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BAT Guide for oil refineries

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0. INTRODUCTION

This guide forms part of the work by the Ministry of Environment and Urbanism of Turkey (MoEU) to align the environmental policies to the standards of the European Union. Within this context, one of the key targets is the alignment with the specifications stated in the Industrial Emissions Directive 2010/75/EU on the establishment of an integrated environmental permits system. According to this Directive, the environmental conditions established in the new integrated environmental permits must be based on the so-called conclusions on Best Available Techniques (BATs) and the Associated Emission Levels (AELs), which are described in a series of BATs Reference Documents (BREFs).

The current target is to start the implementation of the new integrated environmental permits system in 2015, and as the associated environmental standards requested to the industries falling within the scope of this system will be substantially changed, there is a need of awareness and tools that may help them and the environmental authorities to start taking some measures in order to soften this transition.

The excessive length and wide scope of the BREF for mineral oil refineries, plus the importance of this sector in Turkey were the reasons to prepare a BAT National Guide for Crude Oil Refineries, more understandable and adapted to the characteristics of the sector in Turkey, including in addition other information practical for both this industry and the staff of the MoEU. Moreover, it may serve as well to communicate to a broader audience the main characteristics of the sector and its main pollution abatement techniques, given its simple and concise style.

The objectives of this guide are the following:

- Present an overview of the sector in Turkey, and its current position in terms of environmental performance, with reference to the currently applicable environmental legislation (Chapters 1 & 3).
- Describe the processes, technologies and techniques particular of this kind of industry (Chapter 2).
- Discuss the BATs and some emerging techniques to increase the environmental performance, and present the ranges of AELs to them whenever this is possible (Chapters 4 & 6).
- Discuss the available tools and methods to monitor and control the environmental impacts of the installations (Chapter 5).
- Provide in some annexes useful reference tools, such as a check list of the contents that an integrated environmental permit for a crude oil refinery should have.

In this manner, this guide should constitute a reference for both the staff of the MoEU responsible for the issuance of environmental permits for this sector, and for the crude oil refining industry representatives. This guide is not a law stating some emission limit values (ELVs) for certain parameters which have to be respected, but rather a reference on which the environmental authority should base its decisions on the contents of environmental permits issued to installations of this sector, taking of course as well into consideration the relevant applicable environmental legislation in the process of issuance of the new permits.

1 GENERAL INFORMATION OF THE REFINERY SECTOR IN TURKEY

The data and information provided in this Chapter correspond to the year 2012. Currently the evolution of the sector in Turkey is fast, including the construction of a new refinery in Izmir, so updates in the data provided will be needed in following years.

1.1 IMPLEMENTATION OF THE DIRECTIVE ON INDUSTRIAL EMISSIONS IN THE REFINERIES SECTOR

1.1.1 National Legislation transposing the permitting requirements of the Directive on Industrial Emissions. Other sectoral legislation applicable to the sector.

The Ministry of Environment and Urbanism is drafting the By-Law on Integrated Environmental Permits, that will transpose the permitting requirements stated in chapters 1 and 2 of the Directive on Industrial Emissions 2010/75/EU. Explanations about how to implement in practice this new By-Law are provided in the guidance document “Integrated Environmental Permits: Supporting guideline for the Applicants”.

1.1.2 Installations regulated under this legislation and covered by this guidance

The installations covered by this guidance which are subject to the legislation mentioned in section 1.1.1 are the installations dedicated to the refining of oil and crude oil.

1.1.3 Administrative procedure to apply for the Integrated Environmental Permit.

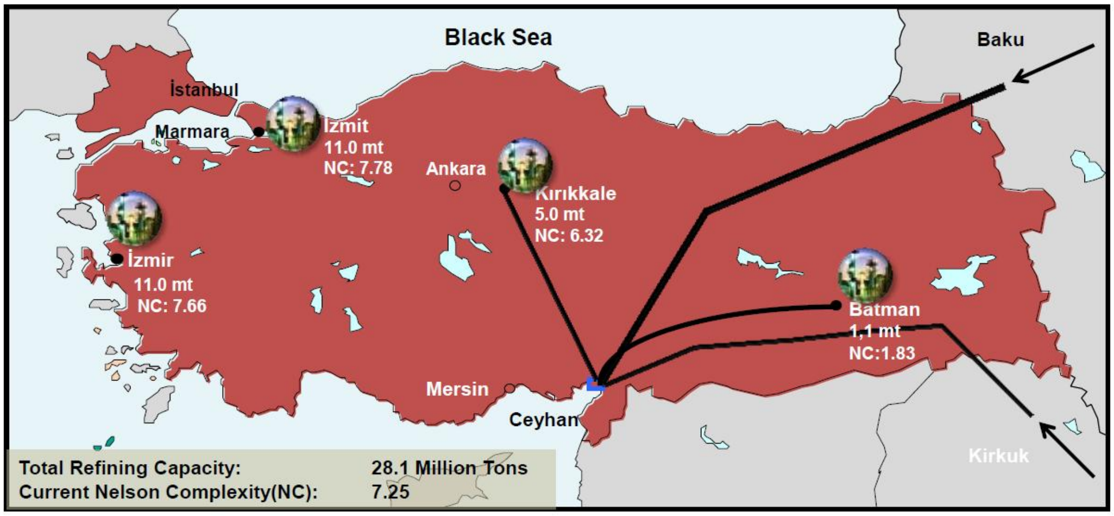
The administrative procedure is explained in detail in chapter 5 of the guidance document “Integrated Environmental Permits: Supporting guideline for the Applicants”.

1.2 General overview of the refinery processes in Turkey

Because of its location, Turkey is an important energy transit country and its relatively large population and growing economy have made the country a significant regional energy consumer in its own right. For these reasons, although Turkey is not a major oil producer, it is increasingly important to world oil markets.

There are four active oil refineries in Turkey in 2012, all owned by the same company: TÜPRAŞ. New refineries may be located in Turkey after 2012.

- İzmit Refinery: Located in Marmara Region, founded in 1961
- İzmir Refinery: Located in Ege Region, founded in 1972
- Kırıkkale Refinery: Located in Central Anatolia Region, founded in 1986
- Batman Refinery: Located in south-eastern Anatolia Region, founded in 1955



The main characteristics of TÜPRAŞ refineries are shown below:

	ANNUAL CAPACITY (MILLION TON /YEAR)	NELSON COMPLEXITY
İzmit Refinery	11	7.78
İzmir Refinery	11	7.66
Kırıkkale Refinery	5	6.32
Batman	1.1	1.83

Refinery		

According to 2011 petroleum requirement of Turkey, 65% of Turkey's needs of petroleum products is met by TÜPRAŞ.

