to resist abrasion and fragmentation in order to reduce dust emissions</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Hydrotreatment of feed</td>
<td>Based on hydrogenation reactions, hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed when upgrading the refinery fractions for compliance with products specifications. See Section 5.21.3</td>
<td>Applicability is limited by availability of hydrogen production and hydrogen sulphide (H\textsubscript{2}S) treatment capacity (e.g. amine and Claus units)</td>
</tr>
</tbody>
</table>

II. Secondary or end of pipe techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Electrostatic separator (ESP)</td>
<td>See Section 5.21.1</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Multistage cyclone separator</td>
<td>See Section 5.21.1</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iii. Third stage blowback filter</td>
<td>See Section 5.21.1</td>
<td>Applicability may be restricted for large size FCC(*)</td>
</tr>
<tr>
<td>iv. Fabric filter</td>
<td>See Section 5.21.1</td>
<td>Fabric filters application to FCC is very restricted because of the pressure drop, the potential for ‘blinding’ of the bags, and inability to face upset conditions. No example was reported in Europe through data collection</td>
</tr>
<tr>
<td>v. Wet scrubbing</td>
<td>See Section 5.21.3</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>

(*) Note to TWG: As applicability needs to be demonstrated for larger than medium size unit capacity, TWG is asked to provide recent examples or information on applicability to commonly sized FCC.

[This BAT conclusion is based on information given in Section 4.5.9.]
BAT associated emission levels. See Table 5.5.

Table 5.5: BAT-associated emission levels for dust and metals emissions from the catalytic cracking process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)((^1))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/Nm(^3)</td>
</tr>
<tr>
<td>Dust</td>
<td>&lt;5 – 25</td>
</tr>
<tr>
<td>Metals (Ni, Sb, V)</td>
<td>To be determined((^1))</td>
</tr>
</tbody>
</table>

(\(^1\)) Soot blowing in CO boiler are excluded as other-than-normal operations. (\(^1\))Note to TWG: TWG is asked to provide metals (Ni, Sb, V) emissions data.

[This BAT conclusion is based on information given in Sections 4.5.6 and 4.5.9.]

25. In order to prevent or reduce SO\(_x\) emissions to air from the catalytic cracking process (regenerator), BAT is to use one or a combination of the techniques given below:

i. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. SO(_x) reducing catalysts additives</td>
<td>Use of a substance which transfers sulphur associated to coke from the regenerator back to the reactor</td>
<td>Applicability may be restricted by regenerator conditions design. Requires appropriate hydrogen sulphide abatement capacity (e.g. SRU)</td>
</tr>
<tr>
<td></td>
<td>See description in 5.21.3</td>
<td></td>
</tr>
<tr>
<td>ii. Hydrotreatment of feed</td>
<td>Hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed. See description in 5.21.3</td>
<td>Applicability is determined by availability of hydrogen production and hydrogen sulphide (H(_2)S) treatment capacity (e.g. amine and Claus units)</td>
</tr>
</tbody>
</table>

ii. secondary or end of pipe flue-gas desulphurisation techniques (FGD) from BAT 59

BAT associated emission levels. See Table 5.6.

Table 5.6: BAT-associated emission levels for SO\(_x\) emissions from catalytic cracking process (regenerator)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_x) expressed as SO(_2)</td>
<td>100 – 500((^1))</td>
</tr>
</tbody>
</table>

(\(^1\))Lower end of the range achievable with feed hydrotreatment and/or flue-gas desulphurisation

Note to TWG: TWG is asked to provide updated information on applicability of hydrotreatment as it appears to be a key operation at refinery site.

[This BAT conclusion is based on information given in Section 3.5.2.1, 4.5.10.1 and 4.25.5.]
26. In order to reduce carbon monoxide (CO) emissions to air from the regeneration of the catalyst, BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>Combustion operation control</td>
<td>See Section 5.21.4</td>
</tr>
<tr>
<td>ii.</td>
<td>Catalysts with carbon monoxide (CO) oxidation promoters</td>
<td>See Section 5.21.4</td>
</tr>
<tr>
<td>iii.</td>
<td>Carbon monoxide (CO) boiler</td>
<td>See Section 5.21.4</td>
</tr>
</tbody>
</table>

BAT associated emission levels. See Table 5.7.

Table 5.7: BAT-associated emission levels for carbon monoxide emissions from partial mode catalytic cracking

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average) (mg/Nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide, expressed as CO</td>
<td>(&lt;100(*))</td>
</tr>
</tbody>
</table>

(*) Not applicable for full combustion mode

[This BAT conclusion is based on information given in Section 4.5 and 3.5.2.1]

5.6 BAT conclusions for the catalytic reforming process

27. In order to reduce emissions of dibenzo-p-dioxins and dibenzofurans to air from the catalytic reforming unit BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>Choice of catalyst promoter</td>
<td>Use of catalyst in order to minimise dioxin-like substances formation during regeneration- See Section 5.21.7</td>
</tr>
<tr>
<td>ii.</td>
<td>Treatment of the regeneration flue-gas,</td>
<td></td>
</tr>
<tr>
<td>a.</td>
<td>Continuous regeneration gas recycling loop with adsorption bed</td>
<td>Waste gas from regeneration step is recycled to the catalyst where chlorinated compounds (e.g. dioxins) are re-adsorbed</td>
</tr>
<tr>
<td>b.</td>
<td>Wet scrubbing</td>
<td>See Section 5.21.3</td>
</tr>
<tr>
<td>c.</td>
<td>Electrostatic separator (ESP)</td>
<td>See Section 5.21.1</td>
</tr>
</tbody>
</table>

Note to TWG: See also BAT 4 on monitoring

[This BAT conclusion is based on information given in Section 4.6 and 3.6]
5.7 BAT conclusions for the coking process

28. In order to reduce NO\textsubscript{x} emissions to air from the coking process (including calcining), BAT is to use one or a combination of the techniques of BAT 32

Specific applicability for coking process:
Primary techniques, e.g. low NO\textsubscript{x} burners, may be restricted to this process due to the fact that heat distribution may causes risk of coking in the furnace.
Application of end of pipe techniques e.g. SCR/SNCR may be restricted.
Note to TWG: TWG is asked to provide possible restrictions of applicability of the general NO\textsubscript{x} end-of-pipe techniques for coking and calcining processes.

29. In order to reduce dust and metals emissions to air from coking process (including calcining), BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.</td>
<td>Collection and recycling of coke fines</td>
</tr>
<tr>
<td>ii.</td>
<td>Handling and storing coke according to BAT 3</td>
</tr>
<tr>
<td>iii.</td>
<td>Use a closed blowdown system</td>
</tr>
<tr>
<td>iv.</td>
<td>Recovering final venting as refinery fuel gas (RFG)</td>
</tr>
</tbody>
</table>

II. Secondary or end of pipe techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Electrostatic separator (ESP)</td>
<td>See standard description in section 5.21.1</td>
<td>Capture efficiency from calciner may be reduced due to difficulty for coke particles to be electrically charged</td>
</tr>
<tr>
<td>ii. Multistage cyclone separator</td>
<td>See standard description in section 5.21.1</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iii. Fabric filter</td>
<td>See standard description in section 5.21.1</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>
BAT associated emission levels. See Table 5.8.

Table 5.8: BAT-associated emission levels for dust and metals emissions from the coking process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>5 – 50</td>
</tr>
<tr>
<td>Metals (Ni, Sb, V)</td>
<td>To be determined</td>
</tr>
</tbody>
</table>

(*) Note to TWG: TWG is asked to provide metals (Ni, Sb, V) emissions data

[This BAT conclusion is based on information given in Section 4.7.]

30. In order to reduce SO\textsubscript{x} emissions to air from the coking process (including calcining), BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Hydrotreatment of feed</td>
<td>Based on hydrogenation reactions, hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed when upgrading the refinery fractions for compliance with products specifications. See Section 5.21.3</td>
<td>Applicability is limited by availability of hydrogen production and hydrogen sulphide ((H_2S)) treatment capacity (e.g. amine and Claus units)</td>
</tr>
</tbody>
</table>

II. secondary or end of pipe flue-gas desulphurisation techniques (FGD) from BAT 60

BAT associated emission levels. See Table 5.9.

Table 5.9: BAT-AELs for SO\textsubscript{x} emissions from the coking process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average) at 3 % O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{x} expressed as SO\textsubscript{2}</td>
<td>&lt; 450</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.7.]
5.8 BAT conclusions for the desalting process

31. In order to reduce water consumption and emissions to water from the desalting process, BAT is to use one or a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Recycling water and optimisation of desalting process</td>
<td>An ensemble of good desalting practices aiming at increasing the efficiency of the desalter and reducing wash water usage e.g. using low shear mixing devices, low water pressure. It includes the management of key parameters for washing (e.g. good mixing) and separation (e.g. pH, density, viscosity, electric field potential for coalescence) steps.</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Multistage desalter</td>
<td>Multistage desalters operate with water addition and dehydration repeated through two stages or more for achieving a better efficiency in the separation and therefore less corrosion in further processes.</td>
<td>Applicable for new units</td>
</tr>
<tr>
<td>iii. Additional separation step</td>
<td>An additional enhanced oil/water and solid/water separation designed for reducing the charge of oil to the waste water treatment plant and recycling it to the process. This includes, e.g. settling drum, the use of optimum interface level controllers.</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>
5.9 BAT conclusions for the combustion units

32. In order to prevent or reduce NO\textsubscript{x} emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

I. primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>i. Selection or treatment of fuel</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Use of gas to replace liquid fuel</td>
<td>See description in See Section 5.21.3 Gas generally also contain less nitrogen than liquid and its combustion leads to lower level of NO\textsubscript{x} emissions</td>
<td>The applicability may be limited by the constraints associated with the availability of low sulphur fuels, which may be impacted by the energy policy of the Member State</td>
</tr>
<tr>
<td>(b) Hydrotreatment of liquid refinery fuels</td>
<td>See Section 5.21.3 Hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed.</td>
<td>Applicability is limited by availability of hydrogen production and hydrogen sulphide (H\textsubscript{2}S) treatment capacity (e.g. amine and Claus units)</td>
</tr>
<tr>
<td><strong>ii. Combustion modifications</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Staged combustion</td>
<td>See Section 5.21.2</td>
<td>Fuel staging for mixed or liquid firing may require specific burner design</td>
</tr>
<tr>
<td>• Air staging</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Fuel staging</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Optimization of combustion</td>
<td>See Section 5.21.2</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>(c) Flue-gas recirculation</td>
<td>See Section 5.21.2</td>
<td>Applicable through the use of specific burners with automatic recirculation of waste gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Applicability may be restricted for retrofitting external flue-gas recirculation in particular for forced draught mode operated devices</td>
</tr>
<tr>
<td>(d) Diluent injection</td>
<td>See Section 5.21.2</td>
<td>Generally applicable where appropriate inert diluents are available.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e) Use of low-NO\textsubscript{x} burners (LNB)</td>
<td>See Section 5.21.2</td>
<td>Generally applicable for new units taking into account, for LNB, the fuel specific limitation (e.g. for heavy oil). Applicability may be restricted for retrofitting existing units where complexity depends on site specific conditions e.g. furnaces design, surrounding devices. In very specific cases heavy modifications may be required.</td>
</tr>
</tbody>
</table>
II. Secondary or end of pipe techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
</table>
| i. Selective catalytic reduction (SCR)         | See Section 5.21.2           | Generally applicable for a new unit  
The applicability for retrofitting existing unit may be constrained by a significant space availability and the requirements for optimal catalyst injection |
| ii. Selective non-catalytic reduction (SNCR)   | See Section 5.21.2           | Generally applicable for a new unit  
The applicability for retrofitting existing unit may be constrained by requirement for the temperature window to be reached by reactant injection |
| iii. Low temperature oxidation                 | See Section 5.21.2           | Applicability may be restricted due to the need for additional scrubbing capacity  
Ozone generation and risk management associated to be properly addressed |
| iv. SNOx combined technique                    | See Section 5.21.5           | Applicable only for high flue-gas flow and when combined NOx and SOx abatements are needed |

BAT associated emission levels. See Tables Table 5.10, Table 5.11, and Table 5.12.

**Table 5.10:** BAT-associated emission levels for NOx emissions from combustion gas turbines

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx expressed as NO2</td>
<td>mg/Nm³ at 15% O2</td>
</tr>
<tr>
<td>(existing turbines)</td>
<td>20 – 90</td>
</tr>
<tr>
<td>(new turbines)</td>
<td>20 – 50</td>
</tr>
</tbody>
</table>

**Table 5.11:** BAT-associated emission levels for NOx emissions from gas firing combustion with the exception of gas turbines

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type of combustion</th>
<th>BAT-AEL (daily average)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx expressed as NO2</td>
<td>Gas firing</td>
<td>mg/Nm³ (at 3 % O2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 – 150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for existing units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 – 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for new units</td>
</tr>
</tbody>
</table>

**Table 5.12:** BAT-associated emission levels for NOx emissions from multi-fuel combustion with the exception of gas turbines

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type of combustion</th>
<th>BAT-AEL (daily average)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx expressed as NO2</td>
<td>Multi-fuel (gas/liquid) firing</td>
<td>mg/Nm³ (at 3 % O2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 – 350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for existing units</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 – 150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for new units</td>
</tr>
</tbody>
</table>
Note to TWG: From 2008 data collection, no detailed information was systematically reported about the size (MWth) and other individual characteristics of the combustion units. The TWG is asked to provide useful additional information for the BAT conclusions.

[This BAT conclusion is based on information given in Section 4.10.4 and 4.23.3]

33. In order to prevent or reduce dust and metal emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

I. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Selection or treatment of fuel</td>
<td>Gas instead of liquid combustion leads also to lower level of dust emissions See Section 5.21.3</td>
<td>The applicability may be limited by the constraints associated with the availability of low sulphur fuels, which may be impacted by the energy policy of the Member State</td>
</tr>
<tr>
<td>(a) Use of gas to replace liquid fuel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Hydrotreatment of liquid refinery fuels</td>
<td>Hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed. See Section 5.21.3</td>
<td>Applicability is limited by availability of hydrogen production and hydrogen sulphide (H2S) treatment capacity (e.g. amine and Claus units)</td>
</tr>
<tr>
<td>ii. Combustion modifications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Optimisation of combustion</td>
<td>See Section 5.21.2</td>
<td>Generally applicable to all type of combustion</td>
</tr>
<tr>
<td>(b) Atomisation of liquid fuel</td>
<td>Use of high pressure to reduce the droplet size of liquid fuel. Recent optimal burner design generally includes steam atomization</td>
<td>Generally applicable to liquid firing</td>
</tr>
</tbody>
</table>

II. Secondary or end of pipe techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Electrostatic separator (ESP)</td>
<td>See Section 5.21.1</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Third stage blowback filter</td>
<td>See Section 5.21.1</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iii. Fabric filter</td>
<td>See Section 5.21.1</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iv. Wet scrubbing</td>
<td>See Section 5.21.3</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>v. Centrifugal washers</td>
<td>See Section 5.21.1</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>
BAT associated emission levels. See Table 5.13

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 3 % O₂</td>
</tr>
<tr>
<td></td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Dust</td>
<td>5 – 50</td>
</tr>
<tr>
<td></td>
<td>for existing units</td>
</tr>
<tr>
<td></td>
<td>5 – 25</td>
</tr>
<tr>
<td></td>
<td>for new unit</td>
</tr>
<tr>
<td>Metals (Ni, Sb, V)</td>
<td>To be determined(*)</td>
</tr>
</tbody>
</table>

(*)Note to TWG: TWG is asked to provide metals (Ni, Sb, V) emissions data

This BAT conclusion is based on information given in Sections 4.10.5, 4.23.4 and 4.5.9.

34. In order to prevent or reduce SOₓ emissions to air from the combustion units, BAT is to use one or a combination of the techniques given below:

i. Primary or process related techniques, such as:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Selection or treatment of fuel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Use of gas to replace liquid fuel</td>
<td>See Section 5.21.3</td>
<td>The applicability may be limited by the constraints associated with the availability of low sulphur fuels, which may be impacted by the energy policy of the Member State</td>
</tr>
<tr>
<td>(b) Treatment of refinery fuel gas (RFG)</td>
<td>See Section 5.21.3</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>(c) Hydrotreatment of liquid refinery fuels</td>
<td>See Section 5.21.3</td>
<td>Applicability is limited by availability of hydrogen production and hydrogen sulphide (H₂S) treatment capacity (e.g. amine and Claus units)</td>
</tr>
</tbody>
</table>

ii. Secondary or end of pipe techniques:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue-gas desulphurisation (FGD) as described in Section 5.19</td>
<td>See Section 5.21.2</td>
<td>Generally applicable for new unit Retrofitting existing unit is possible taking into account the availability of treatment capacity</td>
</tr>
</tbody>
</table>
Chapter 5

BAT associated emission levels. See Tables Table 5.14 and Table 5.15.

Table 5.14: BAT-associated emission levels for SOx emissions from RFG gas firing in combustion units:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/Nm³</td>
</tr>
<tr>
<td></td>
<td>at 3 % O₂</td>
</tr>
<tr>
<td>SOx expressed as SO₂</td>
<td>5 – 35</td>
</tr>
</tbody>
</table>

Table 5.15: BAT-associated emission levels for SOx emissions from multi-fuel firing in combustion units:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/Nm³ at 3 % O₂</td>
</tr>
<tr>
<td>SOx expressed as SO₂</td>
<td>35 – 450 for existing units</td>
</tr>
<tr>
<td></td>
<td>35 – 350(**) for new units from 50 to 100 MWth</td>
</tr>
<tr>
<td></td>
<td>35 – 200 for new units from 100 to 300 MWth</td>
</tr>
<tr>
<td></td>
<td>35 – 150 for new units &gt;300 MWth</td>
</tr>
</tbody>
</table>

(*) taking into account the percentage of gas firing. Upper end of the range for existing units is set for a 75 % gas firing (RFG) and 1 % S content for liquid

(**) Note to TWG: From 2008 data collection, no detailed information was systematically reported about the size (MWth) of the combustion units. For consistency, it is proposed, for new units, to use the ranges for liquid fuels from current LCP BREF.

[This BAT conclusion is based on information given in Sections 4.10.2, 4.10.3, 4.23.5.4 and 4.5.10.]

35. In order to reduce carbon monoxide (CO) emissions to air, BAT is to use combustion operation control (See 5.21.4).

BAT associated emission levels. See Table 5.16.

Table 5.16: BAT-associated emission levels for carbon monoxide emissions from combustion units

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (daily average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/Nm³</td>
</tr>
<tr>
<td>Carbon monoxide, expressed as CO</td>
<td>&lt;100</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Sections 4.10.3]
5.10 BAT conclusions for the etherification process

36. In order to reduce emissions to air from the etherification process, BAT is to ensure appropriate treatment of process off-gases by routing them to acid gas removal.

37. In order to reduce emissions to water from etherification process, BAT is to ensure appropriate treatment of waste water streams by applying the techniques of BAT 9

38. In order to prevent upset of biotreatment, BAT is to use storage tank and appropriate unit production plan management to control the toxic components content (e.g. methanol, formic acid, ethers) of the waste water stream prior to final treatment.

[This BAT conclusion is based on information given in Sections 4.11]

5.11 BAT conclusions for hydrogen consuming process

39. In order to reduce emissions to air from hydrogen consuming units, BAT is to ensure appropriate treatment of process off-gases by routing them to acid gas removal.

40. In order to reduce emissions to air from hydrogen consuming units, BAT is to ensure appropriate treatment of flue-gas by routing them to the FGD system.

41. In order to reduce emissions to water, BAT is to ensure appropriate treatment of waste water streams by applying the techniques of BAT 9.

5.12 BAT conclusions for the isomerisation process

42. In order to reduce emission to air of chlorinated compounds, BAT is to optimise the use of chlorinated organic compounds used to maintain catalyst activity when such a process is in place or to use non chlorinated catalytic systems

[This BAT conclusion is based on information given in Section 4.16.]
Chapter 5

5.13 BAT conclusions for the natural gas plant

43. In order to reduce sulphur emission to air from the natural gas plant, BAT is to apply BAT 59 to BAT 60.

44. In order to reduce nitrogen oxides (NO_x) emission to air from the natural gas plant, BAT is to apply BAT 32.

45. In order to prevent emissions of mercury when present in raw natural gas, BAT is to remove it and recover the mercury-containing sludge for waste disposal.

[This BAT conclusion is based on information given in Section 4.17]

5.14 BAT conclusions for the polymerisation process

46. In order to prevent or reduce waste generation in the polymerisation process BAT is to optimise the catalyst consumption (e.g. phosphoric acid) and reuse it where it is technically possible.

[This BAT conclusion is based on information given in Section 4.18]

5.15 BAT conclusions for the distillation process

47. In order to prevent or reduce waste water flow generation from the distillation process, BAT is to use liquid ring vacuum pumps or surface condensers.

48. In order to prevent or reduce water pollution from the distillation process, BAT is to route sour water to stripping unit in an enclosed system.

49. In order to prevent or reduce emission to air from distillation units, BAT is to ensure the appropriate treatment of process off-gases, especially incondensable, by routing them to acid gas removal prior to further use.

[This BAT conclusion is based on information given in Section 4.19]

5.16 BAT conclusions for the products treatment process

50. In order to reduce emissions to air from the products treatment process, BAT is to ensure the appropriate disposal of off-gases, especially odorous spent air from sweetening units, by routing them to acid gas removal or incineration.

51. In order to reduce waste and waste water generation when a products treatment process using caustic is in place, BAT is to use cascading caustic solution and global management of spent caustic including recycling after appropriate treatment e.g. by stripping.

52. When using hydrotreating as a products treatment, BAT is to apply techniques from BAT 39 to BAT 41.

[This BAT conclusion is based on information given in Section 4.20]
5.17 BAT conclusions for storage and handling processes

53. In order to reduce VOC emissions to air from the storage of liquid hydrocarbon compounds, BAT is to use the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. High efficiency seals in floating roof tanks</td>
<td>Specific device improving the limitation of losses of vapour e.g. improved primary seals, additional multiple (secondary or tertiary) seals</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Tank cleaning procedures working in closed-loop system</td>
<td>For internal inspections tanks have to be periodically emptied, cleaned and rendered gas-free. This cleaning includes dissolving the tank bottom. Closed-loop systems prevent VOC emissions</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.21.4 and 4.21.11]

54. In order to prevent or reduce emission to soil and groundwater from the storage of liquid hydrocarbon compounds, BAT is to use a combination of the techniques given below:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Double bottom tanks</td>
<td>A second impervious bottom that provides a measure of protection against releases from the first material</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Impervious membrane liners</td>
<td>A continuous leak barrier under the entire bottom surface of the tank</td>
<td>Generally applicable for new tanks and during overhaul of existing tanks</td>
</tr>
<tr>
<td>iii. Sufficient tank farm bund containment</td>
<td>An impermeable tank farm bund is designed to contain large spills potentially caused by a shell rupture or overfilling (for both environmental and safety reasons). Size and associated building rules are generally defined by local regulations</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iv. Maintenance programme including corrosion monitoring, prevention and control</td>
<td>A management system including leak detection, inventory control and inspection procedures on tanks at intervals to prove their integrity.</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.21.8, 4.21.9]
55. In order to prevent or reduce VOC emissions to air from loading and unloading operations, BAT is to use one or a combination of the techniques given below to reach a recovery rate of at least 95%:

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Vapour balancing</td>
<td>See Section 5.21.6</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>II. Vapour recovery</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i. Condensation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii. Absorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii. Adsorption</td>
<td>See Section 5.21.6</td>
<td>Generally applicable as alternative in exceptional circumstances (see Directive 94/63/EC), incineration may also be used.</td>
</tr>
<tr>
<td>iv. Membrane separation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>v. Hybrid systems</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note to TWG:** Directive 94/63/EC states that a ‘vapour incineration unit may be substituted for a vapour recovery unit if vapour recovery is unsafe or technically impossible because of the volume of return vapour’

**BAT associated emission levels.** See Table 5.17.

**Table 5.17:** BAT-associated emission levels for non-methanous VOC and benzene emissions to air

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-AEL (hourly values concentration)(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-methanous volatile organic compounds (NMVOC)</td>
<td>0.15 – 10 g/Nm³ **</td>
</tr>
<tr>
<td>Benzene</td>
<td>&lt;1 mg/Nm³</td>
</tr>
</tbody>
</table>

(*) Hourly values in continuous operation expressed and measured according to Directive 94/63/EC. 
(**) Lower value achievable with two-stage hybrid systems-Upper value achievable with single-stage adsorption or membrane system.

[This BAT conclusion is based on information given in Section 4.23.6.2]

**5.18 BAT conclusions for visbreaking and other thermal processes**

56. In order to reduce emissions to air from visbreaking and other thermal processes, BAT is to ensure the appropriate treatment of process off-gases by routing them to acid gas removal prior to final use.

57. In order to reduce emissions to water from visbreaking and other thermal processes, BAT is to ensure the appropriate treatment of waste water streams by applying the techniques of BAT 9.

58. In order to prevent or reduce waste, BAT is to control the sodium content of the feed or use specific additives to decelerate the coke formation.
5.19 BAT conclusions for waste gas sulphur treatment

59. In order to reduce sulphur emissions to air from flue-gases, BAT is to use process specific BAT and/or additional flue-gas desulphurisation (FGD) techniques such as the following:

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Non-regenerative scrubbing</td>
<td>See Section 5.21.3</td>
<td>Generally applicable where the by-products from treatment can be reused or disposed of.</td>
</tr>
<tr>
<td>ii. Regenerative scrubbing</td>
<td>See Section 5.21.3</td>
<td>Generally applicable where regenerated by-products can be market sealable</td>
</tr>
<tr>
<td>iii. SNO₃ combined technique</td>
<td>See Section 5.21.5</td>
<td>Applicable for high flue-gas flow and when combined NOₓ and SOₓ abatements are required</td>
</tr>
</tbody>
</table>

BAT associated emission levels. See Table 5.18.

Table 5.18: BAT-associated SOₓ removal efficiency for flue-gas desulphurisation (FGD)

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Minimum percentage of SOₓ removal efficiency (%) (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non regenerative scrubbing</td>
<td>85</td>
</tr>
<tr>
<td>Regenerative scrubbing</td>
<td>90</td>
</tr>
<tr>
<td>SNO₃ combined technique</td>
<td>95 – 98</td>
</tr>
</tbody>
</table>

(1) Percentage calculation is based on the total quantity of SOₓ removed from the inlet gas

[This BAT conclusion is based on information given in Section 4.23.5.4, 4.23.8]

60. In order to reduce sulphur emissions to air from off-gases containing hydrogen sulphides (H₂S) BAT is to use one or a combination of the following sulphur removal techniques

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Acid gas removal e.g. by amine treating</td>
<td>See Section 5.21.3</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>ii. Sulphur recovery units (SRU) e.g. by Claus process</td>
<td>See Section 5.21.3</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iii. Tail gas treatment unit (TGTU)</td>
<td>See Section 5.21.3</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>

BAT associated emission levels. See Table 5.19.
Table 5.19: BAT-associated sulphur recovery efficiency for waste gas sulphur (H₂S form) removal techniques

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BAT-associated sulphur recovery efficiency(*) (daily average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas removal</td>
<td>Achieve hydrogen sulphide (H₂S) removal in the treated RFG in order to meet gas firing BAT-AEL for BAT 34</td>
</tr>
<tr>
<td>Sulphur recovery efficiency (SRU+TGTU)</td>
<td>99.5 – &gt;99.9 %(*)</td>
</tr>
</tbody>
</table>

(*) Sulphur recovery efficiency is calculated as the fraction of sulphur in the feed which is recovered in the sulphur stream routed to the collection pits

[This BAT conclusion is based on information given in Section 4.23.5.1 and 4.23.5.2]
5.20  BAT conclusions for flares

61. In order to prevent emissions to air from flares, BAT is to use flaring only for emergency situations or non-routine operational conditions (e.g. start-ups, shutdown).

62. In order to reduce emissions to air from flares, BAT is to use the techniques given below

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Correct plant design</td>
<td>See Section 5.21.7</td>
<td>Applicable to new units</td>
</tr>
<tr>
<td>ii. Plant management</td>
<td>See Section 5.21.7</td>
<td>Generally applicable</td>
</tr>
<tr>
<td>iii. Correct flaring devices design</td>
<td>See Section 5.21.7</td>
<td>Applicable to new units</td>
</tr>
<tr>
<td>iv. Monitoring and reporting</td>
<td>See Section 5.21.7</td>
<td>Generally applicable</td>
</tr>
</tbody>
</table>

[This BAT conclusion is based on information given in Section 4.25.7]
Chapter 5

Glossary:

5.21 Description of techniques for the prevention and control of emissions to air

5.21.1 Dust

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrostatic precipitator</td>
<td>Electrostatic precipitators operate such that particles are charged and separated under the influence of an electrical field. Electrostatic precipitators are capable of operating over a wide range of conditions. Abatement efficiency may depend on residence time (size), catalyst properties and upstream particles removal devices</td>
</tr>
<tr>
<td>Bag filter</td>
<td>Bag filters are constructed from porous woven or felted fabric through which gases are flowed to remove particles. The use of a bag filter requires a fabric material selection adequate to the characteristics of the waste gases and the maximum operating temperature</td>
</tr>
<tr>
<td>Multistage cyclone separators</td>
<td>Cyclonic collection device or system installed following the two stages of cyclones. Generally known as a third stage separator, common configuration consists of a single vessel containing many conventional cyclones or improved swirl-tube technology. Performance mainly depends on the particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones</td>
</tr>
<tr>
<td>Centrifugal washers</td>
<td>Centrifugal washers combine the cyclone principle and an intensive contact with water e.g. Venturi washer.</td>
</tr>
<tr>
<td>Third stage blowback filter</td>
<td>Reverse flow (blowback) ceramic or sintered metal filters are devices where after retaining the solids elements at the surface as a cake, it is dislodged by initiating a reverse flow. The dislodged solids are then purged from the filter system</td>
</tr>
</tbody>
</table>

5.21.2 Nitrogen oxides (NOₓ)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
</table>
| Combustion modifications   | The technique is mainly based on the following features:  
  • minimisation of air leakages into the furnace  
  • careful control of air used for combustion  
  • modified design of the furnace combustion chamber |
| Reduction of air/fuel ratio | Air staging – involves substoichiometric firing and the addition of the remaining air or oxygen into the furnace to complete combustion.  
  • Fuel staging – a low impulse primary flame is developed in the port neck; a secondary flame covers the root of the primary flame reducing its core temperature |
| Staged combustion          | Implies the reinjection of waste gas from the furnace into the flame to reduce the oxygen content and therefore the temperature of the flame. The use of special burners is based on the internal recirculation of combustion gases which cool the root of the flames and reduce the oxygen content in the hottest part of the flames |
| Low-NOₓ burners            | The technique (including ultra-Low-NOₓ burners) is based on the principles of reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer (increased emissivity of the flame). It may be associated with a modified design of the furnace combustion chamber |
Optimisation of combustion

Based on permanent monitoring of appropriate combustion parameters (e.g. $O_2$, CO content, fuel/air ratio, unburned components), the technique uses control technology for achieving the best combustion conditions.

Diluent injection

Inert diluents, e.g. flue-gas, steam, water, nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NOx in the flue-gases.

Selective catalytic reduction (SCR)

The technique is based on the reduction of NOx to nitrogen in a catalytic bed by reaction with ammonia (in general aqueous solution) at an optimum operating temperature of around 300 – 450 °C.

One or two layers of catalyst may be applied. A higher NOx reduction is achieved with the use of higher amounts of catalyst (two layers).

Selective non-catalytic reduction (SNCR)

The technique is based on the reduction of NOx to nitrogen by reaction with ammonia or urea at a high temperature. The operating temperature window must be maintained between 900 and 1050 °C for optimal reaction.

Low temperature NOx oxidation

The low temperature oxidation process injects ozone into a flue-gas stream at optimal temperatures below 150 °C, to oxidise insoluble NO and NO2 to highly soluble $N_2O_5$. The $N_2O_5$ is removed in a wet scrubber by forming dilute nitric acid waste water that can be used in plant processes or neutralised for release.