PRODUCTION	OUTPUT (*1000 ton/yr)
LPG	760
Gasoline & Naphta	4594
Jet oil & Gas oil	2923
Diesel	5310
Fuel oil	2871
Bitüm-Bitümlü Bağlayıcı (Asfalt)	2959
Base oil	399
Others	394

1.3 Relevant environmental impacts of oil refining installations

Pollution abatement measures and environmental management have become major issues for refineries in order to reduce the impacts derived from the facilities concerned. The major environmental impacts are atmospheric emissions, water emissions and waste generation.

1.3.1 Air emissions

Refineries are intensive consumers of energy, being the production of energy for the multiple processes the responsible for most of the air emissions. Combustion processes are the most relevant sources of carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NO_x), sulphur oxide emissions (SO_x) and particulate emissions. Despite energy efficiency measures have increased significantly, refinery energy demand has also increased due to changes in the product specifications.

Other units that cause the principal atmospheric pollutants are sulphur recovery units, flares, catalyst changeovers, cokers, oil/water separation units, product loading and handling facilities.

Main air pollutants and their main sources emitted by refineries:,

Main air pollutants	Main sources
Carbon dioxide	Process furnaces, boilers Flare systems Incinerators
Carbon monoxide	Process furnaces and boilers Sulphur recovery units Flare systems Incinerators
Nitrogen oxides (NO, NO2)	Process furnaces and boilers Incinerators Flare systems
Nitrogen peroxide (N2O)	Fluidised catalytic cracking regenerators
Particulates (including metals)	Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators Incinerators
Sulphur oxides	Process furnaces and boilers Sulphur recovery units (SRU) Flare systems Incinerators
Volatile organic compounds (VOCs)	Storage facilities Oil/water separation systems Fugitive emissions (valves, flanges, etc.) Vents Flare systems

1.3.2 Water use and wastewater discharges

Water is also used intensively in the refineries as process water and for cooling purposes. Process waters from activities such as crude desalting, water washing, separation activities or cleaning and purging are in direct contact with either crude oil or other fractions of hydrocarbons and substances. 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) and total metals.

Main **water pollutants** (parameters) generated by refineries:

Main water pollutants	Main sources
Oil	Distillation units, hydrotreatment, spent caustic, utilities (rain)
H_2S (R-SH)	Distillation units, hydrotreatment, hydrocracking, lube oil, spent caustic
NH_3 (NH4+)	Distillation units, hydrotreatment, hydrocracking, sanitary waters
Phenols	Distillation units, spent caustic
Organic Chemicals (BOD, COD, TOC)	Distillation units, hydrotreatment, hydrocracking, spent caustic, utilities (rain), sanitary waters
CN-, (CNS-)	Catalytic cracking, spent caustic
TSS	Distillation units, catalytic cracking, spent caustic, sanitary waters
Amines compounds	CO_2 removal in LNG plants

1.3.3 Waste generation and management

The generation of waste is an inevitable consequence of the operation of refineries and depots. Waste substances generated by oil company sites, fall into two categories:

- Non-hazardous waste, e.g. scrap metal, spent catalytic cracking catalyst or “domestic” waste;

– Hazardous waste, e.g. asbestos, acid tars, sludges with a high lead content or many oil contaminated materials.

Asbestos from any site should be considered hazardous. A too detailed classification of waste is definitely undesirable and use of appropriate lists and other tools as well as discussion with authorised waste management operators use to ensure the correct classification. A list of typical oil industry wastes is:

Oiled materials

– Oily sludges: tank bottoms, biotreatment sludges, interceptor sludges, waste water, treatment sludges, contaminated soils, desalter sludges.

– Solid materials: contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging activated carbon.

Drums and containers

– Metal, glass, plastic, paint.

Spent Catalysts (excluding precious metals)

– FCCU (fluid bed catalytic cracking unit), HDS/HT (hydrodesulphurisation/hydrotreatment), polymerisation unit, residue conversion.

Non-oiled materials

– Resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes (flue gas desulphurisation).

Radioactive wastes

– Catalysts, laboratory waste.

Scales

– Leaded/unleaded scales, rust.

Construction / demolition waste

- Scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood.

Spent chemicals

- Laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/di-ethanol amine), TML/TEL (tetra methyl/ethyl lead).

Pyrophoric wastes

- Scale from tanks/process units.

Mixed wastes

- Domestic waste, green waste (vegetation).

Waste oils

- Lubricating oils, cut oils, transformer oils, recovered oils, engine oils.

Waste production in refineries and terminals represents a high operating cost and potential environmental risk, and as such its minimisation is a priority.

Waste minimisation includes:

- Elimination / Reduction at source
- Recycling of wastes
- Economy of use
- Housekeeping
- Waste Handling

1.3.4 Soil and groundwater pollution

There is a potential for significant soil and groundwater contamination to arise at petroleum refineries. Such contamination may consist of:

- Petroleum hydrocarbons including:

Lighter, very mobile fractions (paraffins, cycloparaffins and volatile aromatics such as benzene, toluene, ethylbenzene and xylenes) typically associated with gasoline and lighter distillates;

middle distillate fractions (paraffins, cycloparaffins and some polyaromatics) associated with diesel, kerosene, some of the lighter fuel oils, which are also of significant mobility;

heavier distillates (long-chain paraffins, cycloparaffins and polyaromatics) associated with lubricating oils and heavy fuel oils;

- Various organic compounds associated with petroleum hydrocarbons or produced during the refining process, e.g. phenols, amines, amides, alcohols, organic acids, nitrogen and sulphur containing compounds.

- Other organic additives, e.g. anti-freezers (glycols), alcohols or detergents.

- Organic lead, associated with leaded gasoline and other heavy metals.

Typical sources of such contamination at petroleum refineries are:

- transfer and distribution points in tankage and process areas, also general loading and unloading areas

- landfarming wastewater treatment areas

- tank farms

- individual Areal Storage Tanks and particularly Underground Storage Tanks

- interceptors (emergency systems to contain anomalous episodes of large wastewater streams)

- pipeline leakages

- drainage leakages

- pump raft/pipe manifold areas

- vehicle washing facilities

- maintenance workshops
- on-site waste treatment impounding basins, lagoons, especially if no additional spill recovery system (like concrete-basement) is .

2 APPLIED PROCESSES AND TECHNIQUES. DESCRIPTION OF THE TECHNOLOGICAL PROCESSES

2.1 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. These impurities, especially salts, can lead to fouling and corrosion of heat exchangers (crude preheaters) and especially the crude distillation unit overhead system. In addition, 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). 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 products 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.