5.21.3 Sulphur oxides (SOx)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment of refinery fuel gas (RFG)</td>
<td>Some refinery fuel gases may be sulphur-free at source (i.e. from catalytic reforming and isomerisation processes) but most other processes produce sulphur-containing gases. These gas streams require an appropriate treatment for gas desulphurisation (e.g. by amine gas removal – see infra – to remove $H_2S$) before being released to the refinery fuel gas system.</td>
</tr>
<tr>
<td>Liquid fuel desulphurisation</td>
<td>In addition to low sulphur crude selection, fuel desulphurisation is made by hydrotreatment process (see infra) where hydrogenation reactions take place and lead to reducing sulphur content.</td>
</tr>
<tr>
<td>Use of gas to replace liquid fuel</td>
<td>Decrease the use of liquid refinery fuel (generally heavy fuel oil containing sulphur, metals,…) by replacing it with on site Liquefied Petroleum Gas (LPG) or refinery fuel gas (RFG) or by externally supplied gaseous fuel (e.g. natural gas) with low level of sulphur and other undesirable substances.</td>
</tr>
<tr>
<td>Use of SOx reducing catalysts additives</td>
<td>Use of a substance (e.g. metallic oxides catalyst) which transfers sulphur associated with coke from the regenerator back to the reactor. It operates most efficiently in full combustion mode rather than in deep partial-combustion mode. Note: SOx reducing catalysts additives might have a detrimental effect on dust emissions by increasing catalyst losses due to attrition and on NOx emissions by participating to the CO promotion together with the oxidation of $SO_2$ to $SO_3$.</td>
</tr>
<tr>
<td>Hydrotreatment</td>
<td>Based on hydrogenation reactions, hydrotreatment aims mainly at producing low-sulphur fuels (e.g. 10 ppm gasoline and diesel) and optimising the process configuration (heavy residue conversion and middle distillate production). It reduces sulphur, nitrogen and metal content of the feed. As hydrogen is required, sufficient production capacity is needed. As the technique transfer sulphur from the feed to hydrogen sulphide ($H_2S$) in the process gas, treatment capacity (e.g. amine and Claus units) is also a possible bottleneck.</td>
</tr>
</tbody>
</table>
Chapter 5

### Acid gas removal e.g. by amine treating

Separation of acid gas (mainly hydrogen sulphide H₂S) from the fuel gases by dissolving it in a chemical solvent (absorption). The commonly used solvents are amines. It is generally the first step treatment needed before elemental sulphur can be recovered in the SRU.

### Sulphur recovery units (SRU)

Specific unit which most often consists of a Claus process for sulphur removal of hydrogen sulphide (H₂S)-rich gas streams from amine treating units and sour water strippers. SRU is generally followed by a tail gas treatment unit (TGTU) for remaining H₂S removal.

### Tail gas treatment unit (TGTU)

A family of techniques, additional to SRU in order to enhance the removal of sulphur compounds. They can be divided into four categories according to the principles applied:
- Direct oxidation to sulphur
  - Continuation of the Claus reaction (sub-dewpoint conditions)
  - Oxidation to SO₂ and recovering sulphur from SO₂
  - Reduction to H₂S and recovering sulphur from this H₂S (e.g. amine process)

### Flue-gas desulphurisation (FGD)

Technique or ensemble of scrubbing techniques where sulphur is removed from flue-gases through various processes generally involving an alkaline sorbent for capturing SO₂ and transforming it into solid sulphur.

#### Wet scrubbing

In the wet scrubbing process, gaseous compounds are dissolved in a suitable liquid (water or alkaline solution). Simultaneous removal of solid and gaseous compounds may be achieved. Downstream of the wet scrubber, the flue-gases are saturated with water and a separation of the droplets is required before discharging the flue-gases. The resulting liquid has to be treated by a waste water process and the insoluble matter is collected by sedimentation or filtration. According to the type of scrubbing solution, it can be:
- a non regenerative technique (e.g. sodium or magnesium based)
- a regenerative technique (e.g. amine or soda solution)

According to the contact method, the various techniques may require e.g.:
- Venturi using the energy from inlet gas by spraying it with the liquid;
- packed towers, plate towers, spray chambers.

Where scrubbers mainly aim at SOx removal, suitable design is needed to also efficiently remove dust.

#### Non-regenerative scrubbing

Sodium or magnesium based solution is used as alkaline reagent to absorb SO₃ generally as sulphates. Techniques are based on e.g
- Wet limestone
- Aqueous ammonia
- Seawater (see infra)

#### Seawater scrubbing

A specific non regenerative type of scrubbing using alkalinity of the seawater as solvent where large amount of seawater is available. Requires generally an upstream abatement of dust.

#### Regenerative scrubbing

Use of specific SOx absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-product during a regenerating cycle where the reagent is reused.

#### Dry or semi-dry scrubbing, in combination with a filtration system

Dry powder or a suspension/solution of alkaline reagent are introduced and dispersed in the waste gas stream. The material reacts with the sulphur gaseous species to form a solid which has to be removed by filtration (bag filter or electrostatic precipitator). In general, the use of a reaction tower improves the removal efficiency of the scrubbing system.
## 5.21.4 Carbone monoxide (CO)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion operation control</td>
<td>The increase in CO emissions due to the application of combustion modifications (primary techniques) for the reduction of NOₓ emissions can be limited by a careful control of the operational parameters.</td>
</tr>
<tr>
<td>Catalysts with carbon monoxide (CO) oxidation promoters</td>
<td>Use of a substance which selectively promotes the oxidation of CO into CO₂ (combustion).</td>
</tr>
<tr>
<td>Carbon monoxide (CO) boiler.</td>
<td>Specific post combustion device where CO present in the flue-gas is consumed downstream of the catalyst regenerator to recover the energy. It is usually used only with partial-combustion FCC units</td>
</tr>
</tbody>
</table>

## 5.21.5 Combined pollutants emissions prevention and control

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet scrubbing</td>
<td>See Section 5.21.3</td>
</tr>
<tr>
<td>SNOx combined technique</td>
<td>Combined technique to remove SOₓ, NOₓ and dust where a first dust-removal stage (ESP) takes place followed by some specific catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NOₓ is reduced to N₂.</td>
</tr>
</tbody>
</table>

## 5.21.6 Volatile organic compound (VOC) emissions prevention and control

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour balancing</td>
<td>Technique in which, to prevent emissions to atmosphere from loading operations, the expelled mixture is returned to the liquid supply tank and replaces the pumped-out volume. Can be used where loading takes place from tanks, vessels or barges. Vapour can be stored prior to vapour recovery or destruction.</td>
</tr>
<tr>
<td>Vapour recovery</td>
<td>Volatile organic compounds which are emitted during loading and unloading operations of most volatile products, especially crude oil and lighter products can be abated by various techniques e.g.:</td>
</tr>
<tr>
<td></td>
<td>• absorption: the vapour molecules dissolve in a suitable absorption liquid (e.g. glycols or mineral oil fractions such as kerosene or reformate). The loaded scrubbing solution is desorbed by reheating in a further step. The desorbed gases must either be condensed, further processed or incinerated</td>
</tr>
<tr>
<td></td>
<td>• adsorption: the vapour molecules are retained by activate sites on the surface of adsorbent solid materials, e.g. activated carbon (AC) or zeolite. The adsorbent is periodically regenerated. The resulting desorbate is then absorbed in a circulating gasoline component stream in a downstream wash column. Residual gas is sent to further treatment.</td>
</tr>
<tr>
<td></td>
<td>• membrane gas separation: the vapour molecules are processed through selective membranes to separate the vapour/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate).</td>
</tr>
<tr>
<td></td>
<td>• two stage refrigeration/condensation: by cooling of the vapour/gas mixture the vapour molecules condense and are separated as a liquid. As the humidity leads to the icing-up of the heat exchanger, a two stage condensation process providing for alternate operation is required.</td>
</tr>
<tr>
<td></td>
<td>• hybrid systems: combinations of available VRUs techniques</td>
</tr>
</tbody>
</table>

*Note: The achievable concentration is expressed for non-methanous VOC (NMVOC) as absorption and adsorption processes cannot notably reduce methane emissions.*
### Vapour destruction

Destruction of VOC can be achieved through e.g. **thermal oxidation** (incineration) or **catalytic oxidation** when recovery is not easily feasible. Safety requirements (e.g. flame arrestors) are needed to prevent explosion.

**Thermal oxidation** occurs typically in single chamber, refractory-lined oxidizers equipped with gas burner and a stack. If gasoline is present, heat exchanger efficiency is limited and preheat temperatures are maintained below 180 °C to reduce ignition risk. Operating temperatures range from 760 to 870 °C and residence times are typically 1 second or less.

**Catalytic oxidation** requires a catalyst to accelerate the rate of oxidation by adsorbing the oxygen and the VOC on the its surface. The catalyst enables the oxidation reaction to occur at lower temperature than required by thermal oxidation: typically ranging from 320° to 540° C. A first preheating step (electrically or with gas) takes place to reach a temperature necessary to initiate the VOCs catalytic oxidation. An oxidation step occurs when the air is passed through a bed of solid catalysts.

### LDAR programme

An LDAR programme is a structured approach to reduce fugitive VOC emissions by detection and subsequent repair or replacement of leaking components. Currently, sniffing and gas imaging methods are available for the identification of the leaks.

### High integrity equipment

**High integrity equipment include e.g.:**
- valves with double packing seals
- magnetically driven pumps/compressors/agitators
- pumps/compressors/agitators fitted with mechanical seals instead of packing
- high-integrity gaskets (such as spiral wound, ring joints) for critical applications.

### 5.21.7 Other emissions prevention and control

**Correct plant design** includes sufficient recovery system capacity, the use of high integrity relief valves and other measures to use flaring only as a safety system for other than normal operations (start-up, shut down, emergency).

**Plant management** includes organizational and control measures to reduce the case of flaring by e.g. balancing RFG system, using advanced process control.

**Flares design** includes height, pressure, assistance by steam, air or gas, type of flare tips, etc. It aims at enabling smokeless and reliable operations and ensuring an efficient combustion of excess gases when flaring from non routine operations.

**Monitoring and reporting:** Continuous monitoring of origin, nature and quantity of gas sent to flaring and associated parameters of combustion (e.g. mixture flow gas and heat content, ratio of assistance, velocity, pollutant emissions). Reporting of flaring events makes possible to use flaring ratio as a requirement included in the EMS and to prevent the future ones.

**Choice of catalyst to avoid dioxins formation**

During the regeneration of the reformer catalyst, organic chloride is generally needed for effective reforming catalyst performance (to re-establish the proper chloride balance in the catalyst and to assure the correct dispersion of the metals). The choice of the appropriate chlorinated compound will have an influence on the possibility of emissions of dioxins and furans.
5.22 Description of techniques for prevention and control of emissions to water

5.22.1 Waste water pre-treatment

<table>
<thead>
<tr>
<th>Pretreatment of sour water streams before reuse or treatment</th>
<th>Send generated sour water (e.g. from distillation, cracking, coking units) to appropriate pretreatment (e.g. stripper unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment of other waste water streams prior to treatment</td>
<td>To preserve treatment performance, appropriate pretreatment may be required</td>
</tr>
</tbody>
</table>

5.22.2 Waste water treatment

| Removal of insoluble substances by recovering oil. | These techniques include generally  
- API Separators (APIs);  
- Corrugated Plate Interceptors (CPIs);  
- Parallel Plate Interceptors (PPIs);  
- Tilted Plate Interceptors (TPIs);  
- Buffer and/or equalisation tanks. |
|---------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| Removal of insoluble substances by recovering suspended solid and dispersed oil | These techniques include generally  
- Dissolved Gas Flotation (DGF);  
- Induced Gas Flotation (IGF);  
- Sand Filtration. |
| Removal of soluble substances including biological treatment (e.g. activated sludge, biofiltration) and clarification | Biological treatment techniques may include:  
- Fixed bed systems;  
- Suspended bed systems.  
One of the most commonly used suspended bed system in refineries WWTP is the activated sludge process. Fixed bed systems may be e.g. biofilter or trickling filter. |
| Additional final treatment step (e.g. nitrification denitrification process) | A specific waste water treatment aiming at complementing the previous treatment steps for e.g. further reducing nitrogen or carbon compounds. Generally used where specific requirements for water preservation are locally needed |
| External waste water treatment | A waste water treatment which is performed by a plant outside the installation |

5.23 Description of techniques for waste generation prevention and waste management

<table>
<thead>
<tr>
<th>Sludge pretreatment</th>
<th>Prior to final treatment (e.g. in a fluidised bed incinerator), the sludge are dewatered and/or de-oiled (by e.g. centrifugal decanters or steam dryers) to reduce their volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reuse of sludge in process units</td>
<td>Certain types of sludge (e.g. oily sludge) can be processed in units (e.g. coking) as part of the feed due to their oil content</td>
</tr>
<tr>
<td>Spent solid catalyst management</td>
<td>Scheduled and handling of the materials used as catalyst (e.g. by contractors) in order to recover or reuse them in off site facilities. These operations depend on the type of catalyst and process</td>
</tr>
<tr>
<td>Removal of catalyst from slurry decant oil</td>
<td>Decant oil sludge from process units (e.g. FCC unit) can contain significant concentrations of catalyst fines. These fines need to be separated prior to the reuse of decant oil as a feedstock.</td>
</tr>
</tbody>
</table>
Chapter 6

6 EMERGING TECHNIQUES

KOM conclusion 6: TWG to review techniques quoted in BREF Chapter 6 and comment (using references, industrial examples, performances, data, and costs) on their status as:

- still emerging (to be retained in BREF Chap. 6)
- worth considering in the determination of BAT (in BREF Chap. 4)

Emerging technique is understood in this document as a novel technique that has not yet been applied in any industrial sector on a commercial basis. This chapter contains these techniques that may appear in the near future and that may be applicable to the refinery sector.

6.1 Refinery activities overview

Throughout its history the refining industry has continuously developed new and improved processes in response to changes in feed quality, product specifications, product slates, new product outlets and economic and environmental requirements. These developments have slowed down in recent years for the following reasons:

1. Large oil companies are cutting down on their R&D budgets, and are more and more relying on third parties for new developments in refinery technology and catalytic processes. These third parties develop techniques for licensing income or for income from catalyst sales. Developments are reported in the technical literature (Hydrocarbon Processing, Chemical Engineering Progress, Oil and Gas Journal, Erdöl, Gas und Kohle, Petroleum Technology Review) and during seminars and conferences (World Petroleum Congress, WEFA, Hart’s Fuel Conference, European Refining Technology Conference, NPRA and API specialist meetings) for the dissemination of these techniques.

2. Technological developments are concentrating on optimising current systems for higher yields (e.g. more selective catalysts and solvents), higher energy efficiency (e.g. improved reactor design and better heat integration) and shorter downtimes (e.g. scavenging of impurities, automatic cleaning systems) rather than novel processes;

3. The current tool box of conversion, separation, treatment and environmental technologies seems adequate and sufficient to meet any desired product slate and product specifications for the coming decade as well as meeting stringent regulatory requirements;

Meanwhile, the upgrading process of the refinery sector to implement existing techniques for meeting new product specifications will continue. The rationalisation process in the refining industry will also continue and low margins will force refineries to look for cost savings.

6.2 Alkylation

Most of the safety and environmental concerns are related to the potential for a large release of HF or H\textsubscript{2}SO\textsubscript{4}. A solid acid catalyst would potentially overcome most of the drawbacks associated with liquid acid catalyst systems and open up a new area of marketing for alkylation. Numerous companies are putting a large R&D effort into the development of a new solid catalyst for the alkylation process.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>Grignard</td>
</tr>
<tr>
<td>SiF\textsubscript{4}/SiO\textsubscript{2}</td>
<td>Circulating bed + washing</td>
</tr>
<tr>
<td>Zeolite H-b</td>
<td>Grignard</td>
</tr>
<tr>
<td>CF\textsubscript{3}SO\textsub{H} fixed in a porous carrier (silica)</td>
<td>Haldor Topsoe A/S</td>
</tr>
</tbody>
</table>


Technology providers claim that these techniques will be ready in the market in one to two years.
6.2.1 Alkylation of parafines

As described in chapter 2 there are four routes on alkylation developments.

6.2.1.1 Sulphuric acid process

The leading one, most used, route of sulphuric did not experience dramatic improvements.

6.2.1.2 Hydrofluric acid (HF) process

The HF route suffered upgrades aiming to reduce hazardous problems (see Chapter 2)

6.2.1.3 Soli-acid technology

There have been substantial achievements in the following 2 options during later years and these processes have become commercially available:

- In Alkyclean process simultaneous reactor do a mild liquid phase regeneration and periodically a reactor undergoes a higher temperature vapour phase h2 strip. No production of acid soluble oils.
- UOP Alkylene is based on increasing the density of catalyst acid sites achieving high reactivation degree. Impurities on feedstock do not need treatment. One contract warded in Azerbayan.
- Exelus Exsact is based on catalyst stable up to 24 hours, with periodic catalyst reactivation.
- Other initiatives are ongoing and reached commercialization (e.g. Fixed Bed of super acid catalyst in solid support by Haldor Topsoe; acid Chevron Isoalky, Eurofuel from Lurgi.)

Text moved from Sections 2.2 and 4.2.3

In the Alkyclean soli-acid process, the reactors operate in the liquid phase at 50 – 90°C at about 21 barg. No chilling is required in this process. The general process scheme (see Figure 6.1 and Figure 6.2) is similar to that used in the case of HF and H₂SO₄ liquid acid alkylation processes. The main difference is the use of a soli-acid catalyst, which does not contain any volatile components. Isobutane is recycled through a set of reactors that contain a fixed- bed catalyst. Olefins are injected in such a way that the olefin is well dispersed in order to keep the olefin concentration low. No corrosive and poisonous liquid acid catalysts are used. The fixed- bed catalyst has a lifetime of several years and therefore catalyst consumption is low, compared to liquid technologies. Furthermore no acid soluble oil waste is formed and no downstream treatment is required to remove traces of liquid acids or halogen compounds from the product. The products will contain no nitrogen, sulphur (H₂SO₄ process) or halogens (HF process). Overall olefin conversion is almost 100 % and yield and quality of the product are similar to what found in case of the liquid acid processes. Regeneration of the catalyst is carried out continuously by cyclic switching from olefins addition to the addition of a small amount of dissolved hydrogen without changing the reactor conditions. Dependent on the severity of operation, the overall conversion of olefins will drop slowly below 99 – 99.5 % after some time. Moderate temperature (about 250 °C) regeneration with hydrogen gas is carried out for the complete restoring of catalyst activity and selectivity.
Figure 6.1: Simplified block diagram of the AlkyClean soli-acid alkylation process

Figure 6.2: Simplified reaction/regeneration scheme of the Alkyclean soli-acid alkylation process

**Achieved environmental benefits:**
The main advantage of the soli-acid alkylation process is the fact that no liquid acids are needed. As a consequence catalyst consumption is the lowest of all processes. The *in situ* regeneration of the catalyst with hydrogen creates a product gas that will be reused in other applications of the refinery, since it contains no acids or halogens. No routine flaring of gas is required. Also, no waste water nor sludge are produced from acid neutralisation units. Furthermore, the absence of liquid acids or any halogens will mean that no product treatment or disposal of acids is needed. There will be no acid soluble oil produced in a soli-acid alkylation unit.

No corrosive or erosive environment is expected in this alkylation process, so on stream reliability is expected to be very high and maintenance low compared to HF and sulphuric
processes. Since there is no corrosive or erosive environment created. This reduces the chance of accidental emissions of hydrocarbons (and acids in the case of HF and H₂SO₄).

**Cross-media effects:**

**Effluent gas emissions**
Gas effluent from regeneration can be used as diluted hydrogen source or in the refinery fuel gas system. Fugitive emissions contain only hydrocarbons and no acids or acid components. Furthermore, since no corrosive environment is created in the case of soli-acid alkylation, maintenance and repairs will be much lower and on stream reliability much higher. This will reduce the overall fugitive emission level of hydrocarbons considerably compared to liquid acid technologies.

**Effluent liquid discharges**
None.

**Waste elimination**
No tars are produced. Only spent catalyst will, after many years of operation, be a solid waste. The catalyst a fixed- bed catalyst that contains zeolite, alumina and a very low concentration of noble metal. Consequently it is relatively harmless and can easily be transported for off-site reclaiming of noble metal. The noble metal is re-utilised, while the solids can be reused in the building industry. The amount of spent catalyst produced by the soli-acid alkylation process AlkyClean is about a factor 100 lower than HF alkylation and a factor 1000 lower than sulphuric alkylation.

**Operational data**
There are no liquid acids or halogens so there are no corrosion issues. Based on demonstration plan, the maintenance costs of equipment are expected to be much lower than in the case of the liquid acid processes.

No special safety precautions are required, other than these for any refinery process unit that processes hydrocarbons.

There is no need for expensive mitigation (acid dump and water spray systems) and vapor pressure suppression facilities that are required for HF units. Compared to H₂SO₄ units, catalyst consumption is very high lower and does not require large daily transports of spent and regenerated acid to external regeneration facilities. In case of smaller scale ‘on-site’ regeneration facilities the cost of regenerated acid will be rather high.

**Applicability**
Unfortunately, the retrofit of conventional HF or H₂SO₄ units with a soli-acid process is impossible. AlkyClean utilises a swing reactor system, which makes on-stream catalyst change out of catalyst possible and thus turnarounds can be tailored to fit the refinery’s schedule. In the case of repairs involving one of the reactors the unit can remain on-stream using the reactors left. In addition, it is to be noted that cycling the reactors frequently between reaction and regeneration may lead to additional cost, operating complexity and reliability challenges.

**Economics**
For soli-acid alkylation, utility and chemical costs will be somewhat higher than reported in the case of hydrofluoric alkylation, but lower than these of the H₂SO₄ process, since the AlkyClean process has much lower catalyst consumption. Table 6.1 shows the data resulting from a US project evaluation in 2008. See also Section 4.2.1 and 4.2.2.
### Table 6.1: Utility and chemical costs of the three alkylation processes

<table>
<thead>
<tr>
<th>Values per tonne of alkylate produced</th>
<th>Sulphuric acid</th>
<th>Hydrofluoric</th>
<th>Solid acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Utilities</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electricity (USD 0.06/kWh)</td>
<td>7.7</td>
<td>1.20 – 3.90</td>
<td>8.02</td>
</tr>
<tr>
<td>Fuel (USD 0.006/MJ)</td>
<td>No</td>
<td>5.7 – 17.06</td>
<td>No</td>
</tr>
<tr>
<td>Steam (USD 0.014/kg)</td>
<td>11.71</td>
<td>1.41 – 14.11</td>
<td>14.50</td>
</tr>
<tr>
<td>Cooling water (USD 0.026/m³)</td>
<td>1.90</td>
<td>1.64</td>
<td>0.02</td>
</tr>
<tr>
<td>Industrial water</td>
<td>negligible</td>
<td>negligible</td>
<td>negligible</td>
</tr>
<tr>
<td><strong>Chemicals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh acid (kg)</td>
<td>25.74 – 39.6(²)</td>
<td>1.64</td>
<td>13.48(¹)</td>
</tr>
<tr>
<td>Caustic (USD 0.55/kg)</td>
<td>0.23</td>
<td>0.31</td>
<td>No</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>47.28 – 61.14</td>
<td>24.6 – 25.96</td>
<td>36.02</td>
</tr>
</tbody>
</table>

(¹) Based on 2008 Pt price and used Pt lease rate 5%
(²) Based on sulphuric acid price of USD 330/tonne

The overall investment and operational costs for a new alkylation unit will be projected by the licensor anyway, to be significantly lower if choosing the solid-acid process instead of an HF unit, due to substantial savings made on necessary safety devices (e.g. leak detection, water spray systems, acid dump facilities) and safety management procedures and equipment to be implemented during HF Units operation.

**Driving force for implementation**

Production of an excellent gasoline blending component with high octane number and low sulphur, nitrogen, benzene and aromatics contents, by using a clean solid-acid catalyst technology that replaces corrosive and poisonous liquid acid technologies. Compared to conventional processes, this technique shows has the potential to provide a dramatic reduction of the environmental impact and risk to refinery employees and nearby communities refineries. This technique was given the ‘Affordable Green Chemistry Award’ in 2010 from the American Chemical Society.

**Example plants**

No full-size commercial unit is in operation yet. However, the technology has been developed over 10-year intensive research and development period, on laboratory and pilot plant scale. During this period Albemarle started a project in cooperation with engineering company Lummus Technology to check and improve the technology from an engineering point of view. After the RandD period the catalyst was produced on a full-size commercial plant scale to demonstrate that commercial production of the catalyst is possible. This resulted in a high performance catalyst that was used to operate a demonstration AlkyClean alkylation plant at Neste Oil’s refinery in Porvoo (Finland).

**Reference Literature**

[52, Broekoven et al. 2008] [53, Van Rooijen et al. 2009]

### 6.2.1.4 Ionic liquids (IL)

Ionikylation is an isobutane alkylation process. The process uses a composite-IL as homogeneous catalyst for alkylation reactions at ambient temperatures and moderate pressures. ILs are ionic, salt-like materials that are liquid at less than 100°C. ILs have been historically used as solvents and homogeneous catalysts due to their negligible vapor pressure, good solubility to a wide range of organic and inorganic compounds, and ability to be recycled for reuse. Acidic chloroaluminate (III) IL has been used as a homogeneous catalyst for isobutane alkylation. Its use eliminates the diffusion limitation present with solid-acid catalyst systems, and alkylated gasoline is more easily separated from the ionic liquid. Active components in alkylate gasoline are iso-octane or trimethylpentanes (TMPs). TMP yield and selectivity, however with conventional-IL-with and without adjusting the IL’s acidity by
varies either the molar fraction of aluminum chloride ($\text{AlCl}_3$) of the IL or adding hydrochloric acid (HCl). A study showed that adding aromatic hydrocarbons and metal chlorides to aluminum chloride-dialkyl ether complex enhanced TMP selectivity. Pilot plant exists in China

Source: OandG Journal

6.2.2 Alkylation aiming to reduce benzene content in gasoline.

See further section 6.14 on Products treatment

6.3 Base oil production

A recently published new technology is the application of membranes for solvent recovery in the solvent extraction/dewaxing processes. Driving force is the reduction in energy consumption. [259, Dekkers, 2000]

6.4 Catalytic cracking

Some promising lines of investigation for the improvement of the environmental performance of cat crackers are:

- the capability to process heavier feedstocks, containing more contaminants (catalyst deactivators) such as vanadium and nickel and having a higher Conradson Carbon Residue (CCR) content. Responses that are being developed are: continue the development of more active catalysts and more effective (e.g. two-stage) catalyst regeneration. Driving forces are the reduction of residue (i.e. enhanced upgrading) and higher overall refinery efficiency (e.g. the elimination of high vacuum unit operation) [259, Dekkers, 2000].

- Currently addressed as a proven technique in section 4.5.8.4 deNO$_x$ additives in cat cracker regenerators. Low NO$_x$ additives. NO$_x$ removal additives are an emerging technology that may have future applicability for NO$_x$ control from FCC regenerators. The additives are added to the regenerator of the FCC to promote the destruction of NO$_x$ by reaction of nitrogen oxides with carbon monoxide or coke. They are often especially promoted SO$_x$ removal additives, providing the ability to simultaneously reduce the NO$_x$ and SO$_x$ emissions from the FCC regenerator. They have been investigated under laboratory conditions but have not been commercially demonstrated. These additives are attractive since they need no capital investment, although the operating cost for additive replacement is expected to be large. Some trials in USA have achieved NO$_x$ reductions of 50\%.

- Addressed as a technique in section 4.5.9.3 hot ceramic filters can be retrofitted to the underflow of third stage cyclones. Ceramic filters are only applied in niche applications.

- Improvement of the catalyst separation by use of a magnet (Kellogg Tech company) [247, UBA Austria, 1998]

- Addresses as a technique in section 4.5.10.2 other flue gas desulphurisation includes CanSolv’s amine scrubbing system for SO$_x$ removal. It has not commercially proven application in FCC, but it’s process appears quite promising and cost effective, especially at high sulphur.

6.5 Catalytic reforming

The current practice of application of continuously improved catalysts (supplied by catalyst manufacturers) is expected to continue. [259, Dekkers, 2000]
6.6 Coking

Total coke gasification is regarded as the future technology for deep desulphurisation and hydrogen production. In that way, crude oil can be refined without the co-production of heavy oil residues.

The interest (research papers and other publications) and investment on refinery use of coke for energy purposes is growing. IGCC and CFB Boiler technologies are being further developed, optimized and applied with the use of coke feedstock.

6.7 Energy system

Some promising lines of investigation for the improvement of the environmental performance of the energy systems are CO₂ abatement techniques (more information in section 6.15 on Waste gas treatments). Others are the heat integration. The search for further energy improvements is continuing, with the current focus on attractive cogeneration opportunities and more complex heat integration.

6.8 Etherification

Methanol to gasoline (MTG) reactions de-hydrate methanol and convert the available carbon and hydrogen into various hydrocarbons:
- The ‘Shape-Selective’ MTG catalyst limits the synthesis reactions to 10 carbons
- Result is sulphur free gasoline with a typical 92 Research Octane Number

First MTG plant (14,500 barrels per day capacity) was operated at Plymouth (New Zealand) from 1985 to 1997 converting natural gas to gasoline. A second generation MTG plant has started in China (Shanxi province)

Source: Exxon Mobil Research and Engineering

6.9 Hydrogen production

Some promising lines of investigation in hydrogen production technologies are:

- the hydrocarb process, in which the residual oil is essentially cracked to carbon and hydrogen. This process can be seen as an internal source of natural gas for a refinery. The process produces carbon, hydrogen and methanol. It has been calculated in a refinery of 4.98 Mt/yr that this process can increase by 40 % the total gasoline production, 1150 m³/d of methanol and 795 m³/d of C/H₂O slurry [32, Steinberg et al. 1992].
- methane pyrolysis, which takes advantage of the thermal decomposition of natural gas and the direct production of hydrogen while sequestering the carbon or using the carbon for other commodity purposes. Consequently the CO₂ generation is completely eliminated [32, Steinberg et al. 1992], [281, Steinberg, 2000].

Some hydrogen purification process developments enable lower cost by using new techniques such as structured adsorbent beds and integrated rotary valves. Rapid cycle pressure swing adsorption (RCPSA) claim
- cheaper erecting costs (30 to 50 %) compared to PSA and low operating costs
- smaller plot space requirement - as little as ¼ of cPSA

Source: Exxon Mobil Research and Engineering
6.10 Hydrogen-consuming processes

Some promising lines of investigation for the improvement of the environmental performance of energy systems are:

- residue hydrotreating and hydroconversion processes (e.g. slurry bed technology). This process has only been demonstrated at semi-commercial scale and no commercial plants are in operation yet.
- gasoline deep desulphurisation techniques with a lower hydrogen consumption are currently under development. Parameters are not yet available.

It is to be noted that, bunker fuel oil desulphurisation is one of the next technical challenge ahead that may probably lead to new techniques or significant improvement in the current ones.

**Deep gasoline and gasoil desulphurisation**

These process has gained importance during recent years. Many of the new design improvements, optimization or new grass root processes are now arriving to commercialization stage.

- In the standard HDS process now operated at higher severity, there are a large amount of new generation catalysts that are more active and more selective. It lead to a direct impact overall process efficiency
- New process developments use less H2-consuming technologies. Reactive adsorption at high temperature using metal oxide sorbent or alumina based adsorption are delivering promising results. Selective extraction or polar adsorption (Irvad process) are also emerging techniques to consider.

**Non H2 desulphurisation techniques**

Oxidative desulphuration may be one of the most promising in this group (see Section 2.13) but still to face some design challenges.

Below there is a list of some other emerging ones techniques:

- Olefin alkylation of thiophinic sulphur (OATS process by BP).
- Polymer membrane (S-Brane technique by Grace)
- Caustic extraction (Exomer process by Exxon)
- Biochemical desulphuration (Energy biosystems)
- Selective adsorption (Penn State SARS)

[ 80, Stanislaus et al. 2010 ] ‘Recent advances in the science and technology of ultra low sulphur diesel (ULSD) production’.

**Selective desulphurisation of main unit feedstock.**
Treating the primary distillation outlet stream is becoming more common.
Feedstock purification before further use in a refining process, as for example:

- C3 or C4 olefinic cut from FCC: alkynes and diolefins selective hydrogenation before further use in an alkylation or oligomerisation process; naphtha from visbreaking, coking: diolefins and olefins selective hydrogenation before further use in the catalytic reforming process;
- Feedstock purification to obtain on-spec products, for example steam-cracked gasoline: selective hydrogenation of dienes is mandatory in order to stabilize the gasoline without octane loss;
- Feedstock purification to produce petrochemical intermediates, for example C2 olefinic cut from steam cracking: selective acetylene hydrogenation in order to produce on-spec ethylene without ethylene yield loss.
6.11 Hydrocracking

Treatment of heavier feedstocks require optimal technical solutions that include catalyst and flow scheme consideration. Hydrotreatment is done before the cracking step.
- Once through (85-90%) conversion is done with minimized investment. Delivers MD and high residue value
- Single stage full conversion requires medium investment but a higher product quality is reached. Higher MD selectivity is achieved
- Two stages full conversion requires the highest investment costs. This scheme delivers highest quality and diesel/kerosene ratio (IFP and UOP developments)

Integrated refinery management

Leak detection technology.
Smart LDAR. This device is able to detect (using laser technology) fugitive hydrocarbon emissions by real-time video imaging of the equipment under surveillance. It allows the user to identify at a refinery the zones in which the greatest emissions are located so that an LDAR using sniffing techniques can focus on the high emission items. An API study has shown that 90% of fugitive emissions comes from 0.13% of the piping components (API analysis of refinery screening data. Publication 310, November 1997). This technology is under development and a number of technical issues need resolving before it is ready for use as a routine tool. The approach would considerably reduce the cost/benefit of a LDAR program by identifying swiftly the high leakers. Nevertheless, these developments over conventional LDAR programmes are likely to come to fruition in the future term and progress should be monitored to see when they can be accepted as a good technique [115, CONCAWE, 1999].