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. Either AC or DC fields may be used and potentials from 15 to 35 kV are used to promote coalescence.

The 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. Many refineries have more than one desalter and 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.

Where bottoms sediments are critical in downstream process units, desalters are equipped with a bottom flushing system to remove settled solids.

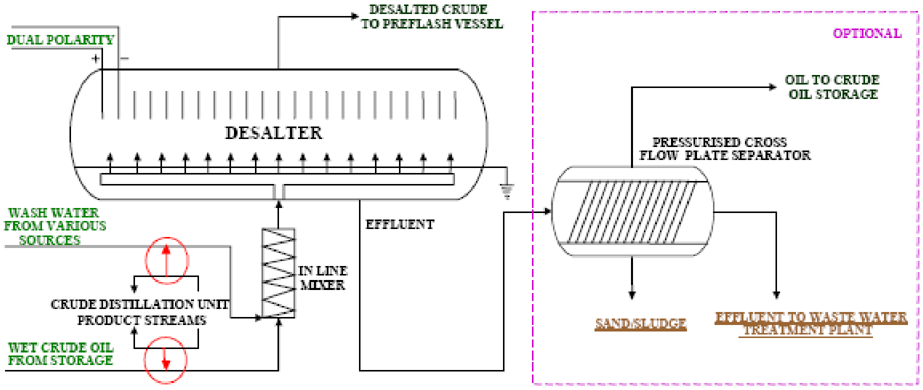


Figure 2.1. Simplified flow diagram of a crude desalter

(Further information in BREF section 2.9)

2.2 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

In Atmospheric Crude Oil Distillation Unit (CDU), 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 CDU bottom of the, which do not vaporise in this column, can be further separated later by vacuum distillation, which 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 products 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})
- 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 hydroprocessing, 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 ºC 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 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. 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. Every refinery has a crude distillation unit designed for a selected crude (mix).

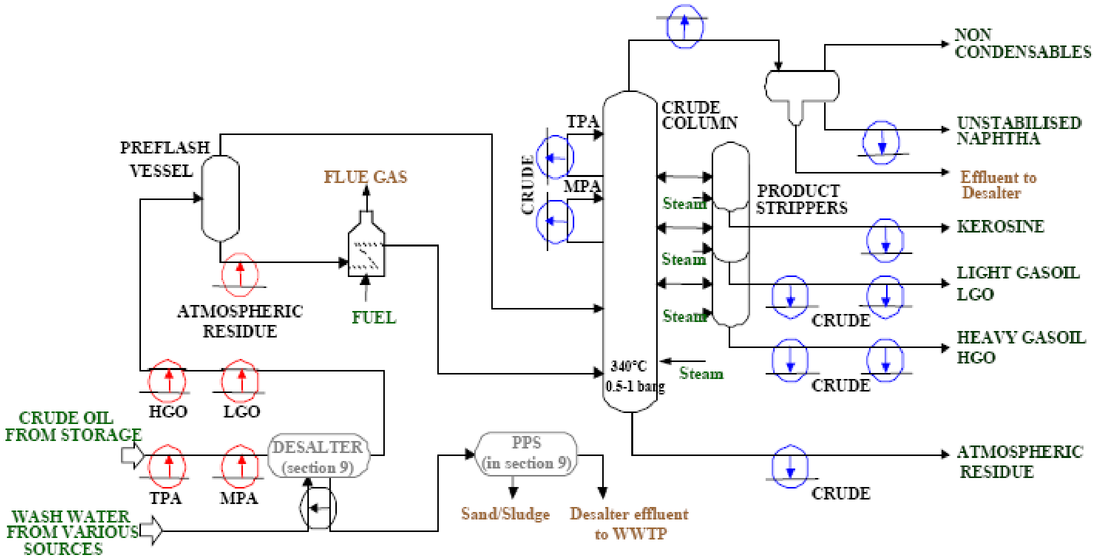


Figure 2.2. Simplified process flow diagram for a crude distillation unit

Vacuum distillation

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/cm^2). 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 (noncondensable) 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.

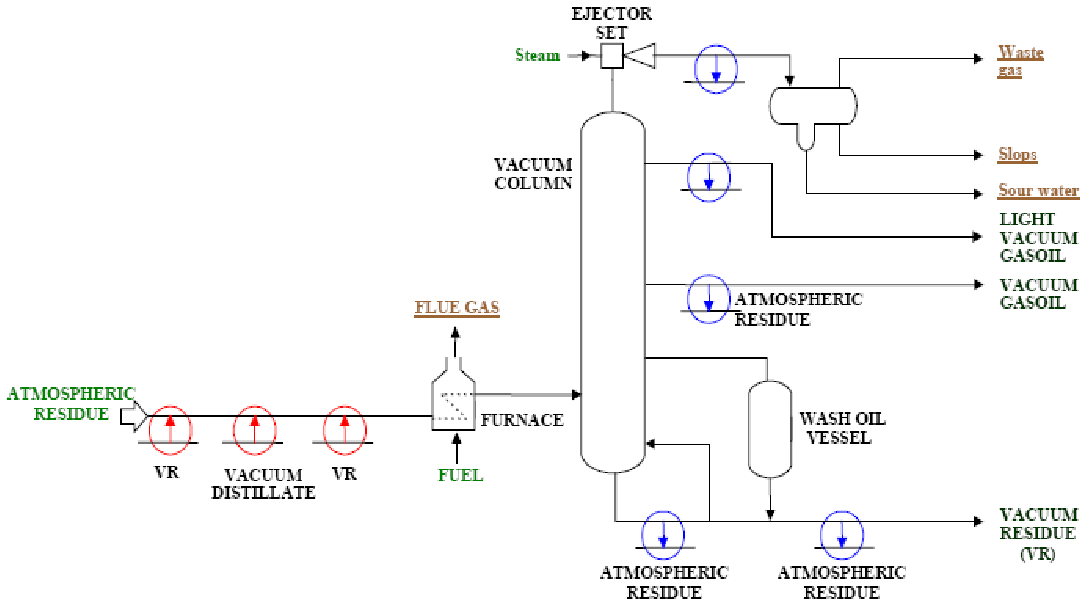


Figure 2.3. Simplified process flow scheme for high-vacuum distillation unit

(Further information in BREF section 2.19)

2.3 Catalytic reforming

Purpose and principle

The purpose of a catalytic reformer is to upgrade the octane of the heavy naphtha leaving the hydrotreating units for use as a gasoline blendstock. The most important characteristic of the reformate product is the octane number. 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 gasoline market is in decline and reformulated specifications 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 products streams

The typical feedstocks to catalytic reformer units are the hydrotreated straight-run heavy naphtha 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 a FCC unit.