6.12 Isomerization

Catalytic hydroisomerisation of long parafins to produce biofuels

This technique using the selectivity of the zeolites will improved the conversion of n-paraffins.

![Biofuels Technology Chart](chart.png)

Figure 6.3 Status of main biofuels technologies (Source: International Energy Agency)
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The bio gasoils are produced from mainly triglyceride containing feedstocks (vegetable oils, used frying oils, animal fats, etc.) by heterogenic catalytic hydrogenation in one or more stages. They contain mainly normal paraffins which are unfavourable (e.g. freezing points of the C16–C18 normal paraffins are between +18°C and +28°C). For this reason, the chemical structure of the n-paraffins is isomerized into isoparaffins having lower freezing points and still high cetane number.

Isomerization dewaxing (Mobil MIDW) is applied to various streams (renewable diesel dewaxing) and is based on catalyst shape selectivity including a zeolite and a metal for dehydrogenation/hydrogenation. Selectively converts long chain paraffins to isoparaffins. Enables fuels to flow at low temperatures. This technique is currently in operation in 8 units.

6.13 Primary distillation

Among developments to reduce the energy consumption by primary distillation in refineries the divided wall column technique is to be distinguished.

Divided wall column

A DWC is a distillation column that has a vertical partition wall in the central section.

- The column may contain either trays or packing.
- The feed side of the two compartments acts as the prefractionator and the product side as the main column.
- In the case of a sharp split, a DWC can be used to produce three pure products from a single tower
- A DWC can handle more than three components.

A DWC typically can cut capital and energy costs by approximately 30% compared to a traditional two-columns system.

6.14 Product treatments

Biodesulphurisation of gas oil and even crude oil: still under development to be mentioned in the [259, Dekkers, 2000]

Reforming gasoline account for 70–85% of the benzene presented in the gasoline pool (US-EPA). Pretreatment technologies that withdraw benzene precursors from the reforming feedstock actually are facing some difficulties: e.g. octane and hydrogen forming reduction, and difficulties for complying with benzene specifications. Removing benzene precursors from reformer feed nearly eliminates (0.3%w) benzene in reformate. Using a dehexanizer with a side column the top composition remain unchanged.

Post-treatment technologies:

- benzene saturation converts benzene to cyclohexane, sometimes coupled with isomerization to increase octane. Some of the saturation technology drawbacks are: hydrogen consumption, loss of octane number and benzene conversions that may not be sufficient to achieve the required level.
- benzene extraction Gasoline volume reductions, need of proprietary solvents that require high level heat, storage facilities and an available market for the extracted benzene are disadvantages of the extraction technology. Expensive.
- benzene alkylation offers increments in octane number and gasoline volume, although the technology is considered pioneer. It is the only benzene reduction option that increases the volume for gasoline and do not lead to consumption of H₂.
6.15 Waste gas treatments

Some developments to be mentioned are:

- Already addressed through regenerative processes:
  - Sulphur dioxide removal by SO$_2$ capture from flue gas and conversion into liquid sulphur.
  - Biological H$_2$S removal [181, HP, 1998]
- Particulate abatement techniques by new developments including ceramic filters (e.g. NGK, Japan) and a rotating particulate separator (Lebon and Gimbrair, the Netherlands).
- CO$_2$ abatement techniques.

Assuming refinery utilisation gradually increases and that product specification and abatement requirements continue to be more stringent, then CO$_2$ releases, if unabated, are likely to continue to rise since measures to meet these requirements will require energy. In principle CO$_2$ emissions can be reduced by separation, collection and finding a useful application. Injection of CO$_2$ aiming at secondary and tertiary oil recovery is a potential possibility. Injection into subsurface formations for storage or supply to greenhouses as a gaseous fertiliser product has also been suggested. However, considering the large quantities of CO$_2$ involved these projects will be very costly indeed. Moreover, these types of solutions can only partly alleviate the CO$_2$ emission issue.

Removal of CO$_2$ from Flue gas Streams
Wet scrubbing using caustic soda for the removal of SO$_2$/NO$_x$ will effectively remove CO$_2$ as a carbonate. It should be noted, however, that to apply wet gas scrubbing for the sole purpose of removal of CO$_2$ would be largely self-defeating as the scrubbing process itself and the production of the scrubbing agents both require energy. A number of other licensed processes are available which will remove CO$_2$ from flue gases using a solvent that can be recycled, typically methylethylamine (MEA). After absorbing the CO$_2$ in a scrubbing system, the solvent is thermally regenerated, releasing the CO$_2$. This could then be compressed, liquefied and sent to underground disposal. Present indications are that the high energy requirements of this type of scheme will discourage its general use.

Disposal of CO$_2$
Unlike the abatement of other pollutants no feasible technology exists for the removal of carbon dioxide from flue gases. A number of disposal options are, however, under scientific consideration. For technical, ecological and economic reasons, a viable solution is not yet available, but this option is currently being investigated by certain major operators and the International Energy Agency (IEA).

Emerging technologies under consideration are:

- Disposal in the deep ocean
- Disposal in deep aquifers
- Disposal in exhausted oil and gas reservoirs
- Disposal as a solid in an insulated repository

Emerging techniques to enable carbon dioxide capture and storage (CCS)
Production of power and other use of fossil energy is the largest source of greenhouse gas emissions. For many years, there has been considerable international interest in development of technology for capture and storage of CO$_2$, particularly from coal-fired power plants. IPCC report points out that the technology for capture and storage of CO$_2$ is not yet mature.

With CCS, a power plant could reduce its CO$_2$ emissions to the atmosphere by approximately 80–90% compared to a plant without CCS. In the same time, CCS leads to a loss in overall efficiency of power plants or industrial processes due to the additional energy required for capture, transport and storage. The additional energy required for CCS depends on intrinsic performances of the capture system and on the energy management in the global installation.
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A power plant equipped with a CCS system would need roughly 10–40 % more energy than a plant of equivalent output without CCS, of which most is for capture and compression. As an example, the range reflects three types of power plants: for Natural Gas Combined Cycle plants, the range is 11–22 %, for Pulverized Coal plants, 24–40 % and for Integrated Gasification Combined Cycle plants, 14–25 % (Source: IPCC report).

**Technique for capturing CO₂**

These techniques are still in the early stages of development. The available technology is highly expensive, and there are many uncertainties linked to the costs and operation of a CO₂ chain.

They can be divided into three main categories:

- post-combustion;
- pre-combustion;
- oxy-fuel.

*Post-combustion* entails separating CO₂ from the exhaust gas from the power plant using chemical cleaning. Because CO₂ is separated from the exhaust gas, this technology can, in principle, be utilised in existing power plants without major modifications of the plant itself. Post-combustion is considered to be the most mature technology, although there is still significant uncertainty surrounding its use.

With the aid of *pre-combustion* technology, CO₂ is captured before combustion. This is accomplished by converting the natural gas to a hydrogen-rich gas mixture. This gas mixture is treated so that CO₂ is captured, and the new fuel is thus ‘decarbonised’ (exhaust gas contains very little CO₂). Pre-combustion requires modification of gas turbines and is considered to be a more complex technology than post-combustion.

With *oxy-fuel*, combustion takes place in the gas turbine with pure oxygen instead of air. This means that the exhaust contains water vapour and CO₂, and the CO₂ can be separated out by cooling the exhaust. Today’s gas turbines suffer from very poor performance with oxygen combustion, and to date there has been little effort to develop new types of turbines that are better suited to oxygen combustion. In addition, production of oxygen is extremely energy-intensive, and the corresponding technology is quite costly. Oxy-fuel is thus an immature technology.

The costs associated with capturing CO₂ from a power plant amount to approximately two-thirds of the costs for the entire CO₂ chain, while transport and storage amount to approximately one-third.

**Transport of CO₂**

CO₂ must be transported from the CO₂ source to the geological structure where the CO₂ will be stored. This transport can be accomplished by pipeline or by ship. Transport is the least complicated element in the CO₂ chain, both as regards technology and the possibility of evaluating realistic costs. Anyhow, the transport of CO₂ requires substantial resources in terms of energy and costs. As CO₂ behaves very differently under various pressures and temperatures, transport must take place in a controlled manner to avoid solid stale and subsequent clogging of pipes or equipment. Choice of means of transport will depend on the specific requirements, including the number of emission sources, the volume of emissions from each source, the distance from the source to the storage place and the volume of CO₂ to be transported. With existing technology, pipeline transport is believed to be the simplest and most cost-effective alternative.

**Storage of CO₂**

There is significant technical potential for storing CO₂ in geological formations around the world. Producing oil and gas fields, abandoned oil and gas fields and other formations are all candidates for such storage. Storage in reservoirs that are no longer in operation is a good solution in terms of geology because these structures are likely to be impermeable after having held oil and gas for million of years. Other formations are also considered to be secure storage alternatives for CO₂.
Chapter 6

Full-scale test in Norwegian refinery
At the Mongstad refinery, a new combined heat and power (CHP) is to be built to produce 280 MW of electricity and 350 MW of heat. Within an agreement with Norway government, a full-scale carbon capture facility is to be built at the Mongstad refinery. At the time of writing this document, it has been reported that this project would need an additional delay (2016).

6.16 Waste water treatment
Emerging techniques on this issue are addressed in the CWW BREF [6, EC 2003].
7 CONCLUDING REMARKS

The EIPPCB will update and finalise this section for the final version of this document.
8 REFERENCES


[25] Pham et al., SOx RECLAIM - Draft Staff Report, California South Coast Air Quality Management District, 2009.


References

[37] Chen, Recent advances in FCC technology , 2006.
[38] INERIS, Démarche globale de surveillance des eaux souterraines dans le cadre du BREF Raffinage, INERIS (France), 2009.
[39] French contribution to TWG (item 4) , Management of a refinery to avoid pollution picks under unfavourable conditions (2 examples), 2009.
[54] Gallauner et al., State of the art of technology in oil and gas refineries - Reference plants in Austria, Umweltbundesamt (Austria), 2009, p. 79.
References

[56] EIGA, Best available techniques for hydrogen production by steam methane reforming, 2009.

[57] Roberts et al., 'SOx-reducing additives for FCC - Results from tests submitted by CONCAWE Member companies (Dec 2009)', Personal Communication, 2009.


[76] Hydrocarbon processing, Hydrocarbon processing, 2011.

[77] REF TWG, Comments from TWG 2010 on DRAFT 1 BREF review, 2010.

[79] Fayruzov et al., 'Oil and Gas Business 2009
ULSD PRODUCTION’, 2009.

[80] Stanislaus et al., ‘Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production’, 2010.


[85] SFT, Emissions to air from flaring, 2009.


[91] JEA, Best Available Control Technology Analysis for JEA – Greenland Energy Center
References


[118] VITO, Contribution from Belgium (Flanders) to the review of the CWW BREF, Flemish Institute for Technological Research (VITO), 2009.

[119] CONCAWE, CONCAWE contribution to the water discharge part of the DRAFT Refinery BREF Revision, 2011.

REFERENCES USED FOR THE ORIGINAL BREF (NOT YET INTRODUCED IN BATIS)


[34a] Italy, (1999). 'The italian refining industry' Ministero dell’Ambiente, Servizio inquinamento atmosferico e acustico e le industrie a rischio., 38 pgs.


[122] REPSOL (2001). 'Technical information of several REPSOL refineries'.


[198] (Hellas), M. O., (1999). 'Contribution of Motor Oil (Hellas) to the BREF' Motor Oil (Hellas), pgs.


References


References


[316] TWG, (2000). 'Comments from TWG members to the second draft of Chapter 4 and Chapter 5.'


[325] Gary and Handwerk 'Petroleum Refining - Technology and Economics'.

[326] Nelson, W. L. 'Petroleum Refinery Engineering'.

[327] Broughson, J. 'Process Utility Systems'.


GLOSSARY
The EIPPCB will update and finalise this section for the final version of this document

Symbols
~ Around, more or less
\( \Delta T \) Increase of temperature, temperature rise
\( \epsilon \) EUR (EU currency)

A
AC Alternating Current
AC Activated Carbon
Amylenes Pentenes
AOC Accidentally Oil Contaminated
^API Density unit (specific density = \( 141.5/(^\text{API} + 131.5) \))
API American Petroleum Institute
API separator Oil/water/sludge separator (developed by American Petroleum Institute)
ASU Activated Sludge Unit
atm Atmosphere. Pressure unit that equals to 101.3 kPa
Auto-Oil Co-operative programmes between the EU and the oil and motor industries to find the most cost-effective way to improve air quality in Europe. These have led to Directives on fuel properties and vehicle emissions.

B
bbl US barrel (159 litres)
bar Pressure unit that equals to 100 kPa (1 bar = 0.987 atmospheres)
barg Bar gauge (relative pressure over the atmospheric pressure)
BBU Bitumen Blowing Unit
BFO Bunker Fuel Oil
BFW Boiler Feed Water to produce steam
BOD Biological Oxygen Demand
bpcd Barrels per calendar day (average flow rates based on operating 365 day per year)
bpsd Barrels per stream day (flow rates based on actual on-stream time of a unit)
BREF Best Available Techniques reference document (Documents developed by the EIPPCB on different IPPC sectors)
BTEX Benzene, Toluene, Ethylbenzene, Xylene
BTX Benzene, Toluene, Xylene

C
CAGR Compound Annual Gross Rate
cat catalytic
cat cracker catalytic cracker (typically refers to fluid catalytic cracker)
CCGT Combined Cycle Gas Turbine
CCR Conradson Carbon Residue (See under Concarbon more information)
CDD/CDF Chlorodibenzoparadioxins/furans
CDU Atmospheric Crude Distillation Unit
CEC Comission of the European Community
CHP Combined Heat and Power
COC Continuously Oil Contaminated
COD Chemical Oxygen Demand
Concarbon Conradson carbon = measurement of carbon residue (expressed in % w/w). Measurement of the tendency of a hydrocarbon to form coke.
CONCAWE European Refinery Association for Environment, Health and Safety
Corinair European Air Emissions inventory
CPI Corrugated Plated Interceptor
C\(_x\) Hydrocarbons with \( x \) number of carbons
CW Cooling Water
Glossary

D
d day
DAF Dissolved Air Flotation
dB(A) Noise unit
DC Direct Current
DCU Delayed Coker Unit
DEA Diethanol Amine
DG Direction General from the European Commission
DGA Diglycolamine
DIAL Differential absorption light detection and ranging
DIPA Di-isopropanol amine
DNB Nitrification/denitrification biotreater
DS Dissolved Solids

E
EC European Community
EFRT External Floating Roof Tanks
EIA Environmental Impact Assessment
EII Energy intensity index (Solomon index. See Section 3.10.1)
EIPPCB European IPPC Bureau
EMS Environmental Management System (see Section 4.15.1)
EOP End-of-pipe
EP European Parliament
ETBE Ethyl tert-butyl ether
EU+ EU countries plus Norway and Switzerland
EUR Euro: EU currency

F
FAME Fatty acid methyl ester (reference: EN 14214)
FBI Fluidised-bed Incinerator
FC Flue Control
FCC Fluidised-bed Catalytic Cracking
FCCU Fluidised-bed Catalytic Cracking Unit
FFU Floculation/flotation unit
FGD Flue-gas Desulphurisation
FGR Flue-gas Recirculation
FOE Fuel oil equivalent (1 tonne FOE = 4.25·10^{10} J)

G
GAC Granular activated carbon
GO Gasoil

H
h hour
HC (1) Hydrocarbon
HC (2) Hydrocracker/ing
HCU Hydrocracker Unit
HDM Hydrodemetallisation
HDS Hydrodesulphurisation
HFO Heavy Fuel Oil
HGO Heavy Gasoil
Horizontal BREF BAT reference documents prepared to deal with topics common to more than one IPPC industrial sector (namely storage, cooling, waste water and waste gas and monitoring)
HORC Heavy Oil and Residue Catalytic cracking
HP High Pressure
Glossary

HSE Health, Safety and Environment
HT High Temperature
HVU High Vacuum Unit
Hydrofiner Selective hydrocracking

I
I-TEQ<sub>DF</sub> International toxic equivalent of dioxins/furans
IAF Induced Air Flotation
IFRT Internal Floating Roof Tank
IGCC Integrated Gasification Combined Cycle
IMO International Maritime Organisation

K
k--- kilo
kg kilogrammes
kero kerosene
KjN Kjeldahl nitrogen (Measure of the total nitrogen content)
kt kilotonne (10<sup>6</sup> kg)

L
LCO Light Coking Oil
LCP Large Combustion Plant BREF
LDAR Leakage Detection and Repair Programme (see Section 4.23.6.1)
LGO Light Gasoil
LP Low Pressure
LPG Liquefied Petroleum Gas
LT Low Temperature
LVGO Light Vacuum Gasoil
LVOC Large Volume Organic Chemicals BREF

M
M--- Million
MAH Mono Aromatic Hydrocarbon
MDEA Mono diethanolamine
MEA Mono ethanolamine
MP Medium Pressure
MS EU Member State
MTBE Methyl Tert-buthyl Ether
Mt/yr Million of tonnes per year
MW<sub>e</sub> MegaWatts electric (energy)
MW<sub>th</sub> MegaWatts thermal (energy)

N
n- normal, linear organic compound
N--- Normal (refers to volume of gases under normal conditions (temperature 0 ºC and pressure of 1 atmosphere (101.3 kPa))
- not applicable
NA not available (typically for data not available within the document).
Highlighted within the document to help next revisions.
N-Kj Nitrogen analysed by Kjendahl method.
Naphthenic The naphthenes contain one or more saturated rings of 5 or 6 carbon atoms in their molecules to which paraffinic-type branches are attached.
NOC Non-oil contaminated
NO<sub>x</sub> Nitrogen Oxides (NO + NO<sub>2</sub>, normally expressed as NO<sub>2</sub>)

P
Pa Pascal (N/m<sup>2</sup>). SI unit for pressure: 1 atm=101.3 kPa
Glossary

PAC  Powdered activated carbon
PAH  Polycyclic aromatic hydrocarbons
PC  Pressure control
PCDD/F Polychlorodibenzoparadioxins/furans
Platformer Type of catalytic reformer
PM Particulate Matter (any finely divided solid or liquid material emitted into the air)

PM$_{10}$ Particulate matter of size less than 10 µm
Poly-unit Polymerisation unit
PPI Parallel Plate Interceptor
ppm parts per million (weight)
ppm v/v parts per million in volume
PPS Pressurised cross flow plate separation of the desalting unit
PSA Pressure-swing adsorption used for purification of hydrogen
psi pounds per inche (British pressure unit 1 bar = 14.5 psi)
psia pounds per inche (absolute pressure)
Pt-based used for catalysts containing platinum
PUF Pick-up factors- kg SO$_2$ removed per kg additive introduced

R
RCC Residue Catalytic Cracker
Residue This term is used in this document as the heaviest fractions of the distillation and conversion units. These fractions are used as feedstock in other processes or as liquid refinery fuel.

RFG Refinery Fuel Gas
RO Reversed Osmosis
RON Research Octane Number
RSH Mercaptan
RVP Reid Vapour Pressure

S
S Sulphur
SF Sand Filter
SO$_x$ Sulphur oxides (SO$_2$ and SO$_3$)
SRU Sulphur Recovery Unit
SS Suspended Solids
SW Sour Water
SWS Sour Water Stripper

T
t Tonne (1000 kg)
t/yr Tonnes per annum (year)
t/d Tonnes per day
TAME Tertiary Amyl Methyl Ether
TBtu Trillion British thermal unit (1 TBtu ~ 1.054 million GJ)
TCDD/F Tetrachlorodibenzoparadioxins/furans (toxicity reference for dioxins)
TEL Tetra ethyl lead
TGT Tail Gas Treatment of the sulphur recovery unit
TML Tetra methyl lead
TOC Total Organic Carbon
TSS Total Suspended Solids (water)
TWG European Technical Working Group on refineries

U
U Unit (used together with names of process)
UF Ultrafiltration
Ultraformer Type of reformer
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>USAEPA</td>
<td>Environmental Protection Agency of the USA</td>
</tr>
<tr>
<td>V</td>
<td>v/v volume per volume</td>
</tr>
<tr>
<td>V.I.</td>
<td>Viscosity Index (see Section 2.3)</td>
</tr>
<tr>
<td>VBU</td>
<td>Visbreaking Unit</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>VR</td>
<td>Vacuum Residue</td>
</tr>
<tr>
<td>VSBGO</td>
<td>Visbreaking Gasoil</td>
</tr>
<tr>
<td>W</td>
<td>w/w weight per weight. Ratio expressed in weight</td>
</tr>
<tr>
<td>WHB</td>
<td>Waste Heat Boiler</td>
</tr>
<tr>
<td>WWTP</td>
<td>Waste Water Treatment Plant</td>
</tr>
<tr>
<td>Y</td>
<td>yr year</td>
</tr>
</tbody>
</table>

**Glossary**
9 ANNEXES

9.1 Annex I. Environmental legislation and emission limit values applied to refineries

Refineries generate emissions to the air, discharges to water and also waste. Most pollutants are emitted to streams that are transboundary in nature. As a consequence many of the environmental policies and regulations with respect to oil refining are to a large extent influenced by international developments (EU directives and other international regulations). These regulations focus on product quality, refinery emissions and, more recently, on environmental reporting. The issue of emergency procedures is normally included in the external safety report and in the permit for the location.

9.1.1 EU and other international legislation

Table 9.1 gives a summary of some of the main EU legislation that is applied to refineries.

<table>
<thead>
<tr>
<th>Name</th>
<th>Concerning</th>
<th>Location</th>
<th>Emission limit values</th>
</tr>
</thead>
</table>
Annexes

<table>
<thead>
<tr>
<th>Name</th>
<th>Concerning</th>
<th>Location</th>
<th>Emission limit values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Directive 94/63/EC</td>
<td>on painting of petrol tanks</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9.1: Main EU legislation affecting refineries

Legislation affecting product specifications

Product specifications (Auto-Oil programmes and IMO)

Concern about the environmental and health impact of fuel combustion has caused changes in environmental regulations with special focus on gasoline and diesel fuel composition as the largest products (Auto-Oil specifications in Table 1.9). The main restrictions on diesel fuels impose limits on sulphur and polynuclear aromatics content. Gasoline specifications include not only sulphur and total aromatics content but also limits for specific compounds, such as benzene, olefins, maximum RVP and, in the USA, minimum oxygen for areas with CO problems.

The specifications for heavy fuel oils are regulated in Council Directive 1999/32/EC relating to the reduction in the sulphur content of certain liquid fuels and amending 93/12/EC. OJ L121/13, 11 may 1999 EU B. For heating oil, the Directive entails a reduction of the sulphur content to 0.1 % in 2008 and for landtrade fuel oils a limitation of the sulphur content to 1 % from 2003 onwards. For seagoing vessels the regulations of Annex VI of the MARPOL treaty, once ratified, imply that as of 2003, in so-called SOx emission control areas, the use of fuel oils may be restricted to fuel oils with a maximum sulphur content of 1.5 %.

Legislation affecting emissions to air

<table>
<thead>
<tr>
<th>Legislation</th>
<th>Concerning</th>
</tr>
</thead>
<tbody>
<tr>
<td>National Emission Ceiling Directive</td>
<td>Important Directive for the reduction of CO2, SO2, NOx and VOC</td>
</tr>
<tr>
<td>Air Pollution Protocol (Gothenburg Protocol, 1 December 1999)</td>
<td>Important protocol for the reduction of SO2, NOx and VOC</td>
</tr>
<tr>
<td>VOC prevention during transfer of liquids</td>
<td>When transferring liquids to vessels at atmospheric pressure, the vapour phase (often air, but also inert) in the receiving vessel is often emitted to atmosphere. Such loading operation is recognised as having an impact on the environment due to the presence of VOC. EU Stage 1 Directive 94/63/EC prescribes emission reduction measures and the application of Vapour Recovery Units (VRU) or Vapour Recovery Systems (VRS) to prevent escape of vapours to the atmosphere.</td>
</tr>
<tr>
<td>Air Quality Directive (AQD)</td>
<td>The Air Quality Directive gives limit values. PM emissions has been agreed upon by the Council of Ministers in second reading and will be published shortly.</td>
</tr>
</tbody>
</table>
Concerning EC Large Combustion Plant Directive

New units (i.e., units which came into existence on or after 1 July 1987) with individual furnaces greater than 50 MWth or multiple heaters where aggregate thermal input is greater than 50 MW, come within the scope of the EC Large Combustion Plant Directive, and must comply with its requirements. However, the Directive does not cover direct refinery processes, e.g., FCC unit regenerators, coking processes or SRUS, nor gas turbines. The Directive requires Member States to introduce programmes for a successive reduction of sulphur dioxide and oxides of nitrogen emissions from large combustion plants operating, or licensed, before 1 July 1987.

Table 9.2: Main legislation affecting emissions to air

<table>
<thead>
<tr>
<th>Compound</th>
<th>Legislation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Concerning</strong></td>
</tr>
<tr>
<td></td>
<td>EC Large Combustion Plant Directive</td>
</tr>
<tr>
<td></td>
<td>New units (i.e., units which came into existence on or after 1 July 1987)</td>
</tr>
<tr>
<td></td>
<td>with individual furnaces greater than 50 MWth or multiple heaters where</td>
</tr>
<tr>
<td></td>
<td>aggregate thermal input is greater than 50 MW, come within the scope of the</td>
</tr>
<tr>
<td></td>
<td>EC Large Combustion Plant Directive, and must comply with its requirements.</td>
</tr>
<tr>
<td></td>
<td>However, the Directive does not cover direct refinery processes, e.g., FCC</td>
</tr>
<tr>
<td></td>
<td>unit regenerators, coking processes or SRUS, nor gas turbines. The Directive</td>
</tr>
<tr>
<td></td>
<td>requires Member States to introduce programmes for a successive reduction of</td>
</tr>
<tr>
<td></td>
<td>sulphur dioxide and oxides of nitrogen emissions from large combustion</td>
</tr>
<tr>
<td></td>
<td>plants operating, or licensed, before 1 July 1987.</td>
</tr>
</tbody>
</table>

Table 9.3 lists, by compound, legislation affecting emissions to air

<table>
<thead>
<tr>
<th>Compound</th>
<th>Legislation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>International Post-Kyoto Protocol UN/Greenhouse gas convention</td>
</tr>
<tr>
<td></td>
<td>EC Directives 93/76/EEC</td>
</tr>
<tr>
<td></td>
<td>93/389/EEC</td>
</tr>
<tr>
<td>Particulate</td>
<td>International EU/UN-UN-ECE</td>
</tr>
<tr>
<td></td>
<td>EC Directives Large Combustion Plant Directive (LCPD), Integrated Pollution</td>
</tr>
<tr>
<td></td>
<td>Prevention Control Directive (IPPC), Air Quality Directives (AQFD)</td>
</tr>
<tr>
<td></td>
<td>Other: UN-UN-UN-ECE, Acidification Strategy</td>
</tr>
<tr>
<td>Sulphur-oxides</td>
<td>International EU/UN-UN-ECE, Acidification Strategy</td>
</tr>
<tr>
<td></td>
<td>EC Directives Large Combustion Plant Directive (LCPD), Sulphur in Liquid</td>
</tr>
<tr>
<td></td>
<td>Fuels Directive (SLFD), Integrated Pollution Prevention and Control</td>
</tr>
<tr>
<td></td>
<td>Directive (IPPC), Air Quality Directives</td>
</tr>
<tr>
<td></td>
<td>Other: UN-UN-UN-ECE, World Health Organisation (WHO), USAEPA/1990 Clean</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>International EU/UN-UN-ECE, Acidification Strategy</td>
</tr>
<tr>
<td></td>
<td>EC Directives LCPD</td>
</tr>
<tr>
<td></td>
<td>IPPC</td>
</tr>
<tr>
<td></td>
<td>Air Quality Directives: AQFD</td>
</tr>
<tr>
<td></td>
<td>N-protocol (93/361/EEC)</td>
</tr>
<tr>
<td></td>
<td>National Ceilings Directives</td>
</tr>
<tr>
<td></td>
<td>Other: UN-UN-UN-ECE, WHO</td>
</tr>
<tr>
<td></td>
<td>USAEPA/1990 Clean-Air Act</td>
</tr>
<tr>
<td>Volatile-organic</td>
<td>International EU/UN-UN-ECE, UN-UN-UN-ECE/VOC Protocol Stage I (Marine VR),</td>
</tr>
<tr>
<td>compounds</td>
<td>Stage II MARPOL Convention Annex VI</td>
</tr>
<tr>
<td></td>
<td>IMO, MARPOL 73/78</td>
</tr>
<tr>
<td></td>
<td>EC Directives Air Quality Directives: AQFD</td>
</tr>
<tr>
<td></td>
<td>94/63/EEC</td>
</tr>
<tr>
<td></td>
<td>National Ceiling Directives Review</td>
</tr>
<tr>
<td></td>
<td>Ozone Strategy</td>
</tr>
<tr>
<td></td>
<td>Other: UN-UN-UN-ECE, WHO</td>
</tr>
<tr>
<td></td>
<td>USAEPA/1990 Clean-Air Act</td>
</tr>
<tr>
<td></td>
<td>Draft EC-Long range transboundary air pollution</td>
</tr>
</tbody>
</table>
Annexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>International</th>
<th>Legislation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>EC directives</td>
<td>IPPC</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>UN-WHO</td>
</tr>
<tr>
<td>Methane</td>
<td>EC directive</td>
<td>UN/Greenhouse gas convention</td>
</tr>
<tr>
<td>Halon and CFC</td>
<td>International</td>
<td>UN/Greenhouse gas convention</td>
</tr>
<tr>
<td>Halon and CFC</td>
<td>International</td>
<td>UN/Montreal Protocol (94/84/EC)</td>
</tr>
<tr>
<td>Nickel</td>
<td>EC directives</td>
<td>UN-ECE protocols on Heavy Metal</td>
</tr>
<tr>
<td>Benzene</td>
<td>EC directives</td>
<td>Air Quality Directives, AQFD</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IPCC</td>
</tr>
<tr>
<td>PAH</td>
<td>EC directives</td>
<td>Air Quality Directives, AQFD</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IPCC</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>UN-ECE POP protocol</td>
</tr>
</tbody>
</table>

Table 9.3: Air pollutants affected by main legislation

### Legislation affecting emissions to water

There is an OSPARCOM Decision (89/5) which sets an oil limit for refinery discharges.

**Legislation affecting other issues**

**Environmental Impact Assessment (EIA)**

An important tool for proactive Environmental Management as imposed by international authorities (in Europe per EC directive) is the Environmental Impact Assessment. Prior to each investment project the expected emissions, waste water and waste and the necessary abatement measures will be defined and the effects and impacts of the projected activities on the environment will be assessed and reported. An approved EIA report is a prescribed input for the permitting procedure for new installations.

**External safety**

On the basis of the post-Seveso guideline of the EU (82/501) refineries are nowadays obliged to prepare an external safety report. The Seveso 1 guideline was implemented in 1999, and involves further requirements on safety reporting. It applies to the refinery as a whole.

**Some EU and international emission limit values**

| Compound | The EC directive on large combustion plants regulating the sulphur content in liquid fuels sets an overall limit of 1700 mg/Nm³ (bubble) for existing plants in the refinery. For new refinery plants the directive on the reduction of emissions from large combustion plants limits the SO₂ emission to 1000 mg/Nm³ flue gas. Moreover, the proposed revision of this directive includes a proposal to lower the SO₂ emission limit for new refinery installations to 450 mg/Nm³. | The EC directive for large combustion plants applies a limit to total emissions of particulate matter (PM) of 50 mg/Nm³. |

### 9.1.2 EU+ national legislation and emission limit values

The remaining tables in this section give a brief summary of the environmental legislation and/or emission limit values affecting refineries in some of the EU+ countries.

**Austria**
### Annexes

#### Medium Legislation Scope

**Air**
  - Clean Air Act for Steam Boilers
  - Clean Air Ordinance for Steam Boilers

**Water**
- Allgemeine Abwasseremissionsverordnung” (BGBl. 1996/186)
- Other ordinances based on the Austrian 'Wasserrechtsgesetz' i.d.F. BGBl. I 155/1999 (water right act).
  - Special ordinance of interest for oil refineries is Verordnung über die Begrenzung von Abwasseremissionen aus der Erdölverarbeitung BGBl. II 1997/314 (Ordinance for the limitation of waste water emissions from oil refining)
  - Other special ordinances for different industrial sectors.

**Waste**
- The principles of waste management in Austria are regulated by the 'waste management act' (BGBl. 325/1990 i.d.F. I 151/1998).

### Table 9.4: Summary of environmental legislation in Austria

<table>
<thead>
<tr>
<th>Medium</th>
<th>Pollutant</th>
<th>Emission limit values</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Sludge</td>
<td>2 m³/t</td>
<td></td>
<td>Limit according to regulation for landfilling</td>
</tr>
<tr>
<td>Waste</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Limit according to regulation for landfilling</td>
</tr>
<tr>
<td>Water</td>
<td>pH</td>
<td>6.5-8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>30 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dissolved solids</td>
<td>30 mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Suspended solids</td>
<td>30 mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>COD</td>
<td>25 mg/l</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BOD</td>
<td>20 mg/l</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TOC</td>
<td>5 mg/l</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>0.5 mg/l</td>
<td></td>
<td>as Sulphur</td>
</tr>
<tr>
<td></td>
<td>NH₄⁺</td>
<td>5 mg/l</td>
<td>mg/l</td>
<td>as Nitrogen</td>
</tr>
<tr>
<td></td>
<td>Oil</td>
<td>2.0/3.0 mg/l</td>
<td>mg/l</td>
<td>2.0 after biological treatment from 2005, today 10 mg/l</td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>0.2 mg/l</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metals</td>
<td>0.5/3.0/5.0/0.02/1.0 mg/l</td>
<td>for Pb/Cu/Co/Ni/Hg/V respectively</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>2.0 mg/l</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surfactants</td>
<td>2.0 mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toxicity</td>
<td>bacteria: 8 Gl fish: 2 Gf</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>0.1/0.1/0.0.1/0.5 mg/l</td>
<td></td>
<td>for CN/total N/P/AOX/BTXE</td>
</tr>
<tr>
<td>Air</td>
<td>H₂S</td>
<td>10</td>
<td></td>
<td>for Claus unit</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>10</td>
<td></td>
<td>for SNCR and SCR</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>100 fuel gas</td>
<td></td>
<td>at 3% O₂ dry</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>475 liquid refinery fuels</td>
<td></td>
<td>2000 FCC</td>
</tr>
</tbody>
</table>

### Table 9.5: Emission limit values

<table>
<thead>
<tr>
<th>Medium</th>
<th>Pollutant</th>
<th>Emission Limit Values</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>SO₂</td>
<td>1700 FCC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600 – Power station – II</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>naphtha – HDS – vacuum</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;50/50 – 300/300 MW at 3% O₂ dry</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Annexes

<table>
<thead>
<tr>
<th>VOC</th>
<th>200-300 fuel gas</th>
<th>400-500 fuel gas</th>
<th>900 power station II (firing heavy residues)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>NO&lt;sub&gt;x&lt;/sub&gt;</th>
<th>200-300 fuel gas</th>
<th>400-500 fuel gas</th>
<th>300 FCC unit regenerator for the respective heat input and fuel at 3% O&lt;sub&gt;2&lt;/sub&gt; dry&lt;sup&gt;1,2&lt;/sup&gt;</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Particles</th>
<th>40/45</th>
<th>50/50</th>
<th>110 power station II (firing heavy residues) for existing/new plants at &gt;5 MW for heavy fuel oil</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Ni:1</th>
<th>Pt:5</th>
<th>V:5</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Table notes:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. for existing plants</td>
</tr>
<tr>
<td>2. 800 mg/Nm³ for refinery power plants</td>
</tr>
<tr>
<td>3. 900 mg/Nm³ for refinery power plants</td>
</tr>
<tr>
<td>4. 700 mg/Nm³ for 1 new boiler within power plant (recently installed)</td>
</tr>
</tbody>
</table>

#### Table 9.5: Emission limit values applied to Austrian refineries

**Belgium**

Air: (Vlarem), water and groundwater: (Vlarem), waste and soil: (Vlarem, Vlarebo and Vlaria) and noise: (Vlarem).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Pollutant</th>
<th>Emission limit values&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Measures against soil pollution related to e.g. the use and storage of chemicals, including construction conditions</td>
<td>Not specific for refineries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>Periodic soil pollution test</td>
<td>Refineries are on the list of activities that entail risks for soil pollution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noise</td>
<td>Immission levels are compared to quality objectives (e.g. industry fields 55 dB(A))</td>
<td>Not specific for refineries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste</td>
<td>Appropriate disposal and processing</td>
<td>Not specific for refineries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Annual reporting to Waste Agency</td>
<td>List of 30 specific waste streams of refineries, annual reporting to Waste Agency</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Water</td>
<td>0.5</td>
<td>m³/t</td>
<td>m³/t crude oil throughput for simple refineries&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>Water</td>
<td>Water</td>
<td>0.6—1.2</td>
<td>m³/t</td>
<td>m³/t crude oil throughput for complex refineries&lt;sup&gt;4&lt;/sup&gt; (0.1 m³/t crude oil per additional treatment to a maximum of 0.7 m³)</td>
</tr>
<tr>
<td>pH</td>
<td>6.5—9.0</td>
<td>Sörensen</td>
<td>6.0—9.5 if discharged in sewer</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>30</td>
<td>°C</td>
<td>45 °C if discharged in sewer</td>
<td></td>
</tr>
<tr>
<td>Dissolved solids</td>
<td>60</td>
<td>mg/l</td>
<td>1000 mg/l if discharged in sewer</td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td>0.5</td>
<td>mL/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>20</td>
<td>mg/l</td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;-extractable, if discharged in sewer 500 mg/l (petroleum-ether extractable)</td>
<td></td>
</tr>
</tbody>
</table>

#### Table notes: |

1. for existing plants |
2. 800 mg/Nm³ for refinery power plants |
3. 900 mg/Nm³ for refinery power plants |
4. 700 mg/Nm³ for 1 new boiler within power plant (recently installed)
<table>
<thead>
<tr>
<th>Medium</th>
<th>Pollutant</th>
<th>Emission limit values</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (ELV at 3% O₂)</td>
<td>SO₂</td>
<td>1300</td>
<td>mg/Nm³</td>
<td>bubble emissions for total of fuel and process emissions, including emissions from cogeneration plants; ELV and scope currently under revision</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1700</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel oil, 50 to 300 MWth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1700 to 400</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel oil, 300 to 500 MWth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel oil, &gt;500 MWth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel gas</td>
</tr>
<tr>
<td>Air (ELV at 3% O₂)</td>
<td>NOₓ</td>
<td>450</td>
<td>mg/Nm³</td>
<td>bubble emissions for total of fuel and process emissions, including emissions from cogeneration plants; ELV and scope currently under revision</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel gas</td>
</tr>
<tr>
<td>Air</td>
<td>dust</td>
<td>150</td>
<td>mg/Nm³</td>
<td>bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>mg/Nm³</td>
<td>new large combustion installations, fuel gas</td>
</tr>
<tr>
<td>Air</td>
<td>CO</td>
<td>150</td>
<td>mg/Nm³</td>
<td>bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2</td>
<td>mg/Nm³</td>
<td>bubble emissions for total of fuel and process emissions, including emissions of cogeneration plants</td>
</tr>
<tr>
<td>Air</td>
<td>Ph</td>
<td>0.05</td>
<td>mg/Ph/l</td>
<td></td>
</tr>
</tbody>
</table>

For complex refineries:

- Phenol: 0.5 mg/l
- Nitrogen: 40 mg-N/l
- Sulphide: + mg-S/l
- Total organic carbon: 200 mg-C/l
- Cr: 0.5 mg Cr/l
- P: 2 mg P/l
- Pb: 0.05 mg Pb/l
- Air (ELV at 3% O₂): SO₂: 1300 mg/Nm³
- NOₓ: 450 mg/Nm³
- H₂S: 10 mg/Nm³
- Dioxins: 0.5 ng TEQ/Nm³

Kjeldahl: 30 mg N/l for complex refineries, no limits if discharged in sewer.

250 mg C/l for complex refineries, no limits if discharged in sewer.
Annexes

<table>
<thead>
<tr>
<th>Media</th>
<th>Regulation</th>
<th>Pollutant</th>
<th>Scope</th>
<th>Limit value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air:</td>
<td>VNp 889/1987</td>
<td>S-emissions</td>
<td>Refineries &lt;3*10^6 t crude/a</td>
<td>12 % of S-content in feed stock</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Refineries &gt;3*10^6 t crude/a</td>
<td>8 % of S-content in feed stock</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VNp 527/1991</td>
<td>NOx</td>
<td>Nat. gas fired boiler P&gt;50 MW</td>
<td>50</td>
<td>ng NOx/MJ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NOx</td>
<td>Oil fired boiler 50&lt;P&lt;150 MW</td>
<td>120</td>
<td>mg NOx/MJ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NOx</td>
<td>Oil fired boiler 150&lt;P&lt;300 MW</td>
<td>80</td>
<td>mg NOx/MJ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NOx</td>
<td>Oil fired boiler P&gt;300 MW</td>
<td>50</td>
<td>mg NOx/MJ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NOx</td>
<td>Oil fired gas turbine P&lt;300 MW</td>
<td>150</td>
<td>mg NOx/MJ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NOx</td>
<td>Oil fired gas turbine P&gt;300 MW</td>
<td>60</td>
<td>mg NOx/MJ</td>
</tr>
<tr>
<td></td>
<td>VNp 453/1992</td>
<td>S-content</td>
<td>Boilers P&gt;300 MW</td>
<td>1</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Boilers 50&lt;P&lt;300 MW</td>
<td>50</td>
<td>mg/m²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Boilers for gaseous fuel</td>
<td>5</td>
<td>mg/m²</td>
</tr>
<tr>
<td></td>
<td>VNp 468/1996</td>
<td>VOC</td>
<td>Petrol storages</td>
<td>0.01</td>
<td>% of throughput</td>
</tr>
<tr>
<td></td>
<td>VNp 142/1997</td>
<td>S-content</td>
<td>Diesel fuel for domestic use</td>
<td>0.05</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Light fuel oil for domestic use</td>
<td>0.2</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>VNp 101/1997</td>
<td>NOx</td>
<td>Burning of waste oil</td>
<td>100</td>
<td>mg/m³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Burning of hazardous wastes</td>
<td>100</td>
<td>mg/m³</td>
</tr>
<tr>
<td></td>
<td>VNp 842/1997</td>
<td>S-content</td>
<td>Burning of hazardous wastes</td>
<td>10</td>
<td>mg/m³</td>
</tr>
</tbody>
</table>

Table 9.6: Summary of emission limit values in Belgium applied to refineries [268, TWG, 2001]

Denmark

Denmark has set SO₂-emission limit values of 1000 mg/Nm³ for residual product fuels, with a maximum of 1 % S in the fuel oil. SO₂ limits for gaseous and LPG fuels have been set at much lower levels (35 mg/Nm³ to 5 mg/Nm³). NOₓ levels have been set at 225 mg/Nm³ for both liquid and gaseous fuels.

Finland

Table 9.7: Summary of environmental legislation and emission limit values in Finland applied to refineries

Note: VNp = Decision of Council of State

France
Air

The maximum allowable SO\textsubscript{2} refinery emission concentration (as bubble) permitted since 2000 is 1700 mg/Nm\textsuperscript{3}.

Water emissions.

According to the different refinery categories, the mass flow limits per tonne of product processed (crude, residues, etc...) are the following:

<table>
<thead>
<tr>
<th>Type of refinery</th>
<th>Mass flow limit (monthly average)</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flow (in m\textsuperscript{3}/t)</td>
<td>0.25</td>
<td>0.65</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Total suspended solids (in g/t)</td>
<td>6</td>
<td>15</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>COD (in g/t)</td>
<td>25</td>
<td>65</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>BOD\textsubscript{5} (in g/t)</td>
<td>6</td>
<td>15</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Total nitrogen (in g/t)</td>
<td>5</td>
<td>12.5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons (in g/t)</td>
<td>1.2</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Phenols (in g/t)</td>
<td>0.06</td>
<td>0.15</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of refinery</th>
<th>Mass flow limit (yearly average)</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flow (in m\textsuperscript{3}/t)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Total suspended solids (in g/t)</td>
<td>5</td>
<td>12.5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>COD (in g/t)</td>
<td>20</td>
<td>50</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>BOD\textsubscript{5} (in g/t)</td>
<td>5</td>
<td>12.5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Total nitrogen (in g/t)</td>
<td>4</td>
<td>10</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons (in g/t)</td>
<td>1</td>
<td>2.5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Phenols (in g/t)</td>
<td>0.05</td>
<td>0.125</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

Notes to the table: These emission limits will apply within 3 years after 2 February 1998.
The water flow is calculated for process water and purging water of the closed-loop cooling system.
(1): refinery with distillations, catalytic reforming and hydro-treatments
(2): (1) + catalytic cracking and/or thermal cracking and/or hydro-cracking
(3): (1) or (2) + steam cracking and/or lubes

Table 9.8: Emission limit values applies to French refineries

French regulatory framework on noise.
French approach: ordinance of the 23rd January 1997
Field: new or modified plants after 01/07/1997

Level of noise not to be exceeded at the limit of the plant
- during the day 70 dBA
- during the night 60 dBA

Consider the additional noise in regulated areas:

<table>
<thead>
<tr>
<th>Level of noise in the regulated areas included the noise generated by the plant</th>
<th>Additional noise limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between 7 h and 22 h except Sundays and days of</td>
<td></td>
</tr>
<tr>
<td>From 35 dBA to 45 dBA</td>
<td>6 dBA</td>
</tr>
<tr>
<td>Greater than 45 dBA</td>
<td>5 dBA</td>
</tr>
<tr>
<td>Between 22 h and 7 h, Sundays and days of</td>
<td></td>
</tr>
<tr>
<td>From 35 dBA to 45 dBA</td>
<td>4 dBA</td>
</tr>
<tr>
<td>Greater than 45 dBA</td>
<td>3 dBA</td>
</tr>
</tbody>
</table>

Distance of 200 m from the plant limit where it cannot be applicable.
Monitoring method: AFNOR NF S 31010
bullet 6 expertise method
bullet 5 control method which need a difference greater than 2 dBA with the reference value to validate the difference.

Former ordinance of the 20 August 1985
Limit concerning additional noise 3 dBA (refineries 5 dBA)

Formula for the noise level requirement at the plant limit: 45dBA + ct (takes into account the different periods of the day) + cz (take into account the type of area)

Different periods of the day (ct):
- day: (+ 0dBA): 7 – 22 h,
- intermediate period: 6 - 7 h and 20 - 22 h (-5 dBA),
- night: 22 – 6 h (-10 dBA)

Cz from 0 to +25 dBA according to the type of area.

Other specific cases linked to impulsive and pure noises

Germany

Important regulations relevant for industrial installations in Germany are laid down in the Federal Immission Control Act [Bundes-Immissionsschutzgesetz – BImSchG], the Federal Water Act [Wasserhaushaltsgesetz – WHG] and the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz – KrW/AbfG]. Germany uses a segregated media permitting system for different environmental media, but the final decision on an application is reached by the assessment of environmental impacts on all media by the local authorities. Also noise requirements are considered in the licensing procedure, whereby Germany aims at favouring pollution prevention. The ‘precautionary principle’ has a legal status which permits the settings of standards. Legal standards are not subject to any negotiation in the licensing process in Germany. The cited regulations are currently amended according to the IPPC Directive.

In compliance with the federal structure of Germany, the implementation of environmental laws and decrees is under the responsibility of the federal states (Bundesländer), which may implement the administrative procedure differently. For new plants, that are regarded as relevant with respect to emissions and releases into the environment, also an environmental impact assessment is required during the licensing procedure (cf. Gesetz über die Umweltverträglichkeitsprüfung [UVPG]).

Table 10.9 gives an overview of the current German legal basis and regulations for environmental protection in German industry alongside the process chain. In the following, the most important acts and regulations are presented.

<table>
<thead>
<tr>
<th>Area</th>
<th>Legal basis</th>
<th>Regulations and ordinances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport</td>
<td>Verkehrsrecht</td>
<td>- Gefahrgutverordnung Straße</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Gefahrgutverordnung Schiene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Gefahrgutverordnung Binnenschifffahrt</td>
</tr>
<tr>
<td>Health and safety at work</td>
<td>Chemikaliengesetz (ChemG)</td>
<td>- Chemikalienverbotsordnung</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Gefahrstoffverordnung</td>
</tr>
<tr>
<td></td>
<td>Gewerbeordnung</td>
<td>- TA Lärm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Arbeitsstättenverordung und -richtlinien</td>
</tr>
<tr>
<td>Emissions into air</td>
<td>Bundes-Immissionsschutzgesetz (BImSchG)</td>
<td>- Bundes-Immissionsschutzverordungen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Bundes-Immissionsschutzverwaltungsvorschriften</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- TA Lärm</td>
</tr>
</tbody>
</table>

Table 10.9
German regulations concerning the air quality

The basic law for air pollution control is the Federal Immission Control Act [Bundes-Immissionsschutzgesetz BImSchG]. The BImSchG is specified by ordinances and the Technical Instructions on Air Quality [TA Luft]. The Federal Immission Control Act and the Technical Instructions on Air Quality are currently being amended according to the IPPC Directive.

Technical Instructions on Air Quality Control (TA Luft):
The Technical Instructions on Air Quality Control (TA Luft) have been set up as general administrative regulations in connection with the §48 BImSchG. The TA Luft further specifies the requirements to be met by installations subject to licensing. Therefore, it prescribes limit values for virtually all air pollutants as well as structural and operational requirements designed to limit fugitive emissions. For the new federal states, the requirements had to be met before 1996, and in special cases by 1999. Table 10.10 shows the limits for main emission control requirements or, if specific regulations for the mineral oil refineries exist, it gives the corresponding more specific requirements laid down in the TA Luft, which are aimed at the avoidance and minimisation of air pollution.

The emitted substances are split into 3 classes (vaporous or gaseous inorganic substances: 4 classes), whereby class I substances are the most toxic and Class III or IV are the least harmful. The emission limit values contained in the TA Luft represent the State of the art for technical measures for reducing emissions (last amended in 1986, currently being amended). These quality values were developed referring to scientific findings and research taking into account toxicological, bioaccumulative and epidemiological aspects. The required concentration limits are given in mass of emitted substances related to the volume of emitted gas under standard conditions (0°C, 1013 mbar) after subtraction of the water vapour content.

<table>
<thead>
<tr>
<th>Emitted-substance (TA Luft section)</th>
<th>Class</th>
<th>Substances</th>
<th>Mass flow threshold [g/h]</th>
<th>Concentration limit [mg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dust</td>
<td></td>
<td></td>
<td>≤500</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;500</td>
<td>≥500</td>
</tr>
<tr>
<td>Inorganic dust</td>
<td>I</td>
<td>sum of substances</td>
<td>1</td>
<td>≥0.2</td>
</tr>
<tr>
<td>Particles</td>
<td>II</td>
<td>(e.g. Hg, Tl)</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>(e.g. Sb, Pb, Cr, Fe, Cu, Mn, Pt, Ru, V, Sn, substances which are strongly suspected to cause cancers)</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>(e.g. Sb, Pb, Cr, Fe, Cu, Mn, Pt, Ru, V, Sn, substances which are strongly suspected to cause cancers)</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>I+II</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I+III, II+III</td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Vaporous or</td>
<td>I</td>
<td>sum of substances</td>
<td>240</td>
<td>4</td>
</tr>
<tr>
<td>gaseous inorganic</td>
<td>II</td>
<td>(e.g. Cl, Cl₂, HCl)</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>Substances</td>
<td>III</td>
<td>(e.g. Cl-compounds as HCl)</td>
<td>300</td>
<td>50</td>
</tr>
</tbody>
</table>
Table 9.10——Emission control requirements laid down in the TA Luft (1986)

<table>
<thead>
<tr>
<th>Inorganic dust particles</th>
<th>Mass concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow (kg/h)</td>
<td>3 kg/h or more</td>
</tr>
</tbody>
</table>

- **Classification**: >0.15 g/m³
- **Total mass flow**: >3 kg/h

Inorganic dust particles of several classes are present, the mass concentration in the emitted gas should not exceed a total of 0.15 g/m³ with a total mass flow of 3 kg/h or more.

- **Technical Instruction on Noise Abatement**
  - The Technical Instruction on Noise Abatement (TA Lärm) sets the limits for noise emissions from the operation of a facility permitted in various areas. Permission for the construction, operation, or altering of a facility is granted only if the emission limits allowed for a specific area are not exceeded and if state-of-the-art noise protection measures are employed.

- **German regulations concerning the water quality**
  - The legal framework for water management is the Federal Water Act (Wasserhaushaltsgesetz—WHG). The WHG applies to waste water generated by various industrial processes. The use of surface, coastal, and groundwater resources requires the approval of the competent authority. Discharges into water are regulated in the Waste Water Ordinance including its Annexes (Abwasserverordnung—AbwV) which is based on art. 7(a) of the Federal Water Act. Here, minimum requirements concerning waste water treatment, requirements concerning techniques of analysis and monitoring as well as limits for the content of specific substances are laid down for different industrial sectors.

- **Issued by the Federal Government in consent with the Federal States (Länder)**, these minimum requirements are binding for the authorities responsible for licensing and governmental control of the discharges. Depending on the local conditions, even more stringent requirements can be established. The minimum requirements are based on the ‘emission principle’ and the precautionary principle, i.e., application of stringent, technically derived emission standards irrespective of the loading reserves of the receiving water bodies resources or the potential effects of the various substances discharged. Additionally, the Federal Ministry of Environment...
Annexes

publishes explanations and comments on the Waste Water Ordinance. Refining of petroleum is dealt with in Annex 45 of this regulation. Table 10.11 gives the main restrictions established in Annex 45 of the AbwV.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit value(a) [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol index after distillation and dye extraction</td>
<td>0.15**</td>
</tr>
<tr>
<td>Total hydrocarbons</td>
<td>2</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>4.5</td>
</tr>
<tr>
<td>Cyanide, easily released</td>
<td>0.1 **</td>
</tr>
<tr>
<td>Sulphide sulphur and mercaptan sulphur</td>
<td>0.6 **</td>
</tr>
<tr>
<td>AOX</td>
<td>0.1 **</td>
</tr>
<tr>
<td>5-day biochemical oxygen demand</td>
<td>25</td>
</tr>
<tr>
<td>COD</td>
<td>80</td>
</tr>
<tr>
<td>Total nitrogen as the sum of ammonia, nitrite and nitrate nitrogen</td>
<td>40</td>
</tr>
</tbody>
</table>

*) Qualified random sample or 2 hours composite sample
**) Requirements apply to the waste water prior to blending with other waste water
Source: AbwV, Annex 45 “Petroleum Refining”

Table 10.11: Limit values for discharges into water for petroleum refining plants

The required loads shall be production-specific loads in relation to the production capacity on which the water discharge licence is based. This should be determined by a qualified random sample or a 2-hour composite sample.

A qualified random sample should refer to a composite sample of at least five random samples taken over a maximum period of two hours at intervals of no less than two minutes, which are then blended. A composite sample should refer to a sample which is taken continuously over a given period, or a sample consisting of several samples taken either continuously or continuously over a given period and then blended. A random sample should refer to a single sample taken from a waste water flow.

Waste water from cooling systems for the indirect cooling of industrial processes is excluded from this regulation. Indirect cooling water is subject to the provisions laid down in Annex 31, AbwV. Table 10.12 gives the relevant requirements for discharges from cooling circuits in Annex 31. If the stated values are not reached, approval for the discharge of waste water will be denied.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum Requirements(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>40 mg/l</td>
</tr>
<tr>
<td>Phosphor compounds, given as P</td>
<td>3 mg/l</td>
</tr>
<tr>
<td>Zinc</td>
<td>4 mg/l</td>
</tr>
<tr>
<td>AOX</td>
<td>0.15 mg/l</td>
</tr>
<tr>
<td>Available residual chlorine</td>
<td>0.3 mg/l</td>
</tr>
<tr>
<td>Chromium compounds</td>
<td>must not be contained</td>
</tr>
<tr>
<td>Mercury compounds</td>
<td>must not be contained</td>
</tr>
<tr>
<td>Nitrite</td>
<td>must not be contained</td>
</tr>
<tr>
<td>Metal organic Compounds (Metal-Carbon-Compound)</td>
<td>must not be contained</td>
</tr>
</tbody>
</table>

*) Qualified random sample or 2 hours composite sample

Source: Annex 31, Abwasserordnung

Table 9.12: Requirements for discharges from cooling circuits of industrial processes

The WHG is complemented by the waste water charges act [Abwasserabgabengesetz—AbwAG]. The charges are related to the mass and possible hazard of the discharged waste water according to Table 10.13. For the discharge of sewage, that exceeds the mentioned threshold values for concentrations or annual loads, the discharging party has to pay a fee related to the given units of measurement.
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<table>
<thead>
<tr>
<th>Hazardous Substances</th>
<th>Units of measurement (relating to a unit of hazard)</th>
<th>Threshold values Concentrations – Annual freights</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical oxygen demand (given as COD)</td>
<td>50 kg Oxygen</td>
<td>20 mg/l</td>
</tr>
<tr>
<td>Phosphor</td>
<td>3 kg</td>
<td>0.1 mg/l</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>25 kg</td>
<td>5 mg/l</td>
</tr>
<tr>
<td>Organic Halogen compounds as AOX</td>
<td>2 kg Halogen, calculated as Cl</td>
<td>100 μg/l</td>
</tr>
<tr>
<td>Mercury and compounds</td>
<td>20 g</td>
<td>1 μg/l</td>
</tr>
<tr>
<td>Cadmium and compounds</td>
<td>100 g</td>
<td>5 μg/l</td>
</tr>
<tr>
<td>Chromium and compounds</td>
<td>500 g</td>
<td>50 μg/l</td>
</tr>
<tr>
<td>Nickel and compounds</td>
<td>500 g</td>
<td>50 μg/l</td>
</tr>
<tr>
<td>Lead and compounds</td>
<td>500 g</td>
<td>50 μg/l</td>
</tr>
<tr>
<td>Copper and compounds</td>
<td>1000 g</td>
<td>100 μg/l</td>
</tr>
<tr>
<td>Fish toxicity</td>
<td>3,000 m³ discharges divided by TF</td>
<td>TF = 2 (dilution factor for non-lethal quantity for fish from the discharge)</td>
</tr>
</tbody>
</table>

Source: Abwasserabgabegesetz

Table 9.13: Thresholds according to the water charges act

German regulations concerning the waste management and disposal of hazardous materials. Regulations concerning the waste management and disposal of hazardous materials are laid down in the Federal Recycling and Waste Management Act [Kreislaufwirtschafts- und Abfallgesetz – KrW-/AbfG] and the Federal Immission Control Act [BImSchG]. According to the BImSchG, an operator of a waste generating installation which is subject to licensing, is obliged to avoid waste production or to make sure that the waste is environmentally soundly recovered. If that is technically or economically not reasonable, the waste has to be disposed of without any harmful effects. The federal States’ working group on immission control (Länderausschuss für Immissionsschutz, LAI) has published examplary administrative regulations for particular industrial sectors containing measures for avoidance and recovery of wastes which are considered as technically and economically reasonable.

The KrW/AbfG states that installations generating more than 2 tonnes of hazardous waste or more than 2000 tonnes of non-hazardous waste (per waste key), must produce a waste management concept and yearly waste balances.

References to the German Legislation

- Abwasserabgabengesetz – AbwAG: Gesetz über Abgaben für das Einleiten von Abwasser in Gewässer, 3.11.1994
- Abwasserverordnung – AbwV: Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer und zur Anpassung der Anlage des Abwasserabgabegesetzes, 09.02.1999; last review 20.02.2001
- Bundes Immissionsschutzgesetz (BImSchG): Gesetz zum Schutz vor schädlichen Umwelteinwirkungen durch Luftverunreinigungen, Geräusche, Erschütterungen und ähnliche Vorgänge, 14.05.1990, last amendment 19.07.1995
- UVPG: Gesetz über die Umweltverträglichkeitsprüfung – UVPG, 12.2.1990, last amendment 23.11.1994

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- *Wasserhaushaltsgesetz* — WHG: Gesetz zur Ordnung des Wasserhaushalts — WHG, 12.11.1996

Ireland

<table>
<thead>
<tr>
<th>Substance</th>
<th>Petroleum Refining</th>
<th>Gas Refining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulphide</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Particulates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Processing</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>- Materials Handling</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>VOCs (as Total Carbon)</td>
<td>Control by Load Minimisation</td>
<td>Control by Load Minimisation</td>
</tr>
<tr>
<td>(excluding particulates)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td>Control by Load Minimisation</td>
<td>350</td>
</tr>
<tr>
<td>SO₂</td>
<td>Control by Load Minimisation</td>
<td>1700</td>
</tr>
<tr>
<td>- Liquid refinery fuel</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>- Vaporised LPG</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>- Other gaseous fuel</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note 1: Achievement of ELV concentrations by the introduction of dilution air is not permitted.

Notes to table:
1. The toxicity of the effluent shall be determined on an appropriate aquatic species. The number of Toxicity Units (TU) = 100/96 hr LC50 in % v/v so that higher TU values reflect greater levels of toxicity. For each TU at least 20 dilutions of the effluent volume must be available in the receiving system.
2. No substance shall be discharged in a manner which, or at a concentration which, following initial dilution causes tainting of fish or shellfish, interferes with normal patterns of fish migration or which accumulates in sediments or biological issues to the detriment of fish, wildlife or their predators.
3. Consent conditions for these parameters for discharge to municipal treatment plants can be established with the Licensing Authority, and different values may apply.

Table 9.14: Emission limit values for air emissions applied in Ireland

<table>
<thead>
<tr>
<th>Constituent group or parameter</th>
<th>Limit value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6-9</td>
</tr>
<tr>
<td>Suspended Solids (mg/l)</td>
<td>30</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>100</td>
</tr>
<tr>
<td>Number of Toxicity Units</td>
<td>5</td>
</tr>
<tr>
<td>EC List 1</td>
<td>As per 76/464/EC and amendments</td>
</tr>
<tr>
<td>Fish Tainting</td>
<td>No Tainting</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>20</td>
</tr>
<tr>
<td>Total Nitrogen (mg/l as N)‡‡</td>
<td>10</td>
</tr>
<tr>
<td>Total Phosphorus (mg/l as P)‡‡</td>
<td>3</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>5</td>
</tr>
</tbody>
</table>

Notes to the table:
These values apply prior to any dilution with e.g. uncontaminated stormwaters or cooling waters. Where appropriate, saline waters to be discharged to sea/lower estuary in compliance with the above standards.
‡‡All values refer to daily averages, except where otherwise stated to the contrary, and except for pH which refers to continuous values.
‡‡Applicable to waters subject to eutrophication. One or both parameters may be limiting, depending on the receiving system.

Table 9.15: Emission limit values for discharges to water applied in Ireland

Italy

The maximum allowable SO₂ refinery emission concentration (as bubble) permitted in 2000 will be 1700 mg/Nm³.
Norway

Emission standards are not generally applied in Norway. The emission limits for the refineries are set according to each case. Norway has introduced a special tax duty to minimise emissions of CO\textsubscript{2} and SO\textsubscript{2}. Heavy fuel oil with more than 1.0 % sulphur is prohibited in the twelve southern and southwestern counties of Norway. In the northern parts of Norway heavy fuel oil is allowed with a maximum 2.5 % sulphur. But due to high sulphur taxes, heavy fuel oil with up to 2.5 % sulphur content is more expensive than the 1.0 % oil, and is therefore hardly used. Noise is regulated to a limit of 45 dB(A).

<table>
<thead>
<tr>
<th>Media</th>
<th>Pollutant</th>
<th>Emission Limit Values</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Sludge</td>
<td>-</td>
<td></td>
<td>Limit according to regulation for landfilling, hazardous waste and groundwater</td>
</tr>
<tr>
<td></td>
<td>Waste</td>
<td>-</td>
<td></td>
<td>Limit according to regulation for landfilling, hazardous waste and groundwater</td>
</tr>
<tr>
<td>Water</td>
<td>pH</td>
<td>6-9</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H\textsubscript{2}S</td>
<td>0.5–1</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oil</td>
<td>5</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>1</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NH\textsubscript{4}+</td>
<td>10–15</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CN (total)</td>
<td>1</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Suspended solids</td>
<td>-</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>COD\textsubscript{1)}</td>
<td>-</td>
<td>tonnes/year</td>
<td>Not regulated but reported in the annual report</td>
</tr>
<tr>
<td></td>
<td>TOC\textsubscript{1)}</td>
<td>-</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metals\textsubscript{1)}</td>
<td>-</td>
<td>kg/day</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P (total)\textsubscript{1)}</td>
<td>-</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>H\textsubscript{2}S</td>
<td>15</td>
<td>mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO\textsubscript{2}</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO\textsubscript{2}</td>
<td>650–1350</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SO\textsubscript{2}</td>
<td>1000–2000</td>
<td>kg/h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO\textsubscript{x}</td>
<td>2150</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CN (total) (cracker)</td>
<td>5</td>
<td>mg/Nm\textsuperscript{3}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particles (cracker)</td>
<td>50</td>
<td>mg/Nm\textsuperscript{3}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particles (cracker)</td>
<td>25</td>
<td>mg/Nm\textsuperscript{3}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Particles (calciner unit)</td>
<td>30</td>
<td>mg/Nm\textsuperscript{3}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N\textsubscript{2}O\textsuperscript{2)}</td>
<td>-</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NMVOC\textsuperscript{2)}</td>
<td>-</td>
<td>tonnes/year</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methane\textsuperscript{2)}</td>
<td>-</td>
<td>tonnes/year</td>
<td></td>
</tr>
</tbody>
</table>

The permit values vary from refinery to refinery due to design, age and local factors. The permits are planned to be under revision in 2001 and 2002.

Sweden

Air

The maximum allowable SO\textsubscript{2} refinery emission concentrations (as bubble) permitted in 2000 will be 800 mg/Nm\textsuperscript{3}. Use of high sulphur fuels (>0.5 %) is prohibited throughout the country. Sulphur recovery must be in excess of 99 % including the flaring of residual tail gas. NO\textsubscript{x} and particulates must be reduced to the minimum feasible level.