A catalytic reformer produces hydrogen, which is essential for use in hydrotreaters (Section 2.5) and may be used in hydrocracking processes. In addition to the hydrogen, products from a reformer include:

- refinery fuel gas
- LPG
- Isobutene
- n-butane
- 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.

Process description

The catalysts used in catalytic reforming processes are usually containing platinium [Pt] and are very expensive, so 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.

Continuous catalytic regeneration (CCR) reforming process

In this process, the catalyst can be regenerated continuously and maintained at a high activity rate.

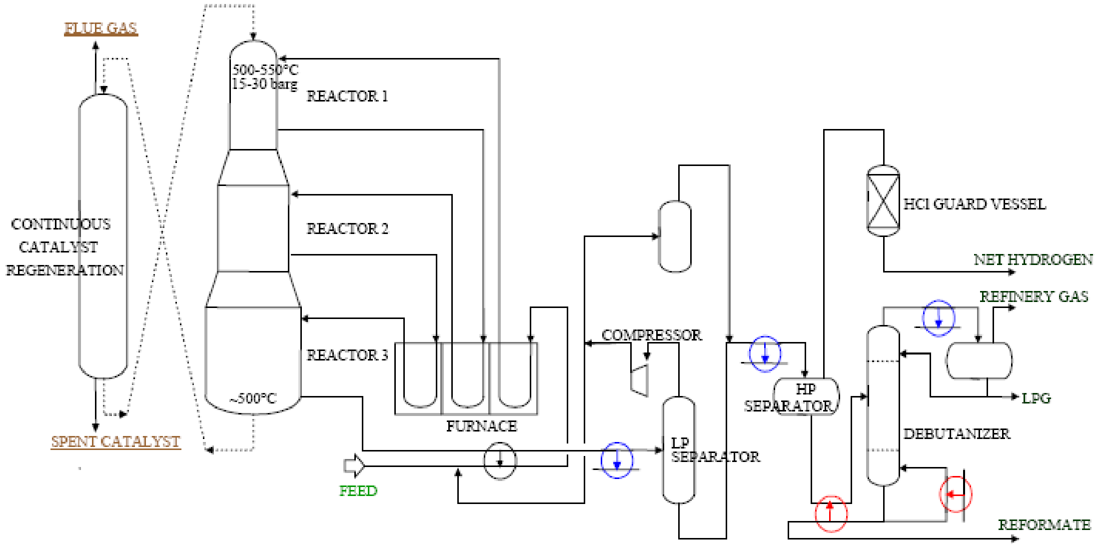


Figure 2.4. Simplified process flow scheme for a continuous catalytic reformer

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 C_3/C_4 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.

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 but the use of a CCR generates more dioxins than a semi-regenerative process during the regeneration of the catalyst.

Cyclic reforming process

The cyclic reforming process is characterised by having a swing reactor in addition to these onstream, 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.

(Further information in BREF section 2.6 and 3.6)

2.4 Hydrotreatment and hydrodesulphurization processes

Purpose and principle

Hydrotreating is used to remove impurities such as sulphur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts and also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. It is 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.

This process uses 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

- 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.

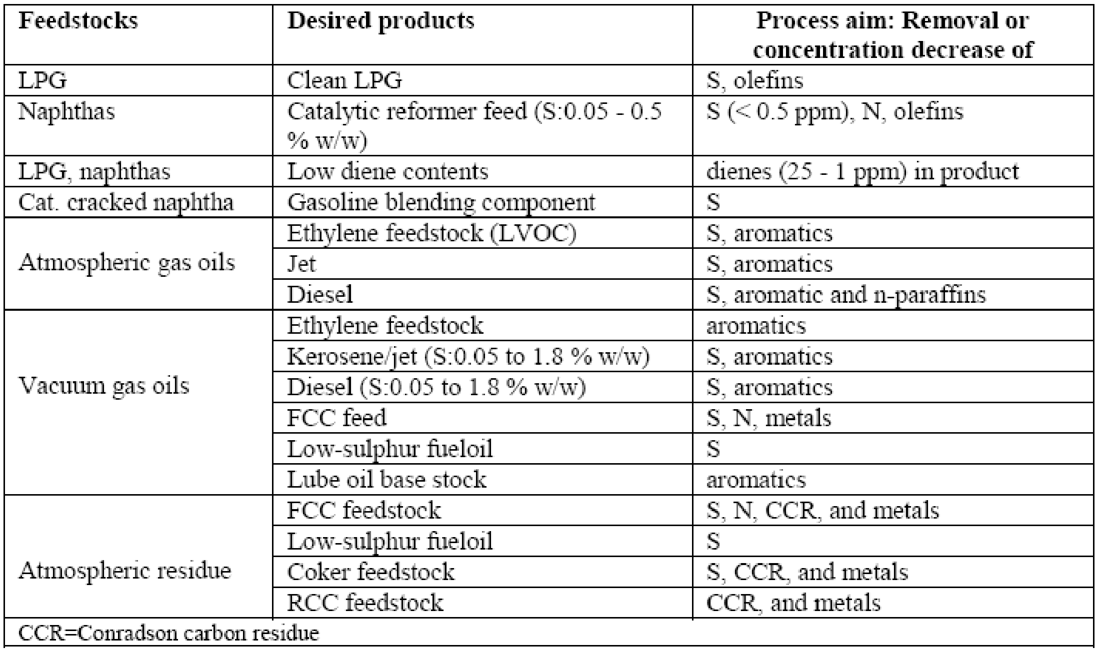
A mid-distillate hydrotreater unit normally has two purposes: desulphurisation and hydrogenation of the mid-distillate stream. Stabilising mid-distillate streams is required when large quantities of cracked components are blended to the mid-distillate pool, and usually requires partial saturation of aromatics and olefins and a reduction of the Ncontent. 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-dimethyldibenzothiophene, 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 H_2S in the product.

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.

Feed and products streams

These processes are applied to a wide range of feedstocks, from LPG up to heavy residue and mixture thereof. Next table summarises the feeds, products and process objectives for each type of hydrotreatment:



Feedstocks	**Desired products**	**Process aim: Removal or concentration decrease of**
LPG	Clean LPG	S, olefins
Naphthas	Catalytic reformer feed (S:0.05 - 0.5 % w/w)	S (< 0.5 ppm), N, olefins
LPG, naphthas	Low diene contents	dienes (25 - 1 ppm) in product
Cat. cracked naphtha	Gasoline blending component	S
Atmospheric gas oils	Ethylene feedstock (LVOC)	S, aromatics
	Jet	S, aromatics
	Diesel	S, aromatic and n-paraffins
Vacuum gas oils	Ethylene feedstock	aromatics
	Kerosene/jet (S:0.05 to 1.8 % w/w)	S, aromatics
	Diesel (S:0.05 to 1.8 % w/w)	S, aromatics
	FCC feed	S, N, metals
	Low-sulphur fueloil	S
	Lube oil base stock	aromatics
Atmospheric residue	FCC feedstock	S, N, CCR, and metals
	Low-sulphur fueloil	S
	Coker feedstock	S, CCR, and metals
	RCC feedstock	CCR, and metals

CCR=Conradson carbon residue

Table 2.1

Process description

Types of reactor technologies applied in hydrotreatment

There are several hydrotreating 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.

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. (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 xx 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 $(NH_4)_2S$ and chlorides NH_4Cl 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 H_2S. 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.

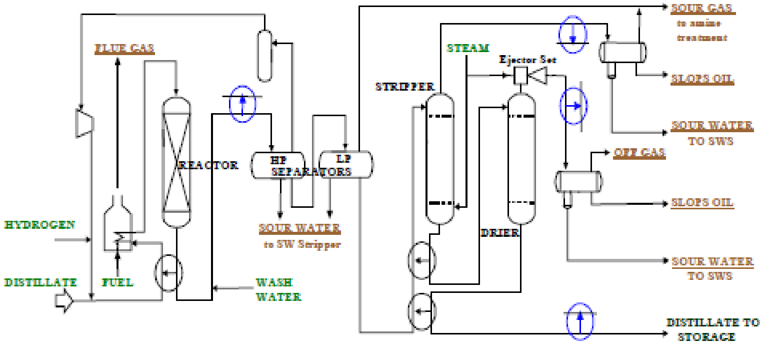


Figure 2.5. Simplified process flow scheme of a distillate hydrodesulphurisation unit

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 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.

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 H_2S and NH_3-rich environment the nickel/molybdenum or nickel/tungsten catalysts are usually applied in the tail reactors. Table XX shows the typical hydrotreatment operating conditions for the different feedstocks:

Table 2.2: Typical hydrotreating operating conditions

Operating conditions	Naphtha	Mid distillate	Light gas oil	Heavy gas oil	Residuum
Liquid hourly space velocity	1.0 – 5.0	1.0 – 4.0	1.0 – 5.0	0.75 – 3.0	0.15 – 1
H_2/HC ratio, Nm^3/m^3	50	135	170	337	300
H_2 partial pressure, kg/cm^2	14	28	35	55	55
Reactor temperature, °C	260 – 380	300 – 400	300 – 400	350 – 425	350 – 425

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.

(Further information in BREF section 2.13)

2.5 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:

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 of the BREF), amine scrubbing for the removal of hydrogen sulphide (included in Section 4.23.5.1 of the BREF) or caustic washing for the removal of acids or mercaptans.

systems where the chemical to be treated is not removed from the stream to be treated.

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:

$$\text{R-SH} + \text{NaOH} \longleftrightarrow \text{NaSR} + \text{H}_2\text{O}$$

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:

$$NaSR + \frac{1}{4} O_2 + \frac{1}{2} H_2O \longleftrightarrow NaOH + \frac{1}{2} RSSR$$

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 2.4).

Process description

Mercaptans are removed from light hydrocarbon streams by a concentrated alkaline wash in an extraction column under elevated pressure (5 barg). If H_2S 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 extraction column. Figure xx shows a simplified process flow diagram of an extraction process.

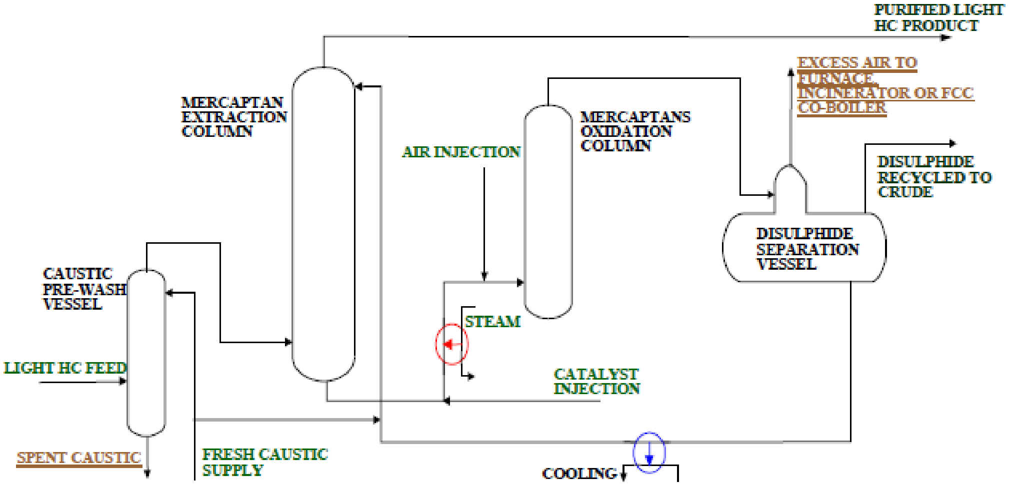


Figure 2.6: Simplified process flow diagram of the mercaptan oxidation extraction process

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.

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, as shown in next figure.

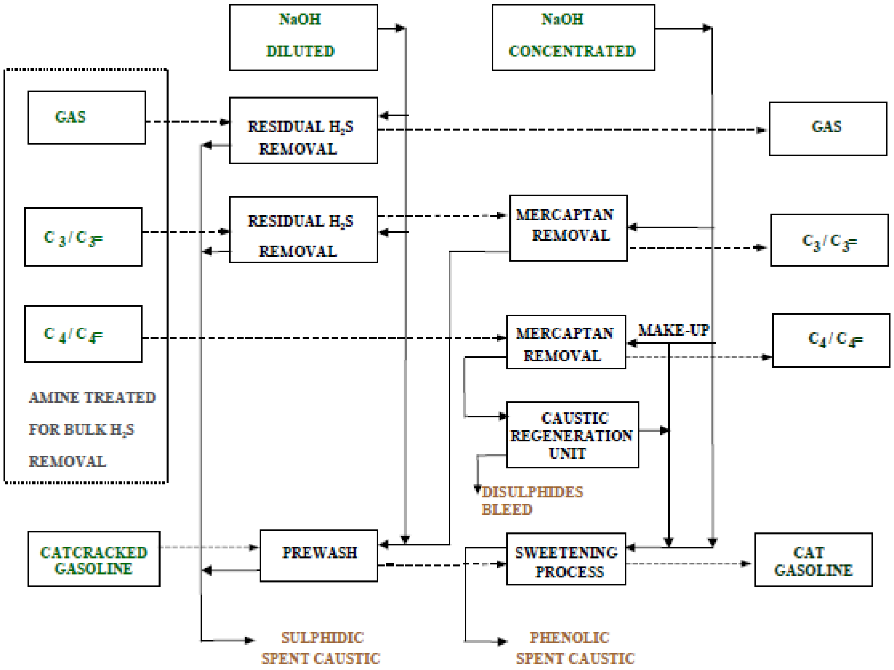


Figure 2.7: Simplified process flow diagram of the caustic cascading system (mercaptan oxidation extraction and mercaptan oxidation sweetening)

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 nearto- 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 2.4).