The total permitted release levels for the Scanraff Refinery are 2000 t/yr SO\textsubscript{2} and 1000 t/yr NO\textsubscript{x}. The absolute limit of particulates from the FCC unit is 75 mg/Nm\textsuperscript{3} (the crude capacity of the refinery is 10 Mt/yr).
The Netherlands

A characteristic of the Dutch regulations and permitting is 'self-regulation with boundaries'. This characteristic stems from a broad support for achieving consensus, and includes as well the environmental policy, both in the way it was brought into existence and in the way it has been implemented.

Air emissions

<table>
<thead>
<tr>
<th>Regulation</th>
<th>Affecting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion Plant Emission Limits Decree (BEES)</td>
<td>SO₂, NOₓ, particulates</td>
</tr>
<tr>
<td>Emission Guidelines for Air (NeR)</td>
<td>Sulphur Recovery Plants</td>
</tr>
<tr>
<td>Hydrocarbons 2000 programme (KWS2000)</td>
<td>VOC</td>
</tr>
</tbody>
</table>

The National Environmental Policy Plan (NEPP, 1997) states as a policy objective that by 2010 the refineries will be gas-fired, or that installations that are still oil-fired will be equipped with FGD, SCR and ESP. The KWS2000 measures comprise preventive maintenance and spills and leaks abatement. Furthermore, vapour recovery for inland barge loading operations of gasoline and double mechanical seals on floating roof tanks are specified as well as improved sealings of pumps, compressors, valves and flanges and covering of open basins. Measures for vapour recovery are also applicable for crude loading and unloading.

Table 9.16 summaries the emission limit values applied to different air contaminants.

<table>
<thead>
<tr>
<th></th>
<th>Load per year (year when the value is applicable)</th>
<th>Emission limit value or performance (New)</th>
<th>Emission limit value or performance (Existing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>53 ktonne</td>
<td>1500 mg SO₂/Nm³ (2000)</td>
<td>1000 mg SO₂/Nm³ (2000)</td>
</tr>
<tr>
<td></td>
<td>36 ktonne (2000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18 ktonne (2010)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur Recovery Plants</td>
<td>99.8 % recovery</td>
<td></td>
<td>99.8 % recovery</td>
</tr>
<tr>
<td>NOₓ (1)</td>
<td>15 ktonne (1997)</td>
<td>NG: 80 mg/Nm³</td>
<td>NG: 150–500 mg/Nm³</td>
</tr>
<tr>
<td></td>
<td>12 ktonne (2000)</td>
<td></td>
<td>LF: 400–700 mg/Nm³</td>
</tr>
<tr>
<td></td>
<td>5–7 ktonne (2010)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulates</td>
<td>5 ktonne (1997)</td>
<td>Combustion plants 50 mg/Nm³</td>
<td>Catcrackers with ESP: 50 mg/Nm³</td>
</tr>
<tr>
<td></td>
<td>0.5–1 ktonne (2010)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC</td>
<td>8.8 ktonne in 2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.2 ktonne in 2010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>11000 ktonne (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NG: Natural Gas

LF: Liquid fuels

(1) Correction factors are used for the determination of the allowed emission level in relation to the quality of the fuel, the extent of air preheat and the prevailing bridge wall temperature.

(2) Emission reduction target for total Dutch economy for year 2010, not specifying individual sectors

Table 9.16: Dutch legislation, regulations and targets

Effluents (emissions to water)

Laws affecting water emissions are: The Surface Water Protection Act (Wvo), Dutch National Environmental Policy Plans (NEPP, NEPP 3), the Third and Fourth Document on Water Management, the Rhine Action Plan/North Sea Action Plan (RAP/NAP) and the ER-heavy metals and blacklist compounds (benzene, toluene, ethylbenzene, xylenes, PAH and heavy metals as Hg and Cd). Limits will be set for other compounds as well, such as nitrogen (total N), phenol, cyanide, sulphides and overall parameters such as COD, BOD and TOC. The PARCOM
recommendations ratified by the Netherlands provide guidance with respect to refinery oil discharges:

Permits normally impose the following obligations on refineries:

- Cooling waters should be separated from other waters and kept uncontaminated by oil
- Storm waters from polluted plant areas should be collected and connected to treatment plants
- Waste waters should be subjected to biological or equally effective treatment.
- Permit values vary from location to location due to differences in design, age and other local factors. The authority aims at uniformity for future permit revisions. A number of permit parameters and typical compliance values for Dutch refineries are (1997): Oil 140 t/yr, Benzene 9 t/yr, Phenol 5 t/yr and N-total 540 t/yr. The parameters and compliance values refer to typical refinery effluent composition (ranges), having passed primary effluent treatment facilities but prior to secondary and/or tertiary treatments.

Waste
Hazardous waste in refineries mainly involves the management of oily sludges, spent catalysts and spent caustic. For these waste categories increased use is made of third-party waste contractors for off-site recovery or disposal. The Environmental Management Act (Wm) governs legal disposal and two EU Directives cover the classification, packing and labelling of hazardous substances. As regards the export of hazardous waste a similar procedure exists as laid down in the Basle Convention on the Control of Transboundary Movements of Hazardous Waste and their Disposal.

Soil and groundwater
Contaminated soil and polluted groundwater are relevant environmental issues for refineries. The Dutch Soil Protection Act (Wbb) stipulates no risk to people and the environment, multifunctionality of the soil, the duty of care, prevention of migration of pollutants beyond location boundaries (isolate, manage and control) in case of historical soil pollution. Soil and groundwater cleaning is obligatory if the so-called intervention values, as defined per component and for each soil type, are exceeded and if the extent of the pollution indicates the seriousness of the pollution. The urgency of the clean-up is determined by the migration rate and the risk to the threatened objects in the actual situation. Contaminated soil is an increasing problem for refineries. In all refineries measures have been taken at least to make an inventory of the soil and groundwater pollution and, where needed, measures are taken to prevent migration. In one refinery preventive measures for soil pollution had been included right from the design stage.

Noise
The Netherlands has an integrated policy for noise, and aims for a proper inventory of noise sources and a planned abatement programme. Germany, Switzerland, Austria, France and the Scandinavian countries are developing similar policies on noise.

Nowadays noise level contour values and monitoring obligations are included in permit requirements of the refineries. Typical for industrial noise requirements in urban areas in most countries are maximum allowable limits between 55 and 73 dB(A) during daytime and 45-66 dB(A) during the night.

United Kingdom
The UK does not have standard emission limit values for refineries, but their guidance notes provide expected BAT levels for new plant units. Existing unit operations should meet BATNEEC standards (Best Available Techniques Not Entailing Excessive Cost).
9.1.3 Non-EU+ legislation and emission limit values

Japan
There are three regulation levels: the State, the Regional Prefecture and the municipality. Japanese refineries are forced to use as liquid fuel an industrial gas oil (so-called A-fuel) containing less than 0.1 % S.

State regulations on NO\textsubscript{x} are: Refinery furnaces, 100 ppm; boilers, 150 ppm; hydrogen production unit, 150 ppm; and FCC, 250 ppm. Municipality emission limit value for NO\textsubscript{x} is 85 Nm\textsuperscript{3}/h (equal to 1396 t/yr) [248, Ademe, 2001]

USA

Air
The US Environmental Protection Agency has set a limit for particulate matter in the FCC generator exhaust gas of 1.0 kg/1000 kg of coke burnt off in the catalyst regenerator (equates approximately to 75 mg/Nm\textsuperscript{3}). The coke-burn-off rate is determined from the volumetric flow rate of regenerator exhaust gas and the content of CO\textsubscript{2}, CO and O\textsubscript{2}. The SO\textsubscript{2} emission limit for New-Source Performance Standards is 700 mg/Nm\textsuperscript{3}.

Water
Strict limits apply to toxic and conventional pollutants for waste water, BOD, COD, TOC, ammonia, sulphides and phenolics.

World Bank
The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance; any deviations from these levels must be described in the World Bank Group project documentation. The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable. All the maximum levels should be achieved for at least 95 % of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. [101, World Bank, 1998]

Air Emissions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum value (mg/Nm\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulate matter (PM)</td>
<td>50</td>
</tr>
<tr>
<td>Nitrogen oxide (NO\textsubscript{x}) (as NO\textsubscript{2})</td>
<td>460</td>
</tr>
<tr>
<td>Sulphur oxide (SO\textsubscript{x}) (as SO\textsubscript{2})</td>
<td>150 for sulphur recovery units and 500 for other units</td>
</tr>
<tr>
<td>Nickel and vanadium (combined)</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>15</td>
</tr>
</tbody>
</table>

* Excluding NO\textsubscript{x} emissions from catalytic units.
Annexes

Liquid effluents

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum-value-milligrams-per-litre (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6–9</td>
</tr>
<tr>
<td>BOD₅</td>
<td>30</td>
</tr>
<tr>
<td>COD</td>
<td>150</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>30</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>40</td>
</tr>
<tr>
<td>Chromium (hexavalent)</td>
<td>0.1</td>
</tr>
<tr>
<td>Chromium (total)</td>
<td>0.5</td>
</tr>
<tr>
<td>Lead</td>
<td>0.1</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.05</td>
</tr>
<tr>
<td>Sulphide</td>
<td>1</td>
</tr>
<tr>
<td>Nitrogen (total)</td>
<td>10</td>
</tr>
<tr>
<td>AT (ºC)</td>
<td>Less than or equal to 3</td>
</tr>
</tbody>
</table>

1. The maximum effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include hydrogenation.
2. The effluent should result in a temperature increase of no more than 3 ºC at the edge of the zone where initial mixing and dilution takes place. Where the zone is not defined, use 100 meters from the point of discharge provided there are no sensitive ecosystems within this range.

Note: Effluent requirements are for direct discharge to surface waters. Discharge to an off-site waste water treatment plant should meet applicable pretreatment requirements.

Solid Wastes and sludges

Wherever possible, generation of sludges should be minimised to 0.3 kg/tonne of crude processed with a maximum of 0.5 kg/tonne of crude processed. Sludges must be treated and stabilised to reduce concentrations of toxics (such as benzene and lead) in leachate to acceptable levels (such as levels below 0.05 mg/kg).

Ambient Noise

Noise abatement measures should achieve either the following levels or a maximum increase in background levels of 3 dB(A). Measurements are to be taken at noise receptors located outside the project property boundary.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Maximum dB(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residential; institutional; educational</td>
<td>Lₚₜ 55</td>
</tr>
<tr>
<td>Industrial; commercial</td>
<td>Lₚₜ(24) 70</td>
</tr>
</tbody>
</table>

The emission requirements given here can be consistently achieved by well designed, well operated and well maintained pollution control systems.
9.2 Annex II. Refinery configurations

Worldwide there are in total approximately 700 refineries. Every year on average between four and six brand-new refineries come on-stream, mainly outside Europe (China, India). On the other hand the origin of some of the oldest refineries still in operation dates back to the end of last century. Many of these refineries have been extended and modernised since. Basically there are about 25 typical refinery processes (excluding treatment) used in the refinery industry. The simplest type, the so-called hydroskimming refinery, comprises a minimum of five processing units. Some large and complex refineries can comprise up to fifteen different processing units or more.

In this section four of the most common refinery schemes or configurations will be discussed in detail. The classification of refineries into these configurations is slightly arbitrary. Other approaches do exist, but the main purpose is to illustrate the great diversity of refinery types in existence.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Units included</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydroskimming (Base Scheme) + Isomerisation Unit</td>
</tr>
<tr>
<td>2</td>
<td>Base Scheme + High Vacuum Unit + Fluid Cracking Unit + MTBE Unit + Alkylation Unit + Visbreaker</td>
</tr>
<tr>
<td>3</td>
<td>Base Scheme + High Vacuum Unit + Hydrocracker Unit + Isomerisation Unit (+ Delayed Coker Unit)</td>
</tr>
<tr>
<td>4</td>
<td>Large complex refinery comprising Scheme 2 + Hydrocracker (+ Hydrogen Residue Cracking unit + IGCC + Petrochemical feedstock production + Flexicoker)</td>
</tr>
</tbody>
</table>

The overall block flow diagrams of the above four configurations are shown in Figure 9.1 to Figure 9.4.

The first diagram is the aforementioned ‘Hydroskimming’ refinery including an Isomerisation Unit. Such a refinery merely produces fuels such as gasoline, kerosene (jet fuel), middle distillates (diesel and light heating oil) and fuel oil, in a ratio determined by the crude oil composition. By adding a Vacuum Distillation Unit and conversion units the atmospheric residue from the Crude Distillation Unit can be converted to lower boiling fuels with higher product values. Two schemes will be discussed, to cover the most commonly used conversion processes, i.e. Fluid Catalytic Cracking and Hydrocracking. The Fluid Cat cracker (FCC) configuration (no. 2) may include on MTBE unit and an Alkylation unit to increase the production and to improve the quality of the gasoline. A Thermal Cracker or Visbreaker unit is often also included in this scheme to reduce the quantity of the heavy fuel oil. The Hydrocracker configuration (no.3) may include a Delayed Coker unit to reduce heavy fuel production and to maximise light fuels production. The last configuration included in this overview is a large, very complex refinery. Besides a Hydrocracker and an FCC unit, this refinery scheme includes units for the conversion of the vacuum residue, a Residue Hydroconversion unit and an Integrated Gasification Combined Cycle Unit.

The complexity of the above 4 configurations (Simple, Complex catcracking, Complex hydrocracking, and Very Complex) can be quantified and various approaches prevail in the Industry. One approach is to express each processing unit in its so-called ‘equivalent distillation capacity’ (EDC), and calculate the sum of these EDCs as a total refinery EDC (the crude distillation unit has an EDC of 1 by definition). The complexity is than the sum of EDCs.

Another approach is to express the conversion (of residual material into distillates) of each conversion unit into its ‘catcracking equivalency’, and then to define the refinery complexity as the sum of all the catcracking equivalencies. In comparing refineries, both the configuration (which units are in) and the complexity (what is the capacity of these units) are important to consider.
Annexes

Energy requirements will generally increase from configuration 1 to 4 and with complexity. Similar generalisations can be made regarding e.g. process water requirements, sulphur production (at same sulphur intake) etc., but qualifications often need to be made. In the schemes that represent the configurations in the following pages, processing units are abbreviated; for more details on these process units, see the Glossary.

9.2.1 Configuration 1: hydroskimming + isomerisation unit

This is the simplest type of refinery, producing fuels by straightforward operations (see Figure 9.1). This type of refinery has a very rigid product distribution pattern; the produced fuels are almost entirely fixed by the type of crude being processed. The production cannot be greatly influenced by changing the operating modes of the various processing units.

Many of the Hydroskimming refineries were built in the fifties and sixties when the demand for all fuels increased significantly, the cost of crude was relatively low and the demand for heavy fuel oil was relatively high. In the seventies and eighties the majority of the Hydroskimming refineries were expanded to include a cracking complex, but quite a lot of Hydroskimming refineries dating from that period are still in operation. In the Crude Oil Distillation Unit the crude oil is fractionated into straight-run naphtha overhead product, kerosene, gas oil side-stream products and atmospheric residue product from the bottom of the column. The straight-run unstabilised naphtha is passed to the Naphtha Hydrotreating Unit to make it suitable for Catalytic Reforming. The hydrotreated naphtha stream is split into a light and a heavy naphtha fraction.

Figure 9.1: Scheme 1:Hydroskimming and isomerisation unit
In the past part of the light naphtha fraction was used as mogas (motor gasoline) blend component, and the balance was sold as feedstock to Naphtha Crackers. More recently, as a result of the lead (TEL) phase-out programme, many Isomerisation Units are included in the Hydroskimming refineries to isomerise the light naphtha stream. The isomerate produced has a roughly 20-25 higher octane number than its feed and compensates for the loss of octane resulting from the lead phase-out. This avoids the complete light naphtha stream being sold as low value feedstock to Naphtha Crackers. The heavy naphtha fraction from the Naphtha Hydrotreater is upgraded in the Catalytic Reformer to a high-octane gasoline-blending component. The hydrogen from the Catalytic Reformer is used to desulphurise the gasoil and naphtha. Normally two grades of gasoline are produced in a refinery, regular and premium gasoline. These grades of gasoline are produced by blending different ratios of isomerate, reformate and butane. Saturated light hydrocarbons from the CDU Naphtha Hydrotreater, Isomerisation Unit and Catalytic Reformer Unit are sent to the Gas Plant. Propane from the Gas Plant is either sold directly as propane product or blended with butane to be sold as LPG. A proportion of the butanes produced in the Gas Plant is used as blend stock for the mogas pool, the remainder of the butanes are either blended with propane to be sold as LPG or directly sold as butane product. The components lighter than propane are sent to the refinery fuel gas system. Straight-run kerosene is often hydrotreated in the Kero Hydrotreating Unit (or kero HDS) and run down as jet fuel. Normally a portion of the hydrotreated kerosene is used as blending component for the automotive diesel oil pool.

Straight-run gas oil is hydrotreated in the Gas Oil Hydrotreating Unit to reduce its sulphur content. Automotive diesel oil is produced by blending desulphurised kerosene with desulphurised gas oil. Heating oil and marine diesel oil (MDO) are produced by blending desulphurised gasoil with straight-run gasoil. Both products have higher maximum allowable sulphur contents than diesel oil. Heavy fuel oil is produced from atmospheric residue with adjustment for viscosity and sulphur content by addition of desulphurised gas oil. In some cases the atmospheric residue is thermally cracked. This is not indicated in the configuration scheme. The sour off-gases from the Naphtha Hydrotreater, the Kerosene and Gas Oil Hydrotreating units (or Gasoil HDS) are treated in the Amine Treating Unit to remove H2S and other sour components present, prior to being sent to the refinery fuel gas system. The sour LPG stream from the Naphtha Hydrotreater is also treated in the Amine Unit to reduce its sulphur content before combining with the sweet LPG stream from the Catalytic Reformers. Sour waste water from all process units is stripped, prior to utilisation as wash water in the Desalter and final purification in Effluent Water Treating facilities. The sour off-gas from the Sour Water Stripper is combined with the H2S rich-off-gas from the Amine Unit and sent to a Sulphur Recovery Unit (SRU), where the H2S is converted to elemental sulphur, and a nearly sulphur-free off-gas is vented to the atmosphere.

### 9.2.2 Configuration 2: cat cracker configuration

Scheme 2 is a configuration whereby the Hydroskimming refinery is extended with a High Vacuum Unit (HVU), a Fluid Catalytic Cracking Unit (FCC unit) and a Visbreaker Unit (VBU). In this refinery configuration a considerable part of the atmospheric residue is converted into lighter fuel components (see Figure 9.2.). As a result the production of residual fuel oil and/or the export of atmospheric residue is considerably reduced. FCC units are specifically designed to increase the production of gasoline. Depending on the refinery market and strategy, a significant quantity of kerosene can also be produced, when the heavier fraction of the cocracked naphtha is separated and hydrotreated along with the straight-run kerosene product. The overall yield of middle distillates is also increased due to the production of ‘light cycle oil’.
Many Cat cracker refineries in Europe include a Visbreaker Unit to reduce the heavy fuel oil production. If no VBU is applied, significant quantities of high value gasoil components will have to be blended to the vacuum residue product, mainly to meet the viscosity specifications of heavy fuel oil. The VBU converts the vacuum residue into a residue which has a much lower viscosity and also produces some naphtha and gas. This type of refinery has a flexible product distribution pattern. The fuel slate can be significantly influenced by changing the operating modes of the various processing units and by the blending of products. This type of refinery configuration is predominant in Europe. Most of these FCC refineries were built in the fifties and sixties as a simple Hydroskimming refinery. In the seventies and eighties, a Cat cracker complex was added to these refineries.

9.2.3 Configuration 3: hydrocracker configuration

Scheme 3 is a Hydroskimming refinery expanded with an HVU, Hydrocracker Unit (HCU) and e.g. a Delayed Coker Unit (DCU, see Figure 9.3.). In this configuration an even larger part of the atmospheric residue is converted into lighter fuel components together with reduced production of residual fuel oil. The addition of a Coker allows this refinery to eliminate the production of residual fuel oil completely. HCU units are specifically used to maximise the production of gasoline and middle distillates. A limited number of Hydrocracker refineries in Europe include a Delayed Coker Unit (DCU) to reduce heavy fuel production and maximise light fuels production. The DCU converts heavy residues in lighter hydrocarbon fractions and petroleum coke. Dependent on the quality, coke is used in the cement and steel or in the aluminium industry. The hydrogen necessary for the HCU is supplied by a Hydrogen Plant. A Catalytic Reformer does not normally produce enough hydrogen for the HCU. Alternatively, the supplemental hydrogen requirement can be provided via partial oxidation of heavy hydrocarbons followed by hydrogen separation.
Figure 9.3: Scheme 3: Hydrocracker configuration

This type of refinery has a higher degree of flexibility with respect to either maximum gasoline or maximum middle distillate production, whereas a FCC configuration is primarily focused on increased gasoline production. About 15% of the existing refinery complexes in Europe have already been extended with a Hydrocracker. It should be noted that such extensions require a relatively high capital investment and high energy consumption compared to the installation of a Cat cracker.

9.2.4 Configuration 4: complex refinery with hydroconversion and IGCC

Scheme 4 is a refinery with a Hydrocracker and additional ‘deep conversion’. With a Residue Hydrocracker and/or a Gasification Unit (IGCC), so that even more conversion capacity for heavier feedstocks is introduced (see Figure 9.4). This is an example of a large complex refinery, and it includes some options to produce high value petrochemical feedstocks. This extended range of heavy residue conversion techniques can in principle eliminate the need for mixing heavy residue to the fuel oil pool or can process more heavy crude oils. The Residue Hydrocracker, i.e. Hycon, H-oil Unit or other types of Residue Hydrocrackers, converts vacuum residues to high-value transportation fuels e.g. gasolines, kerosene and diesel. The addition of a Residue Hydrocracker to a refinery provides considerable flexibility and increases production of gasoline and middle distillate fuels at the expense of fuel oil. The IGCC converts the visbreaker residue to power, steam, hydrogen, and some waste streams. The main advantage of this arrangement is the production of hydrogen by use of low-value vacuum residue instead of the more valuable light naphtha, other light hydrocarbon streams or natural gas. Moreover, the fuel oil production is reduced and the production of LPG and diesel fuels is increased.
Figure 9.4: Scheme 4: Complex refinery with hydroconversion and IGCC

The visbroken residue is sent to the IGCC where it is converted into syngas (H2/CO). The produced hydrogen can partly be used in the Hydrocracker and the Residue Hydrocracker. Remaining syngas may be combusted in a gas turbine followed by a steam turbine for electricity production and a boiler for steam production. This can be an energy efficient alternative to the classic heavy fuel-fired boilers. Waste streams from the IGCC are slag and soot recovered from the soot rework unit. The quantity and quality of the soot depends on the visbroken residue feed quality and ultimately on the crude oil processed.
9.3 Annex III. Refinery feedstock, intermediates and products

Note for the TWG: Please advise on what to do with this Annex
Move relevant part to Chapter 1 or 2
This section contains a brief explanation of the chemical and physical properties of feedstock, intermediates and products available within a refinery. Because some of the terms may vary from country to country, this annex gives a short description of how these names are used within this document. Moreover this annex gives a short overview for non expert readers.

9.3.1 Crude oil

Crude oil is a mixture of hydrocarbon compounds (95 - 99 % w/w) of different chemical composition and molecular structures with some impurities. Most of these impurities, such as sulphur, nitrogen, vanadium and nickel are chemically bound to the hydrocarbon structures. Others, such as sand/clay, water and water-soluble salts of zinc, chromium and sodium are present as inorganic material.

The hydrocarbons in crude oil are a mixture of three chemical groups: paraffins (straight and branched chains are called normal- and iso-paraffins), naphthenes (saturated rings or cycloparaffins) and aromatics (one or more unsaturated rings). The most used rough distinction between crude oil types is sweet or sour. Sweet crude is normally low in sulphur and lightly paraffinic. Sour crude is usually high in sulphur and heavily naphthenic.

The composition of the crude is the most important parameter in establishing the range and quality of products that may be produced from a refinery. The impurities of the crude, which usually make up 1 - 5 % of the total, are also very important in establishing the value of the crude and the difficulties in converting it into marketable products. The most important impurity of crude oil is sulphur, which is present largely in the form of organic compounds such as mercaptans and sulphides. Some elemental sulphur, H₂S, and FeS may also be present but only in small quantities. The total sulphur content may be as low as 0.04 % w/w or as high as 5 % w/w. Crudes containing more than 0.5 % w/w S are commonly referred to as ‘sour’ and the others as being ‘sweet’. In general, the sulphur content increases in the higher boiling fractions.

Examples of crude types processed in European refineries are shown in Table 9.17. A distinct shift in crude oils processed in European refineries took place between 1993 and 1997, from Middle East crude oils to ‘North Sea’ crudes. Market forces mainly caused this and this trend could therefore easily reverse. CONCAWE has reported that the average sulphur content processed in European refineries decreased from 1.45 % in 1979 to approx. 1.0 - 1.1 % from 1985 onwards. The availability and marketing of low sulphur crude oils has helped the European refineries to reduce SO₂ emissions and to some extent also the emissions of NOₓ.

Table 9.17: Examples of crude oil types and compositions

<table>
<thead>
<tr>
<th>Crude origin</th>
<th>Crude Oil</th>
<th>Density kg/m³</th>
<th>Kinnetic viscosity mm²/s</th>
<th>Sulphur % w/w</th>
<th>Vanadium mg/kg</th>
<th>Nickel mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle East</td>
<td>Arabian Light</td>
<td>864</td>
<td>5.18</td>
<td>1.91</td>
<td>23.7</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>Iranian Heavy</td>
<td>870</td>
<td>7.85</td>
<td>1.67</td>
<td>68.2</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>Arabian Heavy</td>
<td>889</td>
<td>14.54</td>
<td>2.92</td>
<td>69.8</td>
<td>22.3</td>
</tr>
<tr>
<td></td>
<td>Iranian Light</td>
<td>860</td>
<td>5.11</td>
<td>1.46</td>
<td>55.2</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>Kuwait</td>
<td>870</td>
<td>6.90</td>
<td>2.47</td>
<td>32.9</td>
<td>9.6</td>
</tr>
<tr>
<td>North Sea</td>
<td>Statfjord</td>
<td>830</td>
<td>2.70</td>
<td>0.26</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Oseberg</td>
<td>845</td>
<td>3.47</td>
<td>0.24</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Russian</td>
<td>Ural</td>
<td>864</td>
<td>5.41</td>
<td>1.55</td>
<td>37.1</td>
<td>12.2</td>
</tr>
</tbody>
</table>
The next two tables show the metal content of crude oil. Nickel and vanadium are present as porphyrin-systems in the crude oil. In order to determine heavy metals in crude, sampling is of crucial importance. More information about that can be found in [43a, Dekkers and Daane, 1999].

Metal content of different crude oils

<table>
<thead>
<tr>
<th>Source</th>
<th>Fe</th>
<th>Ni</th>
<th>V</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Texas</td>
<td>3.2</td>
<td>1.7</td>
<td>12</td>
<td>0.4</td>
</tr>
<tr>
<td>West Texas</td>
<td>5.1</td>
<td>4.8</td>
<td>7.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Miranda</td>
<td>7.6</td>
<td>1.9</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Jackson</td>
<td>4.4</td>
<td>1.8</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Scurry County</td>
<td>3.4</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Wilmington</td>
<td>28</td>
<td>46.0</td>
<td>41.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Santa Maria</td>
<td>17</td>
<td>97.0</td>
<td>223.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Kettleman</td>
<td>24</td>
<td>35.0</td>
<td>34.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Ventura</td>
<td>31</td>
<td>33.0</td>
<td>49.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Tibu-Petrolea</td>
<td>1.6</td>
<td>9.0</td>
<td>60.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Kuwait</td>
<td>0.7</td>
<td>6.0</td>
<td>77.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Mid-Continent</td>
<td>3.8</td>
<td>4.2</td>
<td>7.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Kansas</td>
<td>5.8</td>
<td>5.8</td>
<td>20.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Morocco</td>
<td>0.8</td>
<td>0.6</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Redwater</td>
<td>3.4</td>
<td>10.6</td>
<td>4.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Source: Speight, J 0 - The Chemistry and Technology of Petroleum, Marcel Dekker Inc. 1980

Range of metals content found in crude oils

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>5.0 - 1500</td>
</tr>
<tr>
<td>Ni</td>
<td>3.0 - 120</td>
</tr>
<tr>
<td>Fe</td>
<td>0.04 - 120</td>
</tr>
<tr>
<td>Cu</td>
<td>0.2 - 12.0</td>
</tr>
<tr>
<td>Co</td>
<td>0.001 - 12</td>
</tr>
<tr>
<td>Si</td>
<td>0.1 - 5.0</td>
</tr>
<tr>
<td>Ca</td>
<td>1.0 - 2.5</td>
</tr>
<tr>
<td>Mg</td>
<td>1.0 - 2.5</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5 - 1.0</td>
</tr>
<tr>
<td>Al</td>
<td>0.5 - 1.0</td>
</tr>
<tr>
<td>Ce</td>
<td>0.001 - 0.6</td>
</tr>
<tr>
<td>Zr</td>
<td>0.001 - 0.4</td>
</tr>
<tr>
<td>Ti</td>
<td>0.001 - 0.4</td>
</tr>
<tr>
<td>Sn</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001 - 0.2</td>
</tr>
<tr>
<td>Hg</td>
<td>0.03 - 0.1</td>
</tr>
<tr>
<td>B</td>
<td>0.001 - 0.1</td>
</tr>
<tr>
<td>Ga</td>
<td>0.001 - 0.1</td>
</tr>
<tr>
<td>Ba</td>
<td>0.001 - 0.1</td>
</tr>
<tr>
<td>Sr</td>
<td>0.001 - 0.1</td>
</tr>
</tbody>
</table>

A recent report [43a, Dekkers and Daane, 1999] has shown that the quantity of Cadmium, Zinc, Chromium, Copper and Arsenic in the crudes are indeed much lower than traditionally assumed. Reasons for this include improper analytical techniques and contamination during sampling. The following table shows the results achieved in the above-mentioned report.
Table 9.18: Content of certain metals in some crude compared to other published data

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (µg/kg)</th>
<th>Published data(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>4 – 37</td>
<td>0.2 – 26200</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.40 – 4.9</td>
<td>0.109,1</td>
</tr>
<tr>
<td>Chromium</td>
<td>12 – 240</td>
<td>1.5 – 3170</td>
</tr>
<tr>
<td>Copper</td>
<td>10 – 195</td>
<td>30 – 7180</td>
</tr>
<tr>
<td>Zinc</td>
<td>59 – 1090</td>
<td>25 – 19500</td>
</tr>
</tbody>
</table>

(*) Published data from several sources reflected in the report
Source: [43a, Dekkers and Daane, 1999]

Physical properties and characteristics of crude oil

Crude oil is a mixture of many compounds and, apart from the lightest components, the characterisation by a complete chemical analysis is almost impossible. As a result, the general physical properties are expressed in terms of simple parameters, which can be quickly estimated. The underlying nature of the crude is then derived from this information by comparison with corresponding parameters from known feedstocks. Most of these parameters are not limited to crudes, but may be used for most petroleum products as well. One of the simplest crude properties to measure is the specific gravity, normally expressed in terms of the °API. Crudes are often classified as being ‘heavy’ or ‘light’ according to their °API, the heavy being less than about 28 - 32°API and the light over 32 – 35 °API.

9.3.2 Refinery intermediates and products

There are over a hundred of refinery products, including gaseous and liquid refinery fuels for domestic and industrial use, fuel for most forms of transport, lubricating oils for all types of machinery and the basic raw materials for the petrochemical industry. Individual refineries do not usually supply the full range of possible products, but try to select those most suited to the quality of the crude feed, the available processing equipment and the local market requirements. The composition of a product will vary between refineries, being a function of crude type and refining processes used, but the overall quality will meet the product specifications prevailing for a given market. The major refinery product groups are shown in Table 2.1 by refinery process unit. A short description of the product groups follows.

Refinery fuel gas (RFG)
Refineries use the C1/C2 fraction as refinery gas to cover part or most of their fuel requirements. Refinery gas can also contain H2. An amine wash is normally used to extract H2S.

LPG
Sometimes C3 and C4 components are also used for refinery fuel, but most of the C3 and C4 components will be sold as liquefied petroleum gas (LPG), which is used as a fuel for numerous applications. LPG is sold either as a mixed LPG fraction or as separated C3 and C4 fractions. The liquid propane normally contains a minimum of 95 %w/w C3 compounds, the remainder being C2 and C4. Butanes and butenes are also used as a petrochemical feedstock for the manufacture of MTBE, acetic acid, solvents, polybutylenes, and rubber.

Naphtha and chemical naphtha
Naphtha is the raw gasoline range fraction from crude oil distillation. As well as gasoline production, in some cases, naphtha is used as the feedstock for petrochemicals production.