(Further information in BREF section 2.20)

2.6 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 C_1 - 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 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 2.4) or amine treating (H_2S removal, see Section 4.25.5.1 in BREF). The compounds recovered depend on the composition of the feed and the market requirements. The gas streams are normally separated into C_1 and C_2 fractions for sale or use as refinery fuel gas, LPG (propane and butane) and a light gasoline (C_5 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 C_2-minus components to maximise recovery of C_3-plus components from the feed streams. Figure xx shows a simplified process flow diagram of a gas plant.

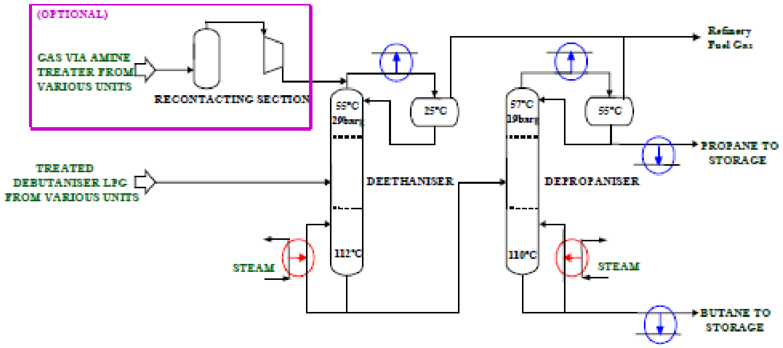


Figure 2.8: Simplified process flow scheme for a part of a gas plant

(Further information in BREF section 2.12)

2.7 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 (C_4-C_6) 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 C_5/C_6 isomerisation unit is normally fractionated so that it includes as much of the C_5/C_6 as possible, while minimising heptanes and heavier compounds.

Process description

Figure xx 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.

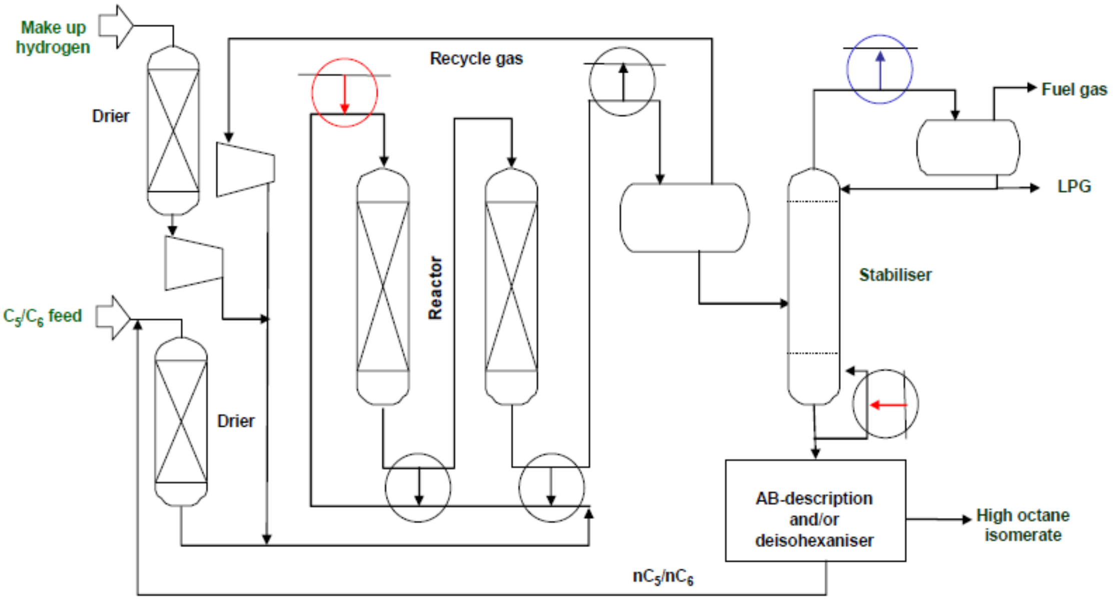


Figure 2.9: Simplified process flow scheme for an isomerisation unit

There are several isomerisation process designs based on three isomerisation catalyst technologies that can be further designed to operate with or without hydrogen recycle and with or without hydrocarbon recycle.

(Further information in BREF section 2.16)

2.8 Visbreaking and other thermal conversions

2.8.1 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 xx 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.

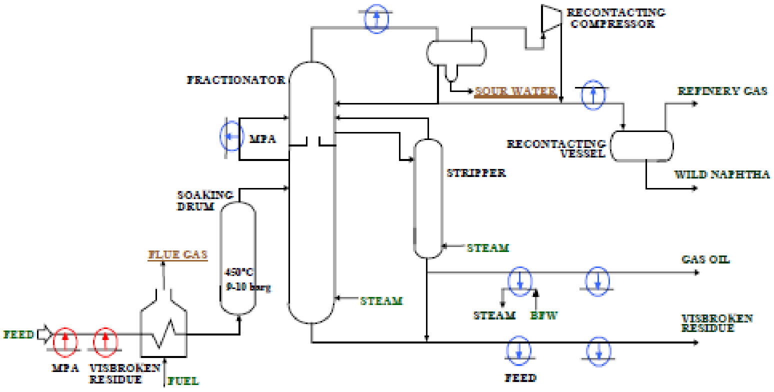


Figure 2.10: Simplified process flow scheme for a visbreaking unit

The feedstock is heated above 500 ºC 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.

2.8.2 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 xx, 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.