Gasoline
Gasoline, the fuel for motor cars and light aircraft, represents the highest volume and one of the more valuable refinery products. Automotive gasoline, which is by far the most important gasoline type, consists of a complex mixture of hydrocarbons ranging from C4 to C10, boiling between 38°C and 205°C. Most refiners produce gasoline in three or four octane grades, the
principal difference being the anti-knock performance. Mogas is a term normally used for motor gasoline.

**Jet fuel (kerosene, avtur)**

Jet fuel is the name given to kerosene or kerosene blends used as fuel in aviation turbines (hence also called Avtur) by both commercial aviation and military aircraft. For most refineries the primary source of jet fuel blending stocks is the straight-run kerosene fraction (C\textsubscript{8} - C\textsubscript{12}) from the atmospheric crude unit. For a refinery with a Hydrocracker, kerosene boiling range hydrocarbons from this unit can also meet jet fuel specifications, and is a major contributor to jet fuel production. Hydrotreated light Coker gas oil and thermally cracked gasoil can also be used as blending stock. In some developing countries kerosene is still the primary fuel for cooking and domestic heating.

**Diesel oil/heating oil/gasoil**

Diesel fuels are produced by blending of kero and gas oil fractions from the crude distillation unit and gas oil fractions of the high vacuum unit and from conversion units. An upgraded and flexible processing scheme for desulphurisation of blending components is necessary in most refineries in order to arrive at the currently required and future sulphur specifications (500 ppm currently, 350 ppm from 2000 and 50 ppm from 2005 onwards). Light heating oils (kero/diesel fraction) are typically used for small domestic applications.

Middle distillates/distillate fuels

Alternative names for the fuels in the kerosene and gasoil boiling ranges.

**Fuel oils**

Fuel oils cover a very wide range of applications and are produced in a variety of grades. Gasoils are sometimes referred to as fuel oils, but in Europe the term is usually used to describe heavy fuel oils (atmospheric residue) which are used for electricity etc. Heavy fuel oil are used for electricity or power generation by utility companies, or sold as bunker fuel oil for seagoing vessels. Refineries use heavier fractions from crude oil distillation, from vacuum distillation or from visbreaking for generation of heat, electricity and steam in their furnaces and boilers.

Heavy fuel oils consist largely of the residue remaining from the distillation of crudes. These residues consist of large hydrocarbon structures containing components that require additional processing to convert them into more valuable, lighter products for use in gasoline and diesel engines. These residues generally have a high sulphur and ash content, are mostly very viscous and will therefore be blended with lighter gasoils in order to sell them as a commercial fuel for ships and utilities.

**Lubricating oils, wax and greases**

Lubricating oil feedstocks are produced from the atmospheric residue by fractionation under vacuum. The oil cuts produced from the vacuum distillation column are further processed to remove unwanted impurities (solvent extraction and dewaxing) and blended with miscellaneous additives (both organic and inorganic in nature) to give lubricating oils of various grades. Lubricating oils can be modified by mixing with thickening agents such as soap, clay or silica gel to produce lubricating greases. Dewaxing yields paraffinic or microcrystalline wax that is usually subjected to hydrofinishing to remove colours, odours and potentially carcinogenic hydrocarbons for domestic applications.

**Bitumen**

Bitumen (referred to as asphalt in the USA) is used mainly for paving roads but also for a number of other applications, such as materials for roofing. The basic source of bitumen is the residue remaining after vacuum distillation of crude. The residue can also be treated by blowing with air at high temperature (bitumen blowing process) to increase the asphaltene content.
**Petroleum coke**

Petroleum coke is the residue remaining after destructive distillation of petroleum residue in a delayed coking unit. It is widely used as fuel in the cement and steel industry. It can also be used as a fuel for power plants if the sulphur content is low enough. Coke also has nonfuel applications as a raw material for many carbon and graphite products.

<table>
<thead>
<tr>
<th>Petroleum coke analysis used in oxygen-blown gasification (*)</th>
<th>% w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate analysis</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>87.1 - 90.3</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.8 - 4.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.5 - 2.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.6 - 2.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.1 - 2.3</td>
</tr>
<tr>
<td>Proximate analysis</td>
<td></td>
</tr>
<tr>
<td>Volatiles</td>
<td>9.0 - 9.7</td>
</tr>
<tr>
<td>Fixed C</td>
<td>80.4 - 89.2</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.9 - 10.2</td>
</tr>
<tr>
<td>Ash</td>
<td>0.2 - 0.4</td>
</tr>
</tbody>
</table>

(*) Source: [166, Meyers, 1997]

**Sulphur**

Sulphur is basically a by-product of refining resulting from the removal of sulphur compounds from the main hydrocarbon product streams. The quantity of sulphur produced by a refinery depends on the amount present in the crude and the desulphurisation and sulphur recovery capacity installed. It is a valuable product which is mainly used as the raw material for sulphuric acid manufacture.

**Relationship between feed (typically crude oil) and products**

As a broad generalisation it is true to say that any crude can be processed into any reasonable selection of products by a suitable choice of refining unit operations. The cost of production will depend on the refining units required, which in turn depend on the crude selected. In theory the production cost can be minimised by careful selection of the crude. In practice, however, refinery designs are often compromised by factors such as: the changing availability, price and composition of crudes and changing market demands for product slate and specifications. A few relatively simple crude properties can indicate the feasibility of processing a particular crude (mix) with a given refinery complex.

In general, it is found that the heavier the crude, the higher the quantities of sulphur, Conradson carbon and heavy metals, and the lower its hydrogen content. Heavy crudes are also more difficult to process. Heavy crude normally results in high fuel-oil production while light crude is more appropriate for a high gasoline and middle distillate production. Other simple property indicators are sulphur content and pour point.

In order to evaluate the properties of the various likely products such as gasoline octane rating, the aromatics content of kerosene, etc., it is necessary to distil the crude and analyse the fractions boiling within different boiling ranges. This will give information on the process units that may be required for quality improvement, such as desulphurisation facilities, a reformer unit or an aromatics extraction plant. The residue fractions can be similarly analysed to give more detailed information on the conversion units that may be appropriate.
Annexes

9.4 Annex IV. Submitted examples on cost-effectiveness of implementation of environmental technologies

Note for the TWG: Please advise on what to do with these Annexes. EIPPCB intention is to delete Annexes 4 to 6 unless the TWG specifically propose to keep some information from it.

9.4 Propose to deletion because updated contributions on cost-effectiveness have been provided

References: [115, CONCAWE, 1999], [268, TWG, 2001], [248, Ademe, 2001], [348, Ashworth Leininger Group, 2001]

It follows some examples submitted by the TWG on the calculation of some cost-effectiveness of the implementation of environmental technologies in the refinery sector. One feasibility study (Section 10.4.4) provided by a TWG member has shown that the cost and the technical solution for the achievement of the same environmental goal (e.g. bubble concept) depends on the local situation.

9.4.1 Calculation of the cost-effectiveness of the implementation of a technique in a hypothetical case

An important consideration of the cost of environmental technologies relates to the changing cost-effectiveness that results for a given technology depending on the point of control from which one starts the cost-effectiveness calculation. Most studies on environmental technologies present the cost and effectiveness (percent of emission reduction or tonnes of emissions reduced) of installing a technology or implementing a technique against an otherwise uncontrolled baseline operation. In this case it is easy to calculate the cost-effectiveness of an environmental technology versus an otherwise uncontrolled facility by simply dividing the cost of the technique by the emissions reduction achieved. Table 10.19 shows a series of various hypothetical controls capable of reaching various percentage emission reductions. For example, technology C would provide a 50% reduction for a cost of 2000 k EUR while technology G would provide 99% reduction for 12000 k EUR.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Percentage of Reduction (%</th>
<th>Remaining emission (tonnes)</th>
<th>Technology cost for a new installation (kEUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>10000</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>8000</td>
<td>1000</td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>5000</td>
<td>2000</td>
</tr>
<tr>
<td>D</td>
<td>60</td>
<td>4000</td>
<td>3000</td>
</tr>
<tr>
<td>E</td>
<td>95</td>
<td>500</td>
<td>4500</td>
</tr>
<tr>
<td>F</td>
<td>95</td>
<td>100</td>
<td>7000</td>
</tr>
<tr>
<td>G</td>
<td>99</td>
<td>100</td>
<td>12000</td>
</tr>
</tbody>
</table>

Table 9.19: Example of abatement technology cost for a new installation, emission reduction and emissions remaining after the application of the technology.

Due to local regulations and/or corporate policies there are many situations where certain levels of control already exist within specific sites. In these cases the cost for achieving a given % emission reduction target is significantly increased over the initial cost-effectiveness values. This needs to be accounted for in determining the cost-effectiveness of a technology/technique. As can be seen in Table 10.19, if technology C is already in place at a location, the additional emissions reduction for going to technology G would be only 49%. The cost of implementing technology G therefore becomes 2.45 kEUR/tonne for the incremental emissions reductions, rather than the 1.21 kEUR/tonne when going to 99% control from 0%. If one were to go to technology G in a location where technology E was in place, the incremental cost would be 13.3 kEUR/tonne. In all of these instances the final situation is to be at 99% control of emissions. The actual cost for going to the 99% level in these situations, if done incrementally, would effectively be the cost of implementing Technology C plus E, plus G, to get the 99% reduction.
Table 10.20 shows the resultant cost of applying various technologies starting from different levels of existing control.

<table>
<thead>
<tr>
<th>Actual level of control</th>
<th>0%</th>
<th>20%</th>
<th>50%</th>
<th>60%</th>
<th>80%</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50%</td>
<td>0.4</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60%</td>
<td>0.5</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90%</td>
<td>0.5</td>
<td>0.46</td>
<td>0.14</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>95%</td>
<td>0.7</td>
<td>0.43</td>
<td>0.33</td>
<td>0.55</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>99%</td>
<td>1.2</td>
<td>0.93</td>
<td>1.55</td>
<td>3.07</td>
<td>13.3</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 9.20: Cost-effectiveness (kEUR/tonne abated) starting from different percentages of reduction and considering that the previous technology should be replaced 100%.

### 9.4.2 Cost-effectiveness data for SRU

Next table gives the data on cost-effectiveness of the application of several sulphur recovery unit techniques.

<table>
<thead>
<tr>
<th>Name of the technique</th>
<th>Specific cost $^1$ EUR/tonne SO$_2$</th>
<th>Specific cost $^2$ EUR/tonne SO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd reactor</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Stand Alone Scot</td>
<td>131.538</td>
<td>12</td>
</tr>
<tr>
<td>Cascade Scot Common regenerator</td>
<td>155.228</td>
<td>22.161</td>
</tr>
<tr>
<td>Super Claus</td>
<td>198.320</td>
<td>22.160</td>
</tr>
<tr>
<td>Super Claus + Claus Stage</td>
<td>171.588</td>
<td>22.160</td>
</tr>
<tr>
<td>Clauspol</td>
<td>253.417</td>
<td>22.160</td>
</tr>
<tr>
<td>Sulfinol</td>
<td>160.300</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ [268, TWG, 2001]

Calculations for this column have been performed based on the following hypothesis:

- The TGCU selling costs include license fee, catalyst and chemical first loads. These investments are financed by a full reimbursable loan. This loan is based on a 10 years basis, with a yearly 6% interest rate.
- The catalyst lifetime is 3 years (part of the operating costs). The related investment every 3 years is financed by a full reimbursable loan. This loan is based on a 3 years basis, with a yearly 6% interest rate.
- The solvent and chemical make-up (part of the operating costs) have been calculated on a yearly basis as a cash expense.
- The utilities consumption and production as well as the supervision manpower costs have been considered constant over the time.
- The sulphur selling price has also been considered constant over the time.

$^2$ [115, CONCAWE, 1999]

Claus plant with a capacity of 20000 t/y sulphur production (sulphur recovery efficiency 94-96% for a two stage unit), a volume of gas treated of 60 million m$^3$/yr, and pollutant initial concentration: 34000 mg SO$_2$/m$^3$.

### 9.4.3 Compendium of cost-effectiveness data for some NO$_x$ abatement techniques

The following graph shows the cost to abate a tonne of NO$_x$ in industry sectors as well as some reference values used in some countries [248, Ademe, 2001].
The following tables show data concerning cost-effectiveness for NO\textsubscript{x} abatement measures:

**NO\textsubscript{x} Control for Fired Heaters and Boilers Firing Refinery Blend Gas**

<table>
<thead>
<tr>
<th>Retrofit of existing unit</th>
<th>Refinery blend gas firing</th>
<th>Uncontrolled NO\textsubscript{x} emissions of 150 ppm at 3% oxygen (300 mg/Nm\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost Effectiveness</td>
<td>EUR/tonne NO\textsubscript{x} Removed (incl. capital charge @ 15%)</td>
<td></td>
</tr>
<tr>
<td>Ultra-Low-NO\textsubscript{x} Burners [6]</td>
<td>650-1200</td>
<td></td>
</tr>
<tr>
<td>SCR [2]</td>
<td>8300-8800</td>
<td></td>
</tr>
<tr>
<td>Ultra-Low-NO\textsubscript{x} Burner plus SCR [2]</td>
<td>12000-130000</td>
<td></td>
</tr>
</tbody>
</table>

---

**NO\textsubscript{x} Control for Fired Heaters/Boilers Firing Residual Fuel Oil**

<table>
<thead>
<tr>
<th>Retrofit of existing unit</th>
<th>Residual Oil firing</th>
<th>Uncontrolled NO\textsubscript{x} emissions of 250 ppm at 3% oxygen (500 mg/Nm\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost Effectiveness</td>
<td>EUR/tonne NO\textsubscript{x} Removed (incl. capital charge @ 15%)</td>
<td></td>
</tr>
<tr>
<td>EPRA RBL [4]</td>
<td>4200-9000</td>
<td></td>
</tr>
<tr>
<td>SCR [3]</td>
<td>8400-10500</td>
<td></td>
</tr>
<tr>
<td>Ultra-Low-NO\textsubscript{x} Burner plus SCR [2]</td>
<td>9000-10500</td>
<td></td>
</tr>
</tbody>
</table>

---

**Notes:**
- **EPRA RBL** clearinghouse listing and California Air Resources Board BACT listings. These listings provide the permitted emission levels in permits granted within the United States or the State of California for alternative control technologies to meet RACT, BACT (Best Available Retrofit Control Technology) and LAER (Lowest Achievable Emission Requirements). The listings cover the period to 1996.
- **Proprietary industry studies**
- **CONCAWE Member Company Information**
- Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4\%/yr have been used in this analysis.

---

Figure 9.5: Some values on the cost for the abatement of NO\textsubscript{x} in different industrial sectors.
### NOx Control for Gas Turbines Firing Natural or Refinery Blend Gas

**Basis:** 85 MW output turbine (representative of a GE Frame 7 size unit) (electrical output) natural gas or refinery blend gas firing

Uncontrolled NOx emissions of 250 ppm at 15% oxygen (350 g/GJ)

<table>
<thead>
<tr>
<th>Cost Effectiveness</th>
<th>SNCR</th>
<th>SCR</th>
<th>Steam injection plus SCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUR/tonne NOx Removed (incl. capital charge @ 15%)</td>
<td>350 (1)</td>
<td>1500 (1)</td>
<td>1700-8000 (2)</td>
</tr>
<tr>
<td>Dry Low-NOx Combustors</td>
<td>1500 (1)</td>
<td>3500 (1)</td>
<td>21000 (2)</td>
</tr>
<tr>
<td>Steam injection plus SCR</td>
<td>2600 (1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Proprietary industry studies
3. Costs from Reference (1) above for SCR increment only with NOx entry to SCR following Low-NOx combustor of 25 ppm.
4. Dry Low-NOx combustors are not available for refinery blend gas containing more than 5 to 10% hydrogen.
5. Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr have been used in this analysis.

### NOx Control for Fluid Catalytic Cracking Units

**Basis:** 30 k bbl/day FCC unit with CO Boiler

800 mg/Nm3 uncontrolled NOx emission

<table>
<thead>
<tr>
<th>Cost Effectiveness</th>
<th>SNCR</th>
<th>SCR</th>
<th>Feedstock Hydrotreating</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUR/tonne NOx Removed (incl. capital charge @ 15%)</td>
<td>1900</td>
<td>3000-3300</td>
<td>38000 (2)</td>
</tr>
</tbody>
</table>
2. Assign all feedstock hydrotreating costs to NOx control. |
3. Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr used in this analysis.

### Cost Effectiveness of some already applied NOx abatement techniques in USA refineries.

<table>
<thead>
<tr>
<th>Cost Effectiveness</th>
<th>Low-NOx Burners (LNB)</th>
<th>Selective Catalytic Reduction (SCR)</th>
<th>Selective Non-Catalytic Reduction (SNCR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUR/tonne NOx Removed</td>
<td>1260-1500</td>
<td>6300-21000 (for process heaters and boilers)</td>
<td>2070-6030 (for process heaters)</td>
</tr>
</tbody>
</table>

### Notes:

1. ULNB are not available for oil-fired heaters and boilers.
2. Costs from Reference (1) above for SCR increment only with NOx entry to SCR following Low-NOx combustor of 25 ppm.
3. Dry Low-NOx combustors are not available for refinery blend gas containing more than 5 to 10% hydrogen.
4. Exchange rate of 1 EUR = 1.25 U.S. dollar and capital and operating costs escalation of 4%/yr used in this analysis.
9.4.4 Feasibility study on the applicability of NO\textsubscript{x} environmental measures in two different refinery sites

A French study, performed by an engineering consultant and sponsored by ADEME/Environment Ministry and French Oil Federation, evaluated the pre-engineering cost of BAT implementation by retrofitting for NO\textsubscript{x} reduction on two existing refinery sites. The study explored the choice mechanism to implement IPPC directive.

For both sites, all the major existing units contributing globally for more than 80\% of the NO\textsubscript{x} emissions from the site have been considered: furnace, boilers, regenerator, etc. The BAT candidates listed in the [115, CONCAWE, 1999] have been considered for each item at the technical, economic and maintenance level.

Summary graphs are presented showing the variable efficiency of considered and validated techniques on different units: low NO\textsubscript{x} burners, flue gas recirculation, SNCR, SCR, reburning, etc. An estimated cost (about 30\%) is expressed for implementation of each BAT candidate in terms of cost per reduced NO\textsubscript{x} tonne per year. A large variation of cost is observed on different units, for various techniques and with different impacts on the global NO\textsubscript{x} emissions reductions of the two sites respectively.

![Image of variable efficiency and cost of retrofitting of existing units (FRF/tonne NO\textsubscript{x} reduced)](image)

*Figure 9.6: Variable efficiency and cost of retrofitting of existing units (FRF/tonne NO\textsubscript{x} reduced)*

*Note: Using feasibility of NO\textsubscript{x} BAT candidates study on two refinery sites (1 Euro = 6.56 FRF)*

Finally, combined scenarios of the potential applicability of these BAT are presented for the both sites and for similar environmental objectives based on a global NO\textsubscript{x} bubble concentration. Cost impact is different for each existing site to be retrofitted and is very expensive according to the environmental objectives to be reached.

This technical feasibility and economic considerations have to be remembered in the context of the BAT associated emissions levels to be proposed, taking into account the complexity of retrofitting due to the difference in the current European existing refinery sites.
### Annexes

<table>
<thead>
<tr>
<th>Site</th>
<th>Objectives</th>
<th>400 mg/Nm²</th>
<th>300 mg/Nm²</th>
<th>200 mg/Nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Site A</strong></td>
<td>Investment</td>
<td>3000</td>
<td>6000</td>
<td>13000</td>
</tr>
<tr>
<td></td>
<td>Annual Cost</td>
<td>1070</td>
<td>2150</td>
<td>4150</td>
</tr>
<tr>
<td></td>
<td>Cost/t NO abated/yr</td>
<td>1170</td>
<td>1680</td>
<td>1860</td>
</tr>
<tr>
<td></td>
<td>techniques</td>
<td>LNB-SNCR</td>
<td>LNB-1 SCR</td>
<td>LNB-3 SCR</td>
</tr>
<tr>
<td><strong>Site B</strong></td>
<td>Investment</td>
<td>3500</td>
<td>8630</td>
<td>12000</td>
</tr>
<tr>
<td></td>
<td>Annual Cost</td>
<td>930</td>
<td>2600</td>
<td>5200</td>
</tr>
<tr>
<td></td>
<td>Cost/t NO abated/yr</td>
<td>1100</td>
<td>1750</td>
<td>2350</td>
</tr>
<tr>
<td></td>
<td>techniques</td>
<td>LNB-recirc.</td>
<td>reburn-SCR</td>
<td>SCR with exch.</td>
</tr>
</tbody>
</table>
9.5—Annex V: Background information from TWG members for the different proposals of SO₂ and NOₓ emission under the bubble concept

The calculation of the emission levels for the bubble concept that can be associated with applying BAT incorporates the various aspects presented in Section 4.15.2 (description of the bubble concept) and the elements described in Chapter 5. The following elements have to be taken into consideration, with due regard to the applicability of each of the elements or options in a particular situation:

- Increased energy efficiency of the various processes integrated with the refinery fuel management system;
- Decrease use of liquid fuels by increased use of gaseous fuels from within the refinery or, where applicable, from additional processing and conversion in the refinery, FCC, IGCC, coker, etc.;
- Lower the S content of liquid fuels (e.g. hydrotreatment) used in the refinery;
- Use of clean gaseous fuels (natural gas or cleaned refinery gas);
- Use of liquid fuels combined with control techniques to clean the flue gases, thereby reducing the emissions of SO₂ and NOₓ;
- Apply BAT to single installations, especially to the sulphur recovery unit (SRU).

It follows some calculations, justifications for the proposals given by some TWG members.

9.5.1—Calculations based on BAT assumptions provided by the Netherlands

In order to illustrate the use of the bubble concept in a refinery, a number of cases and their relevant emissions are calculated along the lines outlined below. The following assumptions are used.

Gas-fired refinery:
There are a few full conversion refineries in Europe that are fully gas-fired. The main source of energy in these cases is cleaned refinery gas. In some cases also natural gas is used as supplementary fuel.

Assumptions for bubble calculation: Full conversion, fully gas-fired refinery, processing 10 million tonne of crude oil with an annual fuel use of 700000 tonnes (7% on intake). SRU applies BAT with 99.8% efficiency and has an annual production of 100000 tonnes of elementary sulphur. The FCC has an annual throughput of 1.5 million tonne (consuming some 12% of the total refinery fuel consumption). The 100% gas case is presented in Tables 10.21-24.

Gas and Liquid-fired Refinery using low sulphur oil (0.5% S)
Most European refineries use a combination of gaseous and liquid fuels from within the refinery. The calculation of the technical achievable emission values in such a refinery is based on a) existence of a combined fuel management system in the refinery, and b) emission values of the combined fuel system with fuels that are either inherently clean (certain refinery gases or natural gas) or refinery gaseous or liquid fuels that can be cleaned relatively easy. It may also cover the situation of the cleaning of the flue gases from fuels that ‘untreated’ will cause pollution to air.

Assumptions for the calculation: Medium conversion, partially gas-fired refinery, processing 10 million tonne of crude oil with an annual fuel use of 400000 tonnes (4% on intake). SRU applies BAT with 99.8% efficiency and has an annual production of 50000 tonnes of elementary sulphur.
sulphur. The FCC has an annual throughput of 1.5 million tonne (consuming some 20% of the total refinery fuel consumption). Several cases are shown (70% gas, 50% gas and 30% gas).

Gas and Liquid-fired Refinery using flue-gas desulphurisation

The following calculations are based on actual data from a complex refinery firing heavy residues in the power plant, whereby all the liquid fuel firing of the refinery is concentrated and the installation is equipped with flue-gas desulphurisation. The remaining installations are gas-fired.

Assumptions for the calculation: Medium conversion, partially gas-fired refinery, processing 10 million tonne of crude oil with an annual fuel use of 400000 tonne (4% on intake). SRU applies BAT with 99.8% efficiency and has an annual production of 50000 tonnes of elementary sulphur. The FCC has an annual throughput of 1.5 million tonne (consuming some 20% of the total refinery fuel consumption). Heavy residue (3.5 wt% S) is fired on the power plant, which is equipped with flue-gas desulphurisation. Two desulphurisation efficiency cases are presented, 90% DeSOx and 95% DeSOx.

The results from the calculations are summarised in Table 10.21. The cases are elaborated in more detail in Tables 10.22-24. It should be explicitly noted that these bubbles are calculated from a technical basis and by taking the ‘bottom up’ approach. It does not take account of process upsets or outages.

### Table 9.21: Summary of calculated SOx and NOx bubbles from the cases described in this section and presented in following tables

<table>
<thead>
<tr>
<th>Description</th>
<th>Unit</th>
<th>100% gas</th>
<th>70% gas</th>
<th>50% gas</th>
<th>30% gas</th>
<th>DeSOx-90</th>
<th>DeSOx-95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery type</td>
<td>XConversion</td>
<td>Full</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Crude throughput</td>
<td>million tonnes/year</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>% of feedstock input</td>
<td>7</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>tonnes per year</td>
<td>700000</td>
<td>400000</td>
<td>400000</td>
<td>400000</td>
<td>400000</td>
<td>400000</td>
</tr>
<tr>
<td>FCC fuel consumption</td>
<td>%</td>
<td>12</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Other fuel pool</td>
<td>%</td>
<td>88</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Gas in fuel pool</td>
<td>%</td>
<td>400</td>
<td>70</td>
<td>50</td>
<td>30</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>Oil in fuel pool</td>
<td>%</td>
<td>0</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>Flue-gas from FCC*</td>
<td>10^2 m^3 ISO dry, 1% O2</td>
<td>1008000</td>
<td>960000</td>
<td>960000</td>
<td>960000</td>
<td>960000</td>
<td>960000</td>
</tr>
<tr>
<td>Flue-gas from gas firing*</td>
<td>10^2 m^3 ISO dry, 1% O2</td>
<td>7392000</td>
<td>2688000</td>
<td>1920000</td>
<td>1152000</td>
<td>1420800</td>
<td>1420800</td>
</tr>
<tr>
<td>Flue-gas from oil firing*</td>
<td>10^2 m^3 ISO dry, 3% O2</td>
<td>0</td>
<td>1152000</td>
<td>1920000</td>
<td>2688000</td>
<td>2419200</td>
<td>2419200</td>
</tr>
</tbody>
</table>

It should be noted that the 100% gas case is the only case that is a full-conversion refinery. The other cases refer to medium conversion refineries, which has a considerable effect on the fuel consumption and thus also on the load bubbles.
## Annexes

<table>
<thead>
<tr>
<th></th>
<th>wt.-%</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
<th>3.5</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-content fuel oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flue-gas desulphurisation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref. product desulphurisation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delta S removed from product</td>
<td>wt.-%</td>
<td>1.25</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SRU efficiency</td>
<td>%</td>
<td>99.8</td>
<td>99.8</td>
<td>99.8</td>
<td>99.8</td>
<td>99.8</td>
<td>99.8</td>
</tr>
<tr>
<td>Sulphur recovery</td>
<td>tonnes per year</td>
<td>100000</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
<td>50000</td>
</tr>
</tbody>
</table>

*The flue-gas flow is calculated from the assumption that the combustion of 1 tonne of oil or 1000 m³ of gas yields a flue-gas flow of 12000 Nm³ (at 3 % O₂)*

Table 9.22: Description of 6 different cases of refinery firing and flue-gas treatment
### Table 9.23: Assumed and calculated SO₂ emissions and bubbles for the different cases described in Table 10.22

<table>
<thead>
<tr>
<th>SO₂² Description</th>
<th>ECC</th>
<th>Gas-firing</th>
<th>Oil-firing</th>
<th>ECC</th>
<th>Gas-firing</th>
<th>Oil-firing</th>
<th>SRI</th>
<th>Total</th>
<th>Concentration bubble</th>
<th>Load-bubble</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 % gas</td>
<td>50</td>
<td>400</td>
<td>5 – 15</td>
<td>30</td>
<td>400</td>
<td>5 – 15</td>
<td>0</td>
<td>400</td>
<td>0.387 – 0.914</td>
<td>0.58 – 1.09</td>
</tr>
<tr>
<td>50 % gas</td>
<td>50</td>
<td>400</td>
<td>5 – 15</td>
<td>850</td>
<td>48 – 384</td>
<td>10 – 20</td>
<td>1439</td>
<td>200</td>
<td>1.190 – 2.245</td>
<td>3.91 – 4.68</td>
</tr>
<tr>
<td>30 % gas</td>
<td>50</td>
<td>400</td>
<td>5 – 15</td>
<td>850</td>
<td>48 – 384</td>
<td>6 – 17</td>
<td>2285</td>
<td>200</td>
<td>2.530 – 2.886</td>
<td>5.20 – 6.01</td>
</tr>
<tr>
<td>DeSOx – 95</td>
<td>50</td>
<td>400</td>
<td>5 – 15</td>
<td>298</td>
<td>48 – 384</td>
<td>7 – 21</td>
<td>720</td>
<td>200</td>
<td>0.925 – 1.325</td>
<td>2.03 – 2.76</td>
</tr>
</tbody>
</table>

²Concentrations are assumed from the application of BAT. Loads and bubbles are calculated accordingly.

### Table 9.24: Assumed and calculated NOₓ emissions and bubbles for the different cases described in Table 10.22

<table>
<thead>
<tr>
<th>NOₓ² Description</th>
<th>ECC</th>
<th>Gas-firing</th>
<th>Oil-firing</th>
<th>ECC</th>
<th>Gas-firing</th>
<th>Oil-firing</th>
<th>SRI</th>
<th>Total</th>
<th>Concentration bubble</th>
<th>Load-bubble</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 % gas</td>
<td>100</td>
<td>150</td>
<td>100 – 150</td>
<td>120</td>
<td>200</td>
<td>96 – 144</td>
<td>330</td>
<td>381</td>
<td>518 – 816</td>
<td>108 – 170</td>
</tr>
<tr>
<td>70 % gas</td>
<td>100</td>
<td>150</td>
<td>100 – 150</td>
<td>120</td>
<td>200</td>
<td>96 – 144</td>
<td>192</td>
<td>288</td>
<td>534 – 854</td>
<td>111 – 178</td>
</tr>
<tr>
<td>50 % gas</td>
<td>100</td>
<td>150</td>
<td>100 – 150</td>
<td>120</td>
<td>200</td>
<td>96 – 144</td>
<td>115</td>
<td>172</td>
<td>534 – 854</td>
<td>111 – 178</td>
</tr>
<tr>
<td>DeSOx – 90</td>
<td>100</td>
<td>150</td>
<td>100 – 150</td>
<td>120</td>
<td>200</td>
<td>96 – 144</td>
<td>142</td>
<td>213</td>
<td>528 – 841</td>
<td>110 – 175</td>
</tr>
<tr>
<td>DeSOx – 95</td>
<td>100</td>
<td>150</td>
<td>100 – 150</td>
<td>120</td>
<td>200</td>
<td>96 – 144</td>
<td>142</td>
<td>213</td>
<td>528 – 841</td>
<td>110 – 175</td>
</tr>
</tbody>
</table>

²Concentrations are assumed from the application of BAT. Loads and bubbles are calculated accordingly.
9.5.2 Example provided by Austria

Hypothesis
The following calculations are based on a complex refinery firing heavy residues in the power plant, which is equipped with flue gas desulphurisation. To allow some flexibility, a gaseous/liquid fuel ratio between 1 and 2 is assumed, which means that between 50 % and 33 % of the total energy used by the refinery is derived from combustion of liquid fuels (there are refineries existing with 100 % gas firing). Average S content of the liquid fuels is assumed to be in the range of 2.8 – 3.5 %. Measures to increase energy efficiency are not included in these calculations.

- Range of input of liquid fuels:
  a. 303000 t with a S content of 2.8 %: S input in the power plant: 8484 t
  b. 500000 t with a S content of 3.5 %: S input in the power plant: 17500 t

- Range of efficiency of FGD: 90 – 95 %
- Highest SO2 concentration in the off-gas of the Claus plant: 1350 mg/m³

Calculations
Assuming the above given parameters, calculated bubble (including all installations, but without flares) concentrations for SO2 are in the range of 109 mg/Nm³ (case a; 95 % efficiency of FGD) and 338 mg/Nm³ (case b; 90 % eff. of FGD). Case b together with an efficiency of FGD of 95 % results in a bubble concentration of 175 mg/Nm³ (corresponding to 235 t/Mt crude throughput).

Corresponding loads are from 126 t SO2/Mt to 455 t SO2/Mt crude throughput.

9.5.3 Two examples provided a TWG member

CASE A: Reduction scenario developed in an existing refinery

Refinery characteristics
A complex refinery processing 15 Mt/yr of crude oil. 15 % fuel oil at an average sulphur content of 1.3 %. 160000 tonnes of fuel oil and 840000 tonnes of gas (RFG + natural gas)

BAT assumptions
50 % reduction of fuel emissions by switching fuel oil to low-S fuel oil or by installing FGD on stacks with highest SO2 fuel emissions.
50 % reduction of cat cracker emissions by reducing sulphur input to cat cracker and/or by installing FGD on stacks of cat cracker
High efficient SRU>99.5 % sulphur recovery

Conclusions
Concentration bubble of 200 mg SO2/Nm³

CASE B: Reduction scenario developed in an existing refinery

Refinery characteristics
A complex refinery processing around 12 Mt/yr of crude oil.
Fuel consumption: 156000 t/yr liquid at 3 % S
400000 t/yr of refinery fuel gas + natural gas
SRU at 99 % SO2-concentration 20000 mg/Nm³

BAT assumptions
Improve the SRU to BAT levels
9.5.4 Italian proposals and justification for the given bubble figures

With respect to environmental benefits, Italy and other Mediterranean countries are characterised by a nearly full compliance with objectives for acidification and very marginal transboundary pollution. In other words, we don’t need very stringent emission ranges for SO\textsubscript{2} and NO\textsubscript{x}.