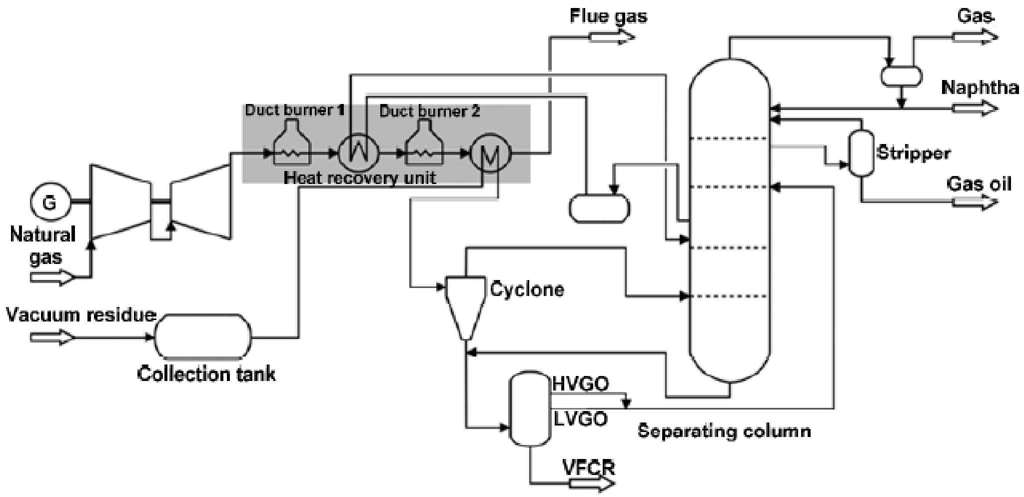


Figure 2.11: Simplified process of a thermal gas oil unit

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.

(Further information in BREF section 2.22)

2.9 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 hydrocracker 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 limited flexibility in changing the product yields even if recent developments in catalysts allow, depending of the catalyst selection, an increase of LPG yield or a further reduction of the bottom products.

Feed and product streams

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.

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 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 C_3 and C_4. Both products are highly olefinic and therefore are ideal feedstreams for the alkylation, etherification and petrochemical industries. One drawback of this process is the very low quality of the mid-distillate products in terms of sulphur, olefins, aromatics and cetane index. 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 (units where fluid passes only once through it). The fluidised- and moving-bed reactors are by far the most prevalent in world refineries and these are which are explained below.

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 next Figure.

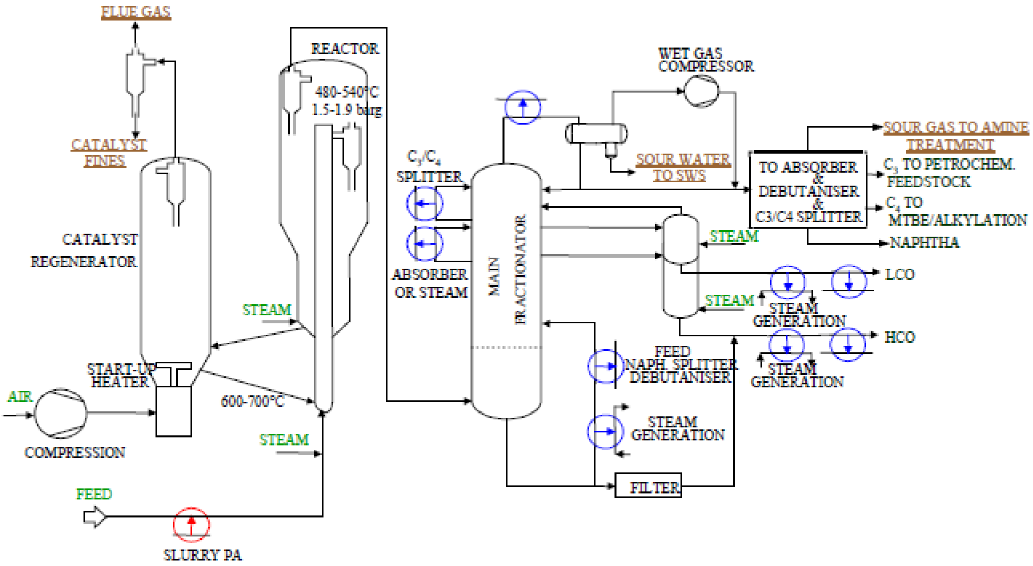


Figure 2.12. Simplified process flow scheme for fluid catalytic cracker

In the FCC process, oil and oil vapour preheated to 250 to 425 °C come into contact with hot catalyst at about 680 – 730°C in the riser reactor. To enhance vaporisation 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 contain zeolites (for more details on zeolites see Annex 9.7 in the BREF) with metals and rare-earths supported by different types of aluminas and clays. The catalyst is in a fine, granular form which mixes intimately with the vaporised feed. The fluidised catalyst and the reacted hydrocarbon vapour are separated mechanically in a (two-stage) cyclone system and any hydrocarbon remaining on the catalyst is removed by steam stripping. The amount of lost catalyst as fines in the reactor and regenerator cyclones 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, 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 twostage 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 vaporisation of the feed and by the heat absorption required for cracking reactions.

The cracked 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 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 2.6) for further separation and the sour water stream is sent to the sour water stripper for purification (Section 2.17.5 of this guide, “Techniques for abatement of emissions”).

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 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.

In the moving-bed process, oil is heated to 400 – 700 ºC 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.

(Further information in BREF section 2.5)

2.10 Coking processes and coke calcination

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[1] 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[2] 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.

Process description

Two types of coking processes exist:

- delayed coking processes: produces coke and is the most extended
- fluid coking processes: produces coke
- flexicoking process: gasifies the coke produced in a fluid coking process to produce coke gas.

Delayed and fluid coking

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[1] Coke produced by the coker is called ‘green’ coke and still contains some heavy hydrocarbons left from incomplete carbonisation reactions.

[2] ConCarbon (Conradson Carbon Number): A measurement of hydrocarbon mixtures tendency to leave carbon deposits (coke) when burned as fuel or subjected to intense heat in a processing unit such as a catalytic cracker.

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

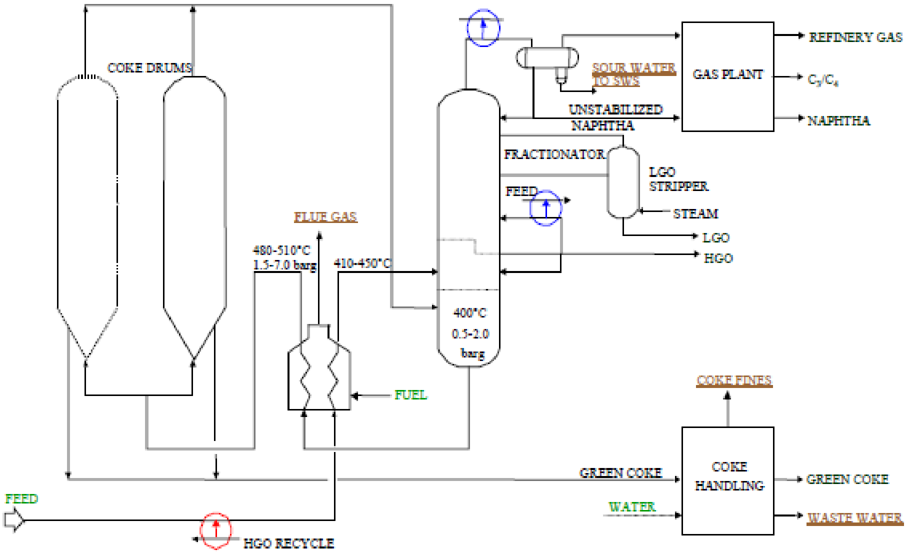

Figure 2.13: Simplified process flow scheme for a delayed coking unit

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 xx). 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 xx).