From the technical and economic point of view, we should consider that the refining sector in the Mediterranean area is characterised as follows:

- 70\% of the European fuel oil market demand is located in the Mediterranean area;
- the current configuration of the existing refineries in this area derives from the actual petroleum products demand that is very different from the North Europe demand;
- the crude oil slate processed is mainly derived from Middle East crude oils that represent the best choice to fit both the market demand and the refinery configuration. The heavy fuel oil produced under these conditions needs to be used internally because any other options (deep conversion, desulphurisation, gasification, etc) are not economically sustainable.

In conclusion we believe that the level associated with BAT should take into account the cost and the advantages associated to different emission ranges and, moreover, BAT must be techniques generally applicable otherwise the competitiveness inside the refining sector in Europe will be distorted.

On the basis of these considerations we propose the following bubble emission ranges:

- SO\textsubscript{2}: 800-1200 mg/Nm\textsuperscript{3} (monthly average all plants included)
- NO\textsubscript{x}: 250-450 mg/Nm\textsuperscript{3} (monthly average all plants included)
- Dust: 30-50 mg/Nm\textsuperscript{3} (monthly average all plants included)

The ranges here proposed for SO\textsubscript{2} and NO\textsubscript{x} are derived from the emission values associated to the BAT considered for the revision of the Large Combustion Plants Directive, recently approved at European level. The BATs adopted for this revision are the most stringent techniques applicable to the new and existing large combustion plants.

In the revision of the Large Combustion Plants Directive the SO\textsubscript{2} emission limit values for new and existing refineries are respectively 600 and 1000 mg/Nm\textsuperscript{3}. Having considered that the bubble emission levels in the BREF are referred to all plants, these emission limit values are slightly increased to include the SO\textsubscript{2} emission also from Claus and Catalytic Cracking plants.

The emission limit values for NO\textsubscript{x}, in the revision of the Large Combustion Plants Directive are defined in the same range we proposed for refinery bubble and this seems enough to justify our proposal.

The above emission values ranges are coherent with the definition of general BAT and so the requirement of more stringent ranges do not have justification.

By the way the techniques that need to be adopted to meet the more stringent ranges will increase the refinery energy consumption and the associated CO\textsubscript{2} emissions.

DeNO\textsubscript{x} in the main stacks

Conclusions

SO\textsubscript{x} bubble concentration of 50 mg/Nm\textsuperscript{3}

NO\textsubscript{x} bubble concentration of <100 mg/Nm\textsuperscript{3}.
9.5.5 Concawe proposals and justifications for the given bubble figures

SO₂-bubble calculations and scenarios

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ratio FO use</th>
<th>S-content of FO</th>
<th>Combustion bubble</th>
<th>Global bubble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>30 %</td>
<td>1.7 %</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td>Scenario 1</td>
<td>30 %</td>
<td>1 %</td>
<td>650</td>
<td>880</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>30 %</td>
<td>0.5 %</td>
<td>255</td>
<td>650</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>100 %</td>
<td>1 %</td>
<td>1960</td>
<td>1950</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>100 %</td>
<td>0.5 %</td>
<td>980</td>
<td>1190</td>
</tr>
<tr>
<td>Scenario 5 + FGD on all units</td>
<td>100 %</td>
<td>3 %</td>
<td>294</td>
<td>650</td>
</tr>
<tr>
<td>Scenario 6 + FGD on 75 % of emissions or major emitters</td>
<td>100 %</td>
<td>2 %</td>
<td>1430</td>
<td>1300</td>
</tr>
<tr>
<td>Scenario 7 + FGD on 75 % of emissions or major emitters</td>
<td>100 %</td>
<td>1.7 %</td>
<td>960</td>
<td>1170</td>
</tr>
<tr>
<td>Scenario 8 + FGD on 50 % of emissions or major emitters</td>
<td>100 %</td>
<td>1 %</td>
<td>1030</td>
<td>1225</td>
</tr>
</tbody>
</table>

Table 9.25: Variation of the Bubble Results from Use of Fuels with Varying Sulphur Content with and without FGD

SO₂-Refinery case – daily-figures

In terms of the regulatory point of view or operating conditions of a single site, the imposed or reachable bubble limit has to take into account the huge variable conditions of operations of a refinery site on a daily basis, particularly on the averaging time considerations.

Figure 2 shows the reported daily variation of a calculated SO₂-global bubble of a representative refinery, all units included, and the corresponding daily use of potential fuels within the site. The annual global average SO₂-bubble is 1200 mg/Nm³, ranging from 500 to 2000 mg/Nm³, the daily variation is given for each type of fuels use (low-sulphur fuel oil, high-sulphur fuel oil, vacuum residue, refinery fuel gas).

In order to avoid making the graph overly complex, it does not reflect the fuels sulphur content which is also varying according to the initial sulphur content in crude feedstock, we observe respectively:

- For LS FO, average S % of 0.7 %, ranging from 0.4 to 1 % by month
- For HS FO, average S % of 1.87 %, ranging from 1.1 to 2.3 % by month
- RSV, average S % of 1.94 %, ranging from 0.9 to 2.7 % by month
- Fuel gas (average S % of 0.05 %)
Concawe SO\textsubscript{2} recommended figures

It is recommended to consider yearly averaged value of the SO\textsubscript{2} bubble in order to maintain the flexibility of the process.

We would believe that very challenging global and annual bubbles for SO\textsubscript{2} in the future, based on local conditions and considering the SO\textsubscript{2} emissions of all the units, could range from 1000 to 1400 mg/Nm\textsuperscript{3}. This leaves flexibility to still respond to market constraints and opportunities on the crude oil, the supply/demand situation for oil products and to operate effectively in a very competitive environment. Individual refineries that have the local opportunity to burn gas only and still remain competitive can go to lower values than this.

In order to avoid any negative local impact on neighbouring communities, this daily variation can be locally controlled by alert procedures based on unfavourable weather forecast conditions, resulting in temporary specific operating constraints for the site.

Achieved NO\textsubscript{x} emissions levels

CONCAWE does not have survey data available on the NO\textsubscript{x} emissions. These values are not only dependent on the fuels management but also from the operating conditions (excess air, temperature, etc.) and processes.

a) REAL NEW REFINERY CASE—Daily Variation of NO\textsubscript{x} single stack ELV
As observed for an SO$_2$ bubble, similar large variations are observed on the short-term basis for single stack: the variation is very sensitive, even on a new built refinery, where feedstock is however not so variable.

<table>
<thead>
<tr>
<th>Stack No</th>
<th>Unit</th>
<th>Equipment</th>
<th>Max. heat performance (MW)</th>
<th>NO$_x$ emission per year (mg/m$^3$) as NO$_2$</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Distillation (atm.)</td>
<td>Stack</td>
<td>130</td>
<td>100</td>
<td>56</td>
</tr>
<tr>
<td>1B</td>
<td>Distillation (vac.)</td>
<td>Stack</td>
<td>73</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>3A</td>
<td>Refiner</td>
<td>Stack</td>
<td>86</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>VGO</td>
<td>Stack</td>
<td>66.5</td>
<td>100</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>FCC Regenerator</td>
<td>-</td>
<td>500</td>
<td>80</td>
<td>53</td>
</tr>
</tbody>
</table>

Table 9.26: Real emissions and legal limits of a EU+ refinery
Source: [248, Ademe, 2001]

NO$_x$ Recommended Figures

We would believe that NO$_x$ annual bubble for a good performing existing refinery (mixed gas/liquid-fired) could be 350 to 500 (based on Low NO$_x$ burners on fuel oil accounting for combustion air preheat). NO$_x$ for a new refinery (gas-fired) possibly 200 can be reached.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ratio FO use</th>
<th>S content of FO</th>
<th>Combustion bubble</th>
<th>Global bubble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>30 %</td>
<td>1.7 %</td>
<td>1000</td>
<td>1200</td>
</tr>
<tr>
<td>Scenario 1</td>
<td>30 %</td>
<td>1 %</td>
<td>590</td>
<td>880</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>30 %</td>
<td>0.5 %</td>
<td>395</td>
<td>650</td>
</tr>
<tr>
<td>Scenario 3</td>
<td>100 %</td>
<td>1 %</td>
<td>1960</td>
<td>1050</td>
</tr>
<tr>
<td>Scenario 4</td>
<td>100 %</td>
<td>0.5 %</td>
<td>980</td>
<td>1190</td>
</tr>
<tr>
<td>Scenario 5 + FGD on all units</td>
<td>400 %</td>
<td>3 %</td>
<td>394</td>
<td>650</td>
</tr>
<tr>
<td>Scenario 6 + FGD on 75 % of emissions or major emitters</td>
<td>100 %</td>
<td>2 %</td>
<td>1130</td>
<td>1300</td>
</tr>
<tr>
<td>Scenario 7 + FGD on 75 % of emissions or major emitters</td>
<td>100 %</td>
<td>1.7 %</td>
<td>960</td>
<td>1170</td>
</tr>
<tr>
<td>Scenario 8 + FGD on 50 % of emissions or major emitters</td>
<td>400 %</td>
<td>1 %</td>
<td>1030</td>
<td>1225</td>
</tr>
</tbody>
</table>

Table 9.27: Variation of the Bubble Results from Use of Fuels with Varying Sulphur Content with and without FGD
9.6——Annex VI. Proposals from two Member States on the implementation of BAT in the refinery sector

These are alternative text proposals given by the French delegation and the Italian delegation for some parts of Chapter 5 related with the emissions of SO\(_2\) and NO\(_x\). The main conclusion, as it can be seen, is that the BAT sections on these two pollutants should be driven by the bubble concept. And consequently the BAT related with these pollutants should only be proposals for the achievement of these environmental goals.

9.6.1——French proposals for the structure of some parts of Chapter 5

**General bat, reduction of so\(_2\) emissions**

The French delegation proposes reducing sulphur oxide emissions by the following steps:

1. Mass balance of sulphur, through the whole refinery, to identify the main sulphur streams (indicated in the graph in Figure 10.9 (see at the end of this Section)) and the overall percentage of sulphur recovered (OPSR) in an inert form or trapped in products in an inert form (OPSR: methodology tool used to appreciate the influence of a technical measure on the sulphur balance)

2. Quantification of the sulphur emissions of the different refinery sources being part of S2 and S4 in order to clarify the bubble concept and to identify the main emitters in each specific case

3. Selection, among the different technical options indicated below (described more precisely in the specific BAT), the technical measures allowing to achieve the following global indicative reference values (bubble benchmark)

   - 600 mg/Nm\(^3\) (Monthly average),
   - 850 mg/Nm\(^3\) (Daily average),

   considering the possible cross-media (extra energy consumption, production of waste and water effluents, atmospheric emissions outside the refinery, increase of residue production, etc...) and the cost effectiveness.

Possible technical measures which could be implemented to fulfill the global environmental goal include the following:

- switch to gaseous fuels if no other reasonable option can guarantee a better evolution of the OPSR,

- improvement of gaseous and liquid fuels and feeds characteristics,

- use of flue gas desulphurisation promoting regenerative techniques or techniques leading to products which can be valorised and trapping sulphur in an inert form (This amount of sulphur has to be taken into account in the OPSR evaluation),

- DeSOx catalyst for the FCC,

- maximisation of the sulphur stream S6,

- flaring optimisation,

- treatment of non condensable gases from the vacuum ejectors

Due to the specific characteristics of the sulphur recovery units for flue-gases, it is additionally considered that BAT is also to apply the specific BAT defined for this type of unit (see Section 5.2.23).

The overall sulphur strategy should also lead to minimise S7 by increasing the conversion of products without specifications with processes like cokers, hydrocracking, gasification, etc..., by improving the characteristics of these products or by having an external use ensuring that the environmental impact is minimised (cement plants, conversion in another refinery for example). This kind of external use has also to be taken into account in the OPSR calculation.
General BAT reduction of \( \text{NO}_x \) emissions
The \( \text{NO}_x \) BAT implementation process needs a prior quantification and characterisation of the emission sources. It follows, having in mind an environmental goal for the whole refinery (150 mg/Nm\(^3\) (Monthly average), 200 mg/Nm\(^3\) (Daily Average)), definition of the priorities to reduce the global emission level taking into account environmental benefits, cost effectiveness and cross-media effects.

Primary measures have generally the highest cost effectiveness but also limited performances especially for liquid fuels. These measures can easily be implemented for new units but may raise important integration problems with existing units. Given the limited cost of this type of measure its promotion may be encouraged where possible.

The limited performance of the primary measures makes necessary to consider secondary measures, whose cost effectiveness considerations are of great importance. Its implementation should be restricted to the main sources, e.g. these representing about 80\% of the emissions of the whole refinery. Secondary measures includes three main abatement techniques: Reburning, SNCR (Selective non catalytic reduction) and SCR (Selective catalytic reduction) with a range of efficiencies (50 to 60 \%, 50 to 70 \% and 80 to 90 \%) and costs per tone of pollutant abated.

BAT can be considered an average abatement rate of 70 \% for the sources representing 80 \% of the whole emission of a refinery. According to the principles described above, the combination of primary and secondary measures allows to reduce the global rough emission level of a refinery by 60 80 \% and to achieve average emission levels in the range of 100-150 mg/Nm\(^3\) on a long-term period.

Other techniques, such as catalytic combustion, or oxyfiring, may need also consideration and could represent relevant technical measures to achieve the global BAT emission level above mentioned.

Other technical options have been implemented in some world areas to achieve lower emission levels. In a refinery in California there was a switch from liquid to gaseous fuels and implementation of secondary measures on gas-fired units, achieving 20-30 mg/Nm\(^3\). In Japan it has been applied hydrotreatment of liquid fuels and feeds combined with the implementation on an important number of SCR units, achieving 60-65 mg/Nm\(^3\).

However, although this type of environmental goal may be locally justified, it is not considered that these experiences represent at the time of writing a general level of BAT in the EU framework because of the direct cost of these measures and the other investments required to manage the great amount of residues produced or to improve their characteristics.

Catalytic cracking new structure
In most cases, the catalytic cracking is a source contributing to a large extend to the emission of \( \text{SO}_x \), \( \text{NO}_x \), dust, metals, CO and \( \text{SO}_2 \) of a refinery. Some measures on this specific unit may be considered fully justified from an environmental point of view in all cases but others have to be evaluated in the global framework of the refinery. For this reason, this section has been splitted in specific BATs and technical options to consider in the global framework of the refinery.

The specific BATs include:

1. A CO furnace boiler for partial oxidation conditions. The associated emission levels are less than 50 mg/Nm\(^3\) for CO and between 100-300 mg/Nm\(^3\) for \( \text{NO}_x \) (see Section 4.5.3),
2. A monitoring and control of the oxygen excess (around 2 \%) for the full combustion mode. The associated emission levels are between 50-100 mg/Nm\(^3\) for CO and between 300-600 mg/Nm\(^3\) for \( \text{NO}_x \) (see Section 4.5.1),
3. A reduction of particulates emission in the range 10-30 mg/Nm\(^3\) (metals (Ni, V, etc...) less than 5 mg/Nm\(^3\)) by a suitable combination of the following techniques:
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- then BAT on particulate emissions
- text BAT on energy conservation,
- text BAT on reduce discharges to water,
- text BAT on reduce waste generation,
- a yearly monitoring of the \( \text{N}_2 \text{O} \) emissions of the regenerator.

In addition, the FCC unit may be a major source of \( \text{NO}_x \) and \( \text{SO}_x \). In this case, several technical options described below have to be considered and evaluated alone or in combination:

- the hydro-treatment of the feedstock (economical and technical viability are described in the Section 4.5.4). The main purpose of this technique is to reduce the sulphur content of the feed but this option has also a positive influence on \( \text{NO}_x \)-metals and on the product quality. Most units around the world (California for example) are designed to achieve 300 to 500 ppm in the feedstock,
- flue-gas desulphurisation; depending on the process considered and the running conditions, the abatement rate may vary between 50 and 90 %. These techniques may produce large amounts of residues and water effluents,
- \( \text{DeSO}_x \) catalyst. This technique may have a limited efficiency and involves an important consumption of catalyst. This option is probably more suitable to solve peak pollution problems,
- \( \text{DeNO}_x \) measures such as SCR (abatement rate between 80-90 %) and SNCR (abatement rate between 50 and 70 %) (these techniques have an associated emission of ammonia which can be limited to 10 mg/Nm\(^3\) and it has to be pointed out that SCR is much more common for FCC units than SNCR) or modifications concerning the design of the unit which can induce a trade-off between \( \text{NO}_x \) and CO emissions.

These technical options allow thus to achieve ranges as low as 50—200 mg/Nm\(^3\) for \( \text{SO}_2 \) as \( \text{SO}_x \) and 50—100 mg/Nm\(^3\) for \( \text{NO}_2 \) as \( \text{NO}_x \). Their combination has to be optimised concerning performances in regard of the different parameters, energy consumption, waste and water effluents and cost effectiveness. They may not be justified in all refinery frameworks but have to be considered to fulfil the whole environmental goal of a refinery.

**BAT process per process energy system**

The energy system is the main source of air pollution of a refinery, however, due to the diversity of the units used (boilers, furnaces, turbines), their characteristics (size, age, type of burners, purpose) and their running conditions (air preheat, fuels used, temperature requirements, oxygen excess and type of control), the strategy to reduce the environmental impact of these units can only be given by the general guidelines described below.

Firstly, it is necessary to have an overview of the fuels used by the refinery, types of combustion units and characteristics of the air emissions (concentration and mass flow) for the main pollutants (\( \text{SO}_x \), \( \text{NO}_x \), dust, metals, carbon oxides).

On these bases, the first step is to consider technical options which seems totally justified from an economical point of view. This category includes specific BATs such as:

- the use of clean refinery gaseous fuels (\( \text{H}_2 \text{~S} \) content between 20 and 100 mg/Nm\(^3\))
- the reduction of \( \text{CO} \) emissions below 50 mg/Nm\(^3\) with efficient combustion techniques, the reduction of dust emissions in the range 10—20 mg/Nm\(^3\) (metal content (\( \text{Ni}, \text{~V}, \text{etc} \) below 5 mg/Nm\(^3\))—applying the suitable following combination of techniques (improvement of fuel characteristics, steam atomisation for liquid fuels, ESP or bag filter),
- the use of primary \( \text{DeNO}_x \) measures for new units, existing ones when these measures can be implemented quite easily and in the other cases during the major rebuilding of these units. The achievable emission levels with primary \( \text{DeNO}_x \) techniques are the following: Gaseous fuels (30 to 100 mg/Nm\(^3\) for boilers and heaters, 50 to 100 mg/Nm\(^3\) at 15 % \( \text{O}_2 \))
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- for gas turbines—the lowest values are more likely achieved with natural gas and the highest with refinery fuel gas but a lot of other parameters may influence the performance level), liquid fuels (200 to 400 mg/Nm$^3$ for boilers and furnaces—the performance level is mainly influenced by the nitrogen content of the fuel even if other parameters need also to be considered.

- It is also considered in this category to (add Section 101).

The second step consists of analysing the relevancy of the following basket of techniques in the global framework of a refinery concerning NO$\textsubscript{x}$ and SO$\textsubscript{x}$ for the main sources (see SO$\textsubscript{x}$ and NO$\textsubscript{x}$ sections of the general BAT):

- improvement of liquid fuels and feeds characteristics,
- use of flue-gas desulphurisation promoting regenerative techniques or techniques leading to products which can be valorised and trapping sulphur in an inert form,
- switch to gaseous fuels if no other reasonable option can guarantee a better evolution of the overall percentage of sulphur recovery (OPSR), of the amount of residue produced and of the SO$\textsubscript{x}$-NO$\textsubscript{x}$ and dust abatement rates. It has to be reminded that gaseous fuels having a higher ratio H/C contribute to lower the SO$\textsubscript{2}$ emissions,
- reburning (for boilers and furnaces), SNCR (Selective non catalytic reduction) and SCR (Selective catalytic reduction) with various efficiencies (50 to 60 %, 50 to 70 % and 80 to 90 %) and costs per tone of pollutant avoided.

These last two techniques induce NH$\textsubscript{3}$ emissions which can be kept below 10 mg/Nm$^3$. The application of these techniques or of a combination of these techniques may allow to achieve emission levels lower than 50 mg/Nm$^3$ for NO$\textsubscript{x}$ (as NO$\textsubscript{2}$) and 100 mg/Nm$^3$ for SO$\textsubscript{x}$ (as SO$\textsubscript{2}$) on any kind of the energy system sources, but the partial or complete implementation of these options on a specific unit has to be examined in the global framework of the refinery.

The technico-economic analysis may lead to select a less ambitious option concerning performances allowing nevertheless to achieve the global environmental target at the refinery level. On the contrary, better performances may be proposed through technical options like catalytic combustion for turbines (NO$\textsubscript{x}$ level lower than 2.5 ppm).

BAT for storage

First proposal is to define an upper limit (volume and pressure) to store a liquid in another way than a pressurised tank designed to prevent any direct organic vapour loss to the atmosphere (connection to a vapour recovery unit with an efficiency of more than 95 %). This limit could be 70 kPa concerning the pressure under storage conditions and 150 m$^3$ for the volume.

Then, a second limit (volume: 150 m$^3$ and pressure under storage conditions: 3.5 kPa) could be indicated concerning the following technical choices: pressurised tank designed to prevent any direct organic vapour loss to the atmosphere (connection to a vapour recovery unit with an efficiency of more than 95 %) or external floating roof with two seals (one above the other) or for new fixed roof storages connection to a vapour recovery unit with an efficiency of more than 95 % and for existing fixed roof storages installation of an internal floating-type cover with two seals or connection to a vapour recovery unit with an efficiency of more than 95 %.

For storages non connected to a vapour recovery unit, BAT is also to paint the external walls and the roof with a material having a radiant heat reflection index of at least 70 %. This BAT could apply to facilities that load organic liquids with a vapour pressure higher than 10500 Pa under loading conditions. Continuous monitoring concerning the vapour recovery unit emissions should also be considered.
9.6.2 Italian proposals for the structure of some parts of Chapter 5.

BAT for the Energy System:

- flue gas Desulphurisation, SCR, SNCR, Electrostatic Precipitators should be considered only options that can be used to meet the bubble limits and not techniques that must be used in any case in conjunction with the high sulphur fuel oil
- providing that the bubble limits are respected, high sulphur fuel oil (3% max. sulphur content) can be used without any other limitation (FGD). High concentration emissions from one stack can be balanced by low concentration emissions from other stacks. Possible health concerns for refinery workers should be considered at local level.
9.7 Description of zeolites

Zeolites are widely used in industrial processes or laboratory (Sherman, 1999). Zeolites are microcrystalline aluminosilicates of natural or synthetic, whose structure is formed by rings consisting of tetrahedral AlO$_4$- and SiO$_4$ are interconnected by oxygen atoms. The negative charges of Tetrahedrons-AlO$_4$ cations are compensated by the compensation, present in various locations within the porous structure, which may be replaced by other cations by ion exchange full or partial (Breck, 1974).

The structure of zeolites is an open structure with large pores and channels. After complete dehydration of a zeolite, the channel can be filled with a variety of other molecules. The adsorption process is selective and depends on the particular structure of the zeolite and the size of molecules to be adsorbed. For this reason, zeolites are also called 'molecular sieves'. Depending on the number of oxygen atoms that form the openings of pores, zeolites can be classified into pore zeolites extra large (>9 Å), large pore zeolites (6 – 9Å), mean pore zeolites (5 -6 Å) and small pore zeolites (3 – 5 Å), where access to the interior of the pore takes place, respectively, through rings 18, 12, 10 or 8 atoms of oxygen (Giannetto, 1990).

The acidity of zeolites is a very important property that depends not only on the material structure, but also other parameters such as total number of Brönsted acid sites and Lewis, and the strength and location of these centers (Serralha, 2001).

The Brönsted acidity is based on the existence of protons as cations compensation. This type of acid depends strongly on the structure and topology of zeolite, the chemical composition and surrounding environment, particularly the molar ratio Si/Al.

There is usually an increase in the strength of Brönsted acid sites with increasing Si/Al ratio. The NaY zeolite has a Si/Al ratio greater than 1.5 (Giannetto 1990), NaA zeolite and a ratio of 1, it is less acidic.
9.8 Soil and groundwater monitoring – An example

Text moved from 4.15.8

Description
See also Section 3.28.
As illustrated in Figure 9.9, the primary objective of a groundwater monitoring network is to:

• provide an access point for measuring groundwater levels;
• collect samples that accurately represent in situ conditions at the specific point of sampling.

![Figure 9.9: Example of a monitoring network in a case of a groundwater pollution](image)

Achieved environmental benefits
When properly designed and implemented, a groundwater monitoring system allows to:

• determine the flow direction and groundwater table profile;
• detect the release of pollutants from a suspected or known source;
• determine the extension of the polluted area;
• help design a management strategy and monitor the effectiveness and efficiency of its implementation;
• act as an alert system (in the event of plume advancement);
• extrapolate the concentration of pollutants in the contaminated area and support a risk assessment.

Cross-media effects
Two important points are to be considered when a monitoring network is implemented:

• the risk of cross-contamination of adjacent groundwater, from one borehole to another and/or vertically within a borehole from a contaminated to an uncontaminated zone;
• the cross-contamination of an adjacent surface water with contaminated purge groundwaters should be prevented. Adequate measures should be taken, and permits should be obtained for the disposal or release of related effluents.
Operational data
The different steps and operational data required to define, implement and use a groundwater monitoring network can be summarised as explained in Figure 9.10. The installation of an adequate monitoring network (steps 1 to 3) is an iterative process, and the interpretation of results (step 6) can lead to modify it.

Steps 1:
the concept model is based on a preliminary analysis of data that should be collected on the following aspects, among which:

- geologic and hydrogeologic conditions (fractured, alluvial or karstic);
- existing observation wells (piezometers), taking into account the eventual accumulation of sediments at the bottom of the well;
- potentially contaminating substances (volatile, miscible or immiscible contaminants), classified as light non-aqueous phase liquids (LNAPLs) or dense non-aqueous phase liquids (DNAPLs);
- other anthropogenic influence (existing pollution, pumping well, irrigation…);
- public priority protection targets.

**Figure 9.10: Main steps for the implementation of a groundwater monitoring system**

**Step 2:**
This information affects the second step and the monitoring design/strategy, in particular on the well locations, screening levels, drilling and installation methods, selection of parameters, purging and sampling frequency and procedures. Usual frequencies are in the range 2 – 6 months, site-specific adaptation may be needed. At this stage, particular precautions and related operational choices may be taken, in particular:

- for each pathway monitored, the implementation of a minimum 3 wells is required (1 upstream for comparison of upgradient conditions to background quality, and 2 downstream for allowing groundwater flow direction by triangulation. (See Figure 9.11);
- in the presence of pure phase, inappropriate purging can lead to redistribute or spread the contaminants: low flow purging is thus recommended (micropurging);
• for a DNAPL, sampling may also need to be performed at the bedrock of the aquifer in order to ensure collecting contaminated groundwater from the plume (as illustrates in Figure 9.12).
• a low-flow sampling method should be preferred in case of volatile compounds. Other specific procedures based on local expert requirements can be used to achieve the same results.

NB: groundwater levels data must be synchronous.

Figure 9.11: Good practice to determine the flow direction and sense

Figure 9.12: Example of DNAPL plume migration in groundwater

Steps 3 to 4: Appropriate standards or guidances might be followed, as for example the ‘Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells’ (US EPA, March 1991) and the ISO 5667 – 11 ‘Guidance on sampling of groundwater’. Laboratories performing the analyses should be accredited for each substance analysed and must achieve the analytical performances settled down (i.e. limit of quantification). Quality control procedures should also cover the prevention of drilling and sampling equipment contamination.

In the case of oil refineries, the following measures and precautions should be in particular taken:
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- the monitoring of the following parameters and substances can be recommended (to be adapted to the context): BTEX, PAH, Total Petroleum Hydrocarbons, pH, temperature and conductivity;
- well construction materials (PVC or HDPE) should be selected in order not to interact with contaminants or modify the composition of the groundwater;
- on sites with aged contamination, multilevel sampling wells can be used for sampling, in order to be able to draw a detailed three-dimensional groundwater contamination profile (e.g. DNAPL).

Steps 5 to 6: the presentation of results will be facilitated using cartographic tools for piezometric and plume mapping, and chronicles of piezometric and concentration data. Figure 9.13 shows an example of groundwater level map based on a rather large number of piezometric wells, and developed using a kriging interpolation software; the rectangle corresponds to the refinery footprint. In more simple cases based on a 3 – 4 set of piezometers, an interpolation may be achieved only by triangulation. Seasonals evolution should be taken into account for the interpretation of these results.

Figure 9.13: Example of groundwater levels map indicating the flow direction and sense (kriging interpolation)
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Applicability
Applicable to any new and existing refinery or part of refinery.

Economics
The cost of this technique varies very much, depending in particular on the number of monitored wells, substances, and measuring campaigns.
As an example, the cost for the implementation of three piezometers at a depth of 8-10 metres (for alluvial aquifer) is estimated (2010) around EUR 8 000 – 12 000 for the steps 1 to 3. The cost of a campaign (3 piezometers, sampling, analysis and interpretation), for steps 4 to 6, is estimated around EUR 1 500 – 2 000 for the monitoring of BTEX, PAH, Total Petroleum Hydrocarbons, pH, temperature, conductivity. The monitoring campaign is usually realised twice a year.

Driving forces for implementation
Prevention and early detection of groundwater pollution. Monitoring of old site historic contamination in order to prevent, reduce and manage potential or actual health and environmental impacts.

Example plants
In France, groundwater monitoring is applied in all refineries.

References
[ 38, INERIS 2009 ] TWG FR 2010
9.9 Air emissions - Bubble approach: a methodology
Text proposal from EIPPCB after considering outcomes of TWG subgroup meetings (May 2010 and May 2011), comments and contributions from TWG received on this topic.
This annex includes 4 appendix named A to D

Introduction
To prevent emission of pollutants in the atmosphere, REF BREF proposed AEL for specific refining process or combustion.
One operator could take appropriate measures in order to comply with these values ‘stack by stack or unit by unit’.
A specific approach based on a ‘bubble concept’ can nevertheless be used by the competent authority to regulate one refining site. It will lead to define a single value as a target for the refiner as a whole.

This approach takes into account the specificity of refining sector, in particular the following factors:

- the recognised complexity of refining sites, with multiplicity of combustion and process units, often interlinked for their feedstock and energy supply
- the frequent (e.g. weekly or even daily) process adjustments required in function of the quality of the crude received
- the technical necessity for many sites to keep burning a part of their internal residues as energy fuels, and to frequently adjust the site fuel mix according to process requirements
- the need for enabling, quantifying and monitoring a net site-level emission reduction for sites where some key specific installation controls are not possible and have to be compensated elsewhere

This approach consists of considering all concerned emissions together, as emitted through a single ‘virtual single stack’.
This approach assume, as prior condition, that the global result on environment should be at least as efficient as if BAT AEL were achieved for every individual processes.

Main definition of the concepts used

What is the ‘bubble approach’ and how it could be applied in a refinery?

the ‘bubble’ approach is a generic tool for expressing and comparing the level of performance achieved or expected at refinery site level, from a clearly identified set of combustion and process units, and for a given substance or parameter.

Bubble perimeter
The exact bubble perimeter to be considered for a given site will depend on the site processes. In the purpose of this document, this methodology is designed to cover, all sources of permanent emissions of a refinery (i.e. combustion plants, cat crackers, sulphur recovery units, coke calciners and other processes where appropriate) as indicated in paragraph 2.

Bubble substances or parameters covered
Based on the work undertaken in 2009 – 2010 for the revision of this document, SO₂ and NOₓ have been recognised as the two parameters which deserve in priority a common methodology for a site-level bubble-expressed AEL calculation, and for which enough supporting information and data have been provided. Therefore the current methodology will address specifically these two substances.
Bubble averaging period
In the particular context of this document, the methodology proposed has been based primarily on a **yearly average**, since a long term period has been considered as the most appropriate for reflecting best performances achievable in normal operating conditions, and giving enough time and flexibility in order to integrate necessary feedstock, process and fuel adjustments. However, the efficient control of a yearly bubble requires a very frequent or continuous monitoring regime of all emissions concerned. A shorter term bubble can, therefore, be derived from the long term bubble using monitoring results. As real examples of bubble regulations already used by some Member States show, an associated **daily average** could be useful.

Methodology to set a bubble level based on individual BAT AEL

The site-level bubble is expressed as a sum of two terms:

- **a first term related to the energy system**, including at least all furnaces, standalone boilers, central CHP or conventional power plants, and gas turbines. This term is driven by suitable AEL concentration ranges expected on each category of installations. It includes emissions from internal power plant where energy is exported and excludes emissions from external (out of permit) power plant.

- **a second term related to the process units** including at least FCC UNIT if any, and SRU. This term should be driven by suitable AEL concentration or specific emission ranges expected on each of them when BAT is applied. It includes emissions from coking: green coke calcination, fluid coking, emissions from SRU (specially SO₂) and PERMANENT emissions of flaring (pilot flames). It excludes emissions from SWS and incondensable untreated gases.

\[
\text{Site Bubble} = \frac{\text{Energy system term} + \sum \text{process units terms}}{	ext{FLcomb x [Comb] + FLfCC x [FCC] + FLSRU x [SRU] + FLother x [other]}}
\]

In the context of this document and for the purpose of expressing meaningful AEL at site level, the bubble determination should always be based on concentration and specific emission ranges expected on all concerned installations when BAT is applied, and should involve the following steps:

1. **Step1.** Exhaustive identification and geographical mapping of all included sources to be done according to Appendix A
2. **Step2.** Determination of the off-gas volumetric contributions expected from all included sources to be done according to Appendix B
3. **Step3.** Determination of the mass contributions expected from all included sources to be done according to Appendix C
4. **Step4.** Determination of the bubble-associated monitoring regime to be done according to Appendix D
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APPENDIX A ON ‘GOOD PRACTICES’ FOR IDENTIFICATION AND MAPPING OF ALL INCLUDED SOURCES

Introduction

Reminder of global methodology steps:

Step 1. Exhaustive identification and geographical mapping of all included sources
Step 2. Determination of the off-gas volumetric contributions expected from all included sources
Step 3. Determination of the mass contributions expected from all included sources
Step 4. Determination of the bubble-associated monitoring regime

The first step of the methodology is crucial as the following steps (calculations) will depend on a clear identification of the sources included in the bubble.

Exhaustive listing of all emitting source (stacks) under the considered bubble area (energy production and processes) including:

- Quick estimation of emission levels for the considered emitted substance (e.g. by using emission factor)
- Prioritizing the sources by ranking
- Listing the currently used monitoring and required for the corresponding source

Methods

Refers to existing mapping e.g. for CO₂ emission trading scheme (ETS) taking into account:
- to get in all combustion processes and identify these using ‘non standard fuels’
- to get in all refining processes as far as they are in the bubble area
- to get out processes that could be on site but are not properly refining, e.g. steam cracker (petrochemical)

Report on map and table all the available operational data (flue-gas volume, load, average or spot concentration measurements,…)

APPENDIX B ON VOLUMETRIC GAS ESTIMATION

Summary of proposed standard flue-gas factors for the bubble calculation

<table>
<thead>
<tr>
<th>Source</th>
<th>Fuel or process feed</th>
<th>Flue-gas factor (dry gas) at 3 % O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion</td>
<td>Refinery fuel oil (RFO)</td>
<td>12.3 Nm³/kg foe(1)</td>
</tr>
<tr>
<td></td>
<td>Refinery fuel gas (RFG)</td>
<td>11.3 Nm³/kg foe</td>
</tr>
<tr>
<td>Sulphur recovery unit (SRU)</td>
<td>Acid gas</td>
<td>1 500 Nm³/t feed</td>
</tr>
<tr>
<td>Fluid catalytic cracking (FCC)</td>
<td>Coke</td>
<td>12.3 Nm³/kg foe</td>
</tr>
<tr>
<td>Coking process</td>
<td>Green coke calcination</td>
<td>Reported as from 1.8 to 3 Nm³ per tonne of coke feed</td>
</tr>
<tr>
<td>Flaring (permanent emissions)</td>
<td>Use combustion emission factor</td>
<td>[ ?? ]</td>
</tr>
<tr>
<td>Sour water stripper (SWS)</td>
<td>flue-gas and non condensables</td>
<td>Not included in the bubble</td>
</tr>
</tbody>
</table>

(1) kg foe: kg of fuel oil equivalent = 41.868 MJ (IEA defines tonne of oil equivalent to be equal to 41.868 GJ)

Source: [77, REF TWG 2010] [127, France 2010]

Calculation details and general explanations

A. 1 FLUE-GAS FLOWRATE - GENERAL

Flue-gas flow rate is rarely measured directly.
Where this is the case the uncertainty in the result of the measurement must be established through a duly documented investigation.

B.1.1 EXPRESSION OF MEASUREMENTS

In all circumstances the quantity of flue-gas has to be expressed under the same conditions as the other parameters to which they relate.
As far as temperature and pressure conditions are concerned, normal conditions will be systematically used, namely:

- Temperature = 273.15 K or 0°C
- Pressure = 101 325 Pa or 1 atm

The normal written form will be used to express these conditions, preceding the unit of volume by the letter N: for example Nm³.
Conversely, the conditions of flue-gas composition in which measurements are expressed will be systematically specified:

- water content: actual content or corrected to 0 % (dry flue-gases),
- oxygen content: actual content or content corrected to a standard value (0 %, 3 % or other value).

Conversion formulae relating to flue-gas composition:

Dry flue-gas flow = wet flue-gas flow x (1- % water in the flue-gas)
Flow at y % O₂ = flow at x % O₂ * (21-x)/(21-y).

B.1.2 USING THE RESULTS
Annexes

Flue-gas flows are used to calculate the quantities of pollutants emitted based on an analysis of flue-gases. **Special care must be taken to ensure that the 2 terms of the product are expressed using the same units and conditions.**

B.2 FLUE-GASES FROM FURNACES AND BOILERS (COMBUSTION)

B.2.1 GENERAL

Flue-gases emitted by these items of plant originate from the combustion of fuels and possibly other fluids.

*The rule below is to be used for fuels: Flue-gas flow = fuel flow x flue-gas factor*

The flow of fuel is to be measured in accordance with the rules described before. Flue-gas factor represents the quantity of flue-gases produced per unit fuel. It is often expressed as Nm³ of dry flue-gas corrected to 3 % O₂ per standard tonne (or tonne of oil equivalent - it is convenient when summing flue-gas volumes generated by different types of fuels (e.g. solid, liquid, gaseous) to express the mass of fuel consumed as tonnes of oil equivalent (toe). The International Energy Agency defines one tonne of oil equivalent (toe) to be equal to be 41.868 GJ, as a result of which an approximate fixed factor can be used regardless of what the fuel is.

The standard flue-gas factor approach is not however sufficiently accurate for complying with the level of uncertainty required by the EU ETS provisions. Statutory obligations for drawing up CO₂ balances have led refineries to obtain a better understanding of the atomic composition of the fuels which they use. The calculations proposed below are based on these characteristics.

B.2.2 FLUE-GAS FACTOR FOR LIQUID FUEL OILS

Liquid fuel oils are analysed on the basis of their compositions by mass:

\[ a \% C + b \% H + c \% S + d \% N + e \% O \]

QFO flue-gases = \[ 0.0889 \times C \% + 0.211 \times H \% + 0.0333 \times S \% + (6.8 \times k + 0.8) \times N \% - 0.02630 \times O \% \] x \( \frac{21}{18} \frac{\text{MJ}}{\text{kg}} \) /NCVFO (MJ/kg)

In Nm³/kg of fuel oil equivalent at 3 % O₂ dry gases

With k the proportion of nitrogen which is wholly oxidised.

**Examples:**

For k = 0.2 (typical value)

The fuels in the table have been taken from the Heavy Fuel oils department survey and the refinery FO analysed in the context of the CO₂ balance.
Corrected stoichiometric formula for nitrogen with a nitrogen % oxidised to 20 % NO₂ (in Nm³/kg)

\[ V_f = 0.0889 \text{ C %} + 0.211 \text{ H %} + 0.0333 \text{ S %} + 0.0216 \text{ N %} - 0.0263 \text{ O %} \]

<table>
<thead>
<tr>
<th></th>
<th>C %</th>
<th>H %</th>
<th>S %</th>
<th>N %</th>
<th>Nf as Nm³/kg neutral</th>
<th>NCV as th/t</th>
<th>Vf as Nm³/kg at 3 % O₂ dry gases</th>
<th>Vf as Nm³/kg foe at 3 % O₂ dry gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF dept FO survey of LSC</td>
<td>87.8</td>
<td>10.2</td>
<td>1.6</td>
<td>0.4</td>
<td>10.02</td>
<td>9650</td>
<td>11.69</td>
<td>12.11</td>
</tr>
<tr>
<td>HF dept FO survey of HVF</td>
<td>86.8</td>
<td>10.1</td>
<td>2.4</td>
<td>0.7</td>
<td>9.94</td>
<td>9400</td>
<td>11.60</td>
<td>12.34</td>
</tr>
<tr>
<td>HSC type HVF</td>
<td>85.5</td>
<td>10.0</td>
<td>3.5</td>
<td>1</td>
<td>9.85</td>
<td>9200</td>
<td>11.49</td>
<td>12.49</td>
</tr>
<tr>
<td>LSC type HVF</td>
<td>87.5</td>
<td>10.5</td>
<td>1</td>
<td>1</td>
<td>10.05</td>
<td>9500</td>
<td>11.72</td>
<td>12.34</td>
</tr>
<tr>
<td>‘LSC’ FO</td>
<td>87.3</td>
<td>12</td>
<td>0.5</td>
<td>0.2</td>
<td>10.31</td>
<td>9900</td>
<td>12.03</td>
<td>12.15</td>
</tr>
</tbody>
</table>

HF = Heavy Fuel oil  
LSC = Low sulphur content  
HSC = high sulphur content  
HVF = high viscosity fuel

It will be noted that there is very little variability in flue-gas factor for liquid fuels. Analysis of liquid fuels composition is performed 6 to 12 times a year.

Flue-gas factor for the calculation of the bubble (combustion component):

Based on the above, it is proposed to take the typical value of 12.3 Nm³/kg of fuel oil equivalent at 3 % O₂ (dry gases) as a standard flue-gas factor for liquid fuels.

B.2.3 FLUE-GAS FACTOR OF GASEOUS FUELS

FG are analysed on the basis of their mass composition:  
a HC + b H₂ + c inerts  
Hydrocarbons are written as the generic form CnHp

\[ Q \text{ flue-gases} = (a \times (4.76n + 0.94p) + b \times 1.88 + c) \times \frac{22.4}{(a \times (12n + p) + b \times 2 + c \times 28)} \]  
as Nm³/kg

This flue-gas volume is expressed per kg of fuel gas at 0 % O₂ (neutral combustion) on dry gases.  
In order to have the factor expressed in Nm³/kg foe, the result has to be divided by the fuel Net Calorific Value.  
See above the formula to convert the result at a different O₂ content.

Examples:
The table below also indicates the Net Calorific Values for the various molecules and expresses flue-gas factor (dry gases) in relation to quantity of energy.
The table below provide values for a typical FG corresponding to the averaging of 700 measurements of different FG with varying composition. The measurements were performed on 12 different units coming from 3 refineries (average of 58 measurements for each unit).

<table>
<thead>
<tr>
<th>%vol</th>
<th>MM</th>
<th>%m</th>
<th>Dry flue-gas at 3 % O₂ Nm³/kg dry gases</th>
<th>NCV</th>
<th>Dry flue-gas at 3 % O₂ Nm³/kg std dry gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>25.0%</td>
<td>16</td>
<td>23%</td>
<td>13.92</td>
<td>50.01</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>19.0%</td>
<td>30</td>
<td>33%</td>
<td>13.23</td>
<td>47.79</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>7.0%</td>
<td>44</td>
<td>18%</td>
<td>12.95</td>
<td>46.36</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>3.5%</td>
<td>58</td>
<td>12%</td>
<td>12.81</td>
<td>45.75</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>1.0%</td>
<td>72</td>
<td>4%</td>
<td>12.70</td>
<td>45.35</td>
</tr>
<tr>
<td>H₂</td>
<td>40.5%</td>
<td>2</td>
<td>5%</td>
<td>24.57</td>
<td>120</td>
</tr>
<tr>
<td>N₂</td>
<td>3.5%</td>
<td>28</td>
<td>6%</td>
<td>0.93</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>0.5%</td>
<td>28</td>
<td>1%</td>
<td>2.47</td>
<td>10.11</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>17.5</td>
<td>100%</td>
<td>13.02</td>
<td>48.07</td>
</tr>
</tbody>
</table>

Flue-gas factor for the calculation of the bubble (combustion component):

*Based on the above, it is proposed to take the typical value of 11.3 Nm³/kg of fuel oil equivalent at 3 % O₂ (dry gases) as a standard flue-gas factor for gaseous fuels.*

**B.3 FLUE-GASES FROM SOUR WATER STRIPPER (SWS) GASES**

Flue-gases from SWS gases and incondensables are not taken into account in the calculation of the flue-gas volume used for determining the bubble.

As it has been considered that such practices cannot be BAT, including such emissions in a permanent bubble calculation could have a counter productive effect by tolerating them over time and preventing the operator to take drastic actions.
B.4 FLUE-GASES FROM SULPHUR RECOVERY UNITS

The calculations are a simplified formulation based on the flow of acid gas (AG) feeding the unit. The molar composition of acid gas is modelled as three main families, to which ammonia must be added if SWS gases are treated: a H₂S + b HC + c inert.

Where:

\[ a = \%_v H_2S \]
\[ b = \%_v \text{hydrocarbons} \]
\[ c = \%_v \text{inerts} \]
\[ a + b + c = 1 \]

For simplicity the HC are considered to be C2H6 (MM= 30) and the inert components are essentially CO₂ (MM = 44). These approximations generally have little effect on the result (with a low HC content).

B4.1 MAKE-UP FUEL GAS

Fuel Gas (FG) is injected in the incinerator in order to entirely burn residual H₂S. The flow of FG is represented by the ratio: \( j = \%_m \text{of FG to AG} \)

B.4.2 ANALYSERS

Gas analysers are mainly:

- H₂S and SO₂, in the tail gas (TG) downstream of the main reaction zone,
- SO₂ and O₂ in the flue-gas at the exit of the incinerator.

In the following, unless specified otherwise, concentrations are given on dry gases.

B.4.3 CALCULATIONS

Taking into account the actual conversion in the sulphur unit, the molar flow (corresponding to 1 Mol of AG) of the dry residual gas for 0 % O₂ is:

\[ f = Q_{\text{TG mol}} = \frac{1.88a + 15.2b + c}{1 - 4.76*%\text{SO}_2\text{TG} + 0.88*%\text{H}_2\text{S TG}} \]

Flue-gas volume exiting the incinerator:

\[ Q_{\text{incin vol}} = (1 + 5.64 \times %\text{H}_2\text{S TG}) \times \frac{1.88a + 15.2b + c}{1 - 4.76*%\text{SO}_2\text{tg} + 0.88*%\text{H}_2\text{S tg}} + j \times Q_{\text{GA}} \times 1000 \times PF \text{ (Nm}^3\text{/h of dry flue-gas at 0 % O}_2\text{)} \]

Examples:

a) Complete conversion:

<table>
<thead>
<tr>
<th>Molar composition</th>
<th>H₂S</th>
<th>HC</th>
<th>Inerts</th>
<th>MM AG</th>
<th>Mol flue gas/mol AG</th>
<th>Flue-gases Nm³/t AG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>34</td>
<td>1.88</td>
<td>1 239</td>
</tr>
<tr>
<td>Case 2</td>
<td>90%</td>
<td>0.5%</td>
<td>9.5%</td>
<td>35</td>
<td>1.86</td>
<td>1 208</td>
</tr>
<tr>
<td>Case 3</td>
<td>80%</td>
<td>1%</td>
<td>19%</td>
<td>36</td>
<td>1.85</td>
<td>1 178</td>
</tr>
</tbody>
</table>

In the table above, cases 1 and 3 correspond to extreme values: case 1 would be an AG flux originating from amine treatment of FG, while case 3 would be an AG flux from an FCC, with a...
Annexes

high CO₂ content. In practice these fluxes are mixed and case 2 reflects a typical AG composition.
Flue-gas factor increases inversely with the inerts content and in the same direction as HC concentration. In the 3 situations above the 2 parameters partly cancel out and the resulting variability is small.

b) Actual conversion:

Qvol dry flue-gas with combustion of FG in incinerator in Nm³ dry/t AG at 3 % O₂

<table>
<thead>
<tr>
<th>FG=50 % m C₁, 50 % m C₂</th>
<th>PF (moles dry flue-gas at 3 % O₂/g FG)</th>
<th>Composition AG</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.52</td>
<td>20.87</td>
<td>2</td>
</tr>
<tr>
<td>%S [= %vol SO₂/₉ + % vol H₂S]→</td>
<td>0.25 %</td>
<td>1.00 %</td>
<td>2.00 %</td>
</tr>
<tr>
<td>Mass ratio FG/GA</td>
<td>0 %</td>
<td>1 517</td>
<td>1 529</td>
</tr>
<tr>
<td></td>
<td>1 %</td>
<td>1 652</td>
<td>1 665</td>
</tr>
<tr>
<td></td>
<td>2 %</td>
<td>1 788</td>
<td>1 800</td>
</tr>
<tr>
<td></td>
<td>3 %</td>
<td>1 924</td>
<td>1 936</td>
</tr>
<tr>
<td></td>
<td>4 %</td>
<td>2 060</td>
<td>2 072</td>
</tr>
</tbody>
</table>

This method should be used for reporting purposes.

Simplified calculation of flue-gas volume from SRU:
This simplified method allows expressing the flue-gas volume with a reduced number of parameters.

Qincin VOL = (2 + 5.76 x %S TG + j % x 18.32) x QGA/MMGA x 22.4 x 103 x 21/18 (at 3 % O₂ dry gases)
The table above allows determining the flue-gas volume emitted by SRU as a function of the mass ratio of make-up fuel gas in the incinerator to the acid gas feeding the unit.

The variability of the result is twofold for a given sulphur content in tail gas. However a typical mass ratio FG/AG of 4% can be considered an average value, as it reflects operational constraints (need to ensure an excess of FG to convert residual H2S) as well as energy efficiency constraints (need to minimize FG consumption as much as possible).

This ratio is very specific to SRU configurations and operating parameters.

### B.4.4 FLUE-GAS FACTOR FOR THE CALCULATION OF THE BUBBLE (SRU COMPONENT)

A simplified flue-gas factor which can easily apply to all SRU, regardless of their specificities, has to be established in order to determine the proportion of flue-gas generated by SRU.

Such flue-gas factor should be:

- Independent from variable parameters such as the quantity of FG burnt in the incinerator, which anyway is already taken into account in the refinery fuel balance (even if it is a negligible amount as compared to combustion).
- Based on available, verifiable, commonly used parameters (like quantity of AG feeding the unit and sulphur recovery efficiency).

### B.4.5 DETERMINATION OF THE FLUE-GAS VOLUME AS A FUNCTION OF SULPHUR RECOVERY EFFICIENCY

By definition efficiency is:

$$\eta = 1 - \%H_2S \text{ unconverted}$$

for 1 mole of AG it gives %S incin mol expressed as a function of η:

$$%S \text{ incin mol} = (100\% - \eta) \times a/Q \text{ incin mol} \quad (i)$$

$$%S \text{ incin} = (100\% - \eta) \times a/(f_0 + 4.76 \times (100\% - \eta) \times a)$$

$$Q \text{ incin vol} = (f_0 + 4.76 \times (100\% - \eta) \times a) \times 22400/MMGA$$

in Nm³ of dry flue-gas at 0 % O₂/t of AG

With $f_0 = 1.88a + 15.2b + c$
Let’s consider the standard case where:
- \( b = 1 \) (HC in AG = 1 % and HC is \( \text{C}_2\text{H}_6 \))
- make up FG is \( \text{CH}_4 \) (\( \text{PF} = 11.93 \text{Nm}^3/\text{kg} \))
- \( f_0 = 1.88a + 0.152 + (100\% - a - 1\%) \)
- \( f_0 = 0.88a + 1.142 \)

The calculations lead to the following results:

**Sulphur recovery efficiency**

<table>
<thead>
<tr>
<th>H(_2)S content of AG (%vol)</th>
<th>Flue-gas volume (Nm(^3) at 3 % O(_2))/t of AG</th>
<th>( \text{MM}_\text{GA} ) (g)</th>
<th>( f_0 )</th>
<th>99.90 %</th>
<th>99.50 %</th>
<th>99.00 %</th>
<th>98.00 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>99 %</td>
<td>34.0</td>
<td>2.01</td>
<td>1 553</td>
<td>1 567</td>
<td>1 585</td>
<td>1 619</td>
<td></td>
</tr>
<tr>
<td>90 %</td>
<td>34.9</td>
<td>1.93</td>
<td>1 453</td>
<td>1 466</td>
<td>1 481</td>
<td>1 511</td>
<td></td>
</tr>
<tr>
<td>80 %</td>
<td>35.9</td>
<td>1.85</td>
<td>1 348</td>
<td>1 359</td>
<td>1 372</td>
<td>1 399</td>
<td></td>
</tr>
</tbody>
</table>

**B.4.6 STANDARD FLUE-GAS FACTOR FOR THE DETERMINATION OF THE BUBBLE (SRU COMPONENT)**

The variability of the previous result is relatively small (less than 15 % for a given recovery efficiency).

It can be show that even with a 30 % variability on the flue-gas volume from SRUs, the influence on the bubble value is very limited (average standard deviation is 1.3 %).

**Based on this, it is proposed to take the typical value of 1 500 Nm\(^3\)/t of acid gas at 3 % O\(_2\) (dry gases) as a standard flue-gas factor for SRU.**

It corresponds to a H\(_2\)S content of 95 % and a sulphur recovery efficiency of 99.5 %, but as mentioned the variability of the factor is small even when AG composition and efficiency vary.

**B.4.7 DETERMINATION OF THE SRU SO\(_2\) EMISSION LEVEL AS A FUNCTION OF SULPHUR RECOVERY EFFICIENCY**

Using the same calculations and knowing \( \%\text{Sincin} \), it is possible to determine the SO\(_2\) emission level for SRU expressed as a concentration of SO\(_2\) at the exit of the incinerator (without dilution from the make up fuel gas).

The SO\(_2\) emission level is then directly related to the recovery efficiency of the unit:

\[
\text{[SO}_2\text{]} = \%\text{Sincin} \times \frac{64}{22.4} \times 106 \times \frac{18}{21} \text{ mg/Nm}^3 \text{ at 3 % O}_2 \text{ dry gases}
\]

Leading to the following results:

<table>
<thead>
<tr>
<th>SO(_2) (mg/Nm(^3) at 3 % O(_2)) in cin</th>
<th>Flue-gas volume (Nm(^3) at 3 % O(_2))/t of AG</th>
<th>( \text{MM}_\text{GA} ) (g)</th>
<th>( f_0 )</th>
<th>99.90 %</th>
<th>99.50 %</th>
<th>99.00 %</th>
<th>98.00 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>99 %</td>
<td>34.0</td>
<td>2.01</td>
<td>1 201</td>
<td>5 952</td>
<td>11 768</td>
<td>23 009</td>
<td></td>
</tr>
<tr>
<td>90 %</td>
<td>34.9</td>
<td>1.93</td>
<td>1 137</td>
<td>5 636</td>
<td>11 150</td>
<td>21 826</td>
<td></td>
</tr>
<tr>
<td>80 %</td>
<td>35.9</td>
<td>1.85</td>
<td>1 059</td>
<td>5 252</td>
<td>10 399</td>
<td>20 385</td>
<td></td>
</tr>
</tbody>
</table>

**B.5 FLUE-GAS FLOW FROM THE FCC**

The methodology presented under is the most precise and is used within the framework of the ETS reporting. However it requires a significant amount of data, including measurements which are site and unit-specific.
This is why a simplified method is presented further, based on a standard flue-gas factor. This latter method will be the one used for determining the flue-gas volume contribution of FCC UNIT to the total flue-gas of the refinery for the bubble calculation.

**B.5.1 GENERAL CASE**

In the catalytic cracking process there is a build-up of coke on the catalyst during the reaction. The coke is burned in the regenerator, which provides the heat necessary for the reaction and re-establishment of the normal activity of the catalyst.

**FCC simplified diagram**

\[
Q_{\text{vol flue-gases}} = \frac{Q_{\text{mass of entering air}} \times 0.79 \times \frac{1}{MM_{\text{dry air}} + MM_{H_2O} \times \frac{\% \text{water}}{1 - \% \text{water}}} - Q_{N_2 \text{ mass to fraction}} \times \frac{1}{MM_{N_2}} \times 22.4 \times 1000}{%N_2 \text{ flue gases}} \text{ as Nm}^3/\text{h}
\]

Where:
- \(Q_{\text{mass entering air as t/h moist air}}\)
- \(MM_{\text{dry air}} = 28.97 \text{ kg/kMol}\)
- \(MM_{H_2O} \times \% \text{water}/(1 - \% \text{water}) = 0.25 \text{ kg/kMol for air at 20 °C and 60% relative humidity}\)
- \(Q_{N_2 \text{ mass to fraction as t/h}}\)
- \(MM_{N_2} = 28 \text{ kg/kMol}\)

Let:

\[
Q_{\text{vol flue-gases}} \approx \frac{Q_{\text{mass of entering air}} \times 605 - Q_{N_2 \text{ mass to fraction}} \times 800}{%N_2 \text{ flue gases}} \text{ as Nm}^3/\text{h dry flue-gas with the measured O}_2\text{ content}
\]

Note 1: if the atmospheric pollutant analyser is located in a different place from the other analysers involved in the calculation of flue-gas flow, the quantity of gas entering the flue-gas circuit between the 2 measuring points must be added to the calculated flue-gas flow above.
Annexes

Note 2: the above formula is based on an assumed mean water content corresponding to 60 % relative humidity at 20°C. The accurate formula is to be preferred, as the corresponding parameters are generally available. Note also that the temperature conditions at the point where the air flow is measured may differ from these for the air sampled.

B.5.2 PARTICULAR CASE OF CO BOILERS

If the atmospheric pollutant analyser is located on the flow on the boiler output, the quantity of flue-gases to take into account is the sum of that from the regenerator and that from the combustion of the fuels in the boiler.

The first function (flue-gases from FCC) is calculated as from the above formula by adding the additional flue-gas generation by combustion of the CO in the same way as for the other fuels. Both functions must be expressed under the same excess air conditions, which shall be taken as nil (that is to say, stoichiometry) to simplify the formulae.

CO + ½ O₂ → CO₂

As the volume flowrate of the CO₂ is equal to that of the CO. The additional quantity of flue-gases generated by CO combustion is:

Qflue-gas CO = quantity of nitrogen in air used for combustion of the CO.

Hence:

Qflue-gas CO = %CO x Qvol flue-gas x \( \frac{1}{2} \times \frac{0.79}{0.21} = %CO x Qvol flue-gas \times 1.88 \)

Qvol flue-gas at 0 % O₂ = Qvol flue-gas x \( \frac{21\% - %O₂ \times 21\%}{21\%} \)

Qflue-gas CO = %CO x Qvol flue-gas x = %CO x Qvol flue-gas x 1.88

Qvol flue-gas at 0 % O₂ = Qvol flue-gas

%O₂ being the content in O₂ on the regenerator output (measurement point) used in the expression for Qvol flue-gas.

The total volume of flue-gases generated by the FCC, expressed for 0 % O₂ becomes:

\[
Q_{\text{total flue-gas}} = Q_{\text{vol flue-gas}} \times \left[ \frac{21\% - %O₂ \times 21\%}{21\%} + %CO \times 1.88 \right] \text{ in Nm}^3/\text{h dry flue-gas for 0 % O₂}
\]

B.5.3 FLUE-GAS FACTOR FOR THE CALCULATION OF THE BUBBLE (FCC UNIT COMPONENT)

Coke consumption is an easy-to-obtain variable as its annual consumption in FCC UNIT regenerator is reported to the authorities. It is established on the basis of the methods used for ETS reporting (coke burnt is deducted from quantities of CO₂ emitted) which offer the best accuracy.

A benchmark based on 6 FCCs, shows a very little variability of the flue-gas volume generated by 1 kg of coke as fuel oil equivalent (foe).

Note: The standard flue-gas factor may also be expressed per tonne of feed processed, but the factor will have a larger variability as the quality of the feedstock can vary significantly. It is therefore proposed to take the value of 1.2 Nm³/kg of coke (foe) at 3 % O₂ (dry gases) as a standard flue-gas factor for FCC UNIT.
APPENDIX C ON MASS/LOAD EMISSION ESTIMATION

Table determined from relevant BAT-AEL (Chapter 5)

SO$_2$ emissions

<table>
<thead>
<tr>
<th>Source</th>
<th>Type</th>
<th>BAT-AEL/EPL Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas firing</td>
<td></td>
<td>5 – 35 mg/Nm$^3$</td>
</tr>
<tr>
<td>Combustion</td>
<td>Multi-fuel (gas-liquid) firing</td>
<td>Existing: 35 – 450 mg/Nm$^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>New units:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35 – 350 mg/Nm$^3$ for new units from 50 to 100 MWth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35 – 200 mg/Nm$^3$ for new units from 100 to 300 MWth</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35 – 150 mg/Nm$^3$ for new units &gt;300 MWth</td>
</tr>
<tr>
<td>Sulphur recovery unit (SRU)</td>
<td>Sulphur recovery efficiency</td>
<td>99.5% – &gt;99.9%</td>
</tr>
<tr>
<td>Fluid catalytic cracking (FCC)</td>
<td></td>
<td>&lt;500 mg/Nm$^3$</td>
</tr>
<tr>
<td>Coking process</td>
<td></td>
<td>&lt;450 mg/Nm$^3$</td>
</tr>
<tr>
<td>Flares (permanent emissions only)</td>
<td></td>
<td>Use combustion values</td>
</tr>
</tbody>
</table>

NO$_x$ emissions

<table>
<thead>
<tr>
<th>Source</th>
<th>Type</th>
<th>BAT-AEL/EPL Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas firing</td>
<td></td>
<td>Existing: 30 – 150 mg/Nm$^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>New: 30 – 100 mg/Nm$^3$</td>
</tr>
<tr>
<td>Combustion</td>
<td>Multi-fuel (gas-liquid) firing</td>
<td>Existing: 200 – 350 mg/Nm$^3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>New: 30 – 150 mg/Nm$^3$</td>
</tr>
<tr>
<td>Sulphur recovery unit (SRU)</td>
<td>NO$_x$ emissions considered negligible</td>
<td></td>
</tr>
<tr>
<td>Fluid catalytic cracking (FCC)</td>
<td></td>
<td>&lt;30 – 200 mg/Nm$^3$</td>
</tr>
<tr>
<td>Coking process</td>
<td></td>
<td>&lt;350 mg/Nm$^3$</td>
</tr>
<tr>
<td>Flares (permanent emissions only)</td>
<td></td>
<td>Use combustion values</td>
</tr>
</tbody>
</table>
APPENDIX D BUBBLE MONITORING

Setting appropriate monitoring requirements to each stack identified in the mapping

Fully benefit from ETS CO\textsubscript{2} monitoring plan to identify the relevant sources and assess emissions level (both volumetric and mass contributions) for each substance covered by the bubble.

Define the type of monitoring in accordance with the relevant tier, as for example, following a growing level of emissions:

- use of emission factor and activity parameter monitoring;
- idem + periodic stack measurements;
- idem + continuous stack measurements.

The following requirements can be associated to the correspondent emissions sources:

<table>
<thead>
<tr>
<th>Source</th>
<th>Type of monitoring</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion</td>
<td>Continuous direct measurements of SO\textsubscript{2} or calculation based on S % in fuel</td>
<td>Technical provisions on monitoring of IED Annex V may be applicable</td>
</tr>
<tr>
<td></td>
<td>Continuous direct measurements of NO\textsubscript{x}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Periodic measurements of SO\textsubscript{2} and NO\textsubscript{x} for the smallest sources</td>
<td></td>
</tr>
<tr>
<td>Sulphur recovery unit (SRU)</td>
<td>Continuous direct measurements of SO\textsubscript{2}</td>
<td>Possible calculation from fixed S % recovery and S inlet measurement</td>
</tr>
<tr>
<td>Fluid catalytic cracking (FCC)</td>
<td>Continuous direct measurements of SO\textsubscript{2} or calculation based on S % in feed/coke</td>
<td>Measurements generally required when using deSo\textsubscript{x} and/or DeNO\textsubscript{x} catalysts</td>
</tr>
<tr>
<td></td>
<td>Continuous direct measurements of NO\textsubscript{x}</td>
<td></td>
</tr>
<tr>
<td>Coking process</td>
<td>Continuous direct measurements of SO\textsubscript{2} and NO\textsubscript{x}</td>
<td></td>
</tr>
<tr>
<td>Flares</td>
<td>Permanent emissions of flares monitored from additional fuel consumptions</td>
<td></td>
</tr>
</tbody>
</table>

Elaborating a formal monitoring plan

The monitoring plan shall contain the following contents:

(a) the description of the process to be under monitoring;

(b) a list of emissions sources and source streams to be monitored for each process;

(c) a description of the calculation-based methodology or measurement-based methodology to be used and the associated level of confidence.

(d) a description of the measurement systems, and the specification and exact location of the measurement instruments to be used at emission source, i.e. the points of measurement, frequency of measurements, equipment used, calibration procedures, data collection and storage procedures and the approach for corroborating calculation and the reporting of activity data and, emission factors.