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 petroleumcoke 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 reprocessed 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 2.12) 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 ºC, 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. Hotflue-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 xx). 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.

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.

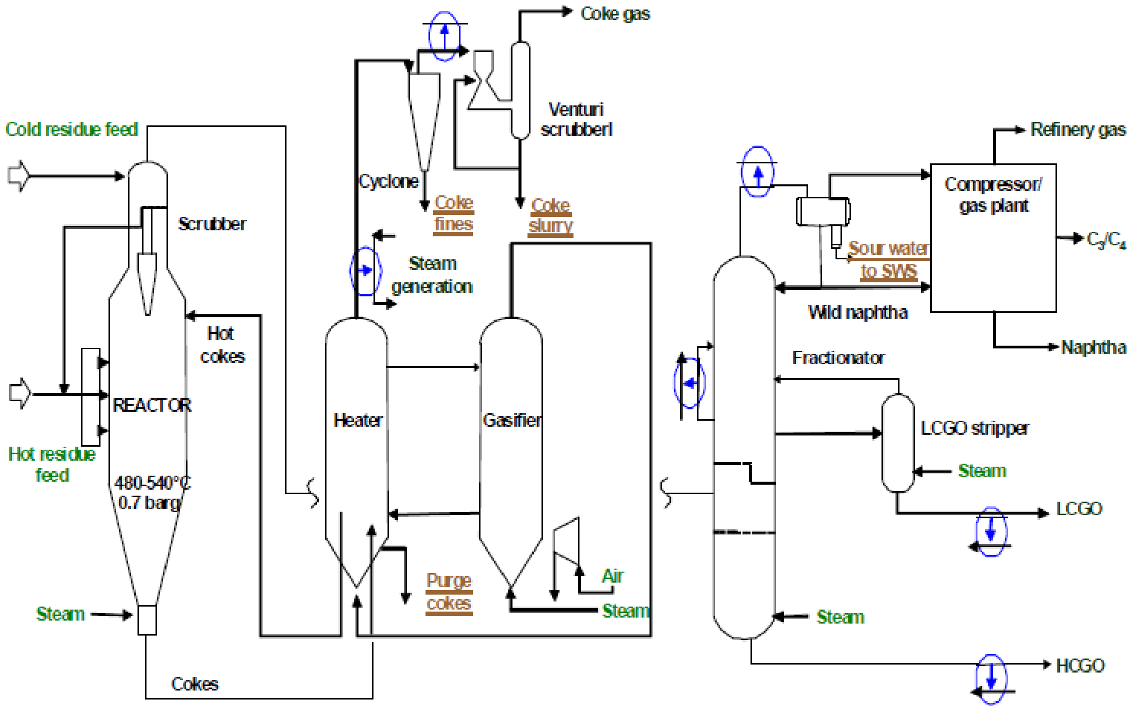

Figure 2.14: Simplified process flow scheme for a flexicoker

Regarding polycyclic aromatic hydrocarbons (PAH), a research study was made in a Turkish refinery about the presence and control of PAHs in petroleum coke drying and calcination plants (Dokuz Eylül University, Kaynaklar Campus, 35160 Buca, İzmir). From this work it was concluded that the storage, shipment, handling, as well as drying and calcination of petroleum cokes might create serious health risks. This material should be processed and handled with care not only because of the excessive dust emissions it causes, but also because it may emit hazardous and carcinogenic volatile compounds. In this study, PAH emissions from a petroleum coke drying and calcination unit in Turkey were investigated. Rotary kiln exhaust gases were found to contain 10 of the 16 EPA priority PAHs[3]. These emissions were identified and evaluated by using the Turkish regulatory limits after certain pollution control measures were implemented. For control of PAHs and other incomplete combustion products in the stack gases incinerators equipped with liquefied petroleum gas (LPG) burners were installed into the drying and calcination gas outlet ducts

(Further information in BREF section 2.7)

2.11 Hydrocracking

Purpose and principle

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 2.14). 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;

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[3] The 16 EPA priority PAHs are the following ones: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]flouranthene, benzo[a]pyrene, dibenz(ah)anthracene, benzo[ghi]perylene, and indeno(1,2,3-cd)pyrene.

- heavy products that are hydrogen-rich for feed FCC units, ethylene plants (LVOC), or lube oil dewaxing and finishing facilities (Section 2.14).

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.

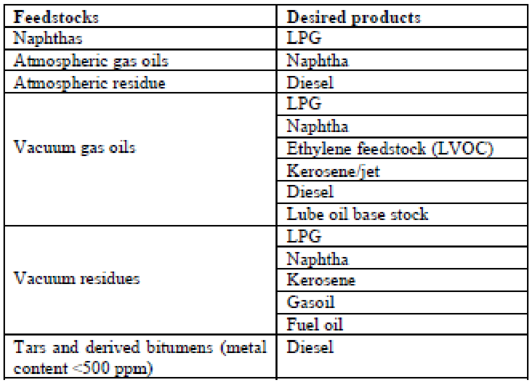
Feed and products streams

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 xx, 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 2.3: Feedstocks and desired products of hydrocracking processes



Feedstocks	Desired products
Naphthas	LPG
Atmospheric gas oils	Naphtha
Atmospheric residue	Diesel
Vacuum gas oils	LPG
	Naphtha
	Ethylene feedstock (LVOC)
	Kerosene/jet
	Diesel
	Lube oil base stock
Vacuum residues	LPG
	Naphtha
	Kerosene
	Gasoil
	Fuel oil
Tars and derived bitumens (metal content <500 ppm)	Diesel

Process description

Hydrocracking normally uses a fixed-bed catalytic reactor with cracking occurring under substantial pressure (35 to 200 kg/cm_2) 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 (H_2S, NH_3, H_2O) 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 lowlevels 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 xx 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 xx. 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.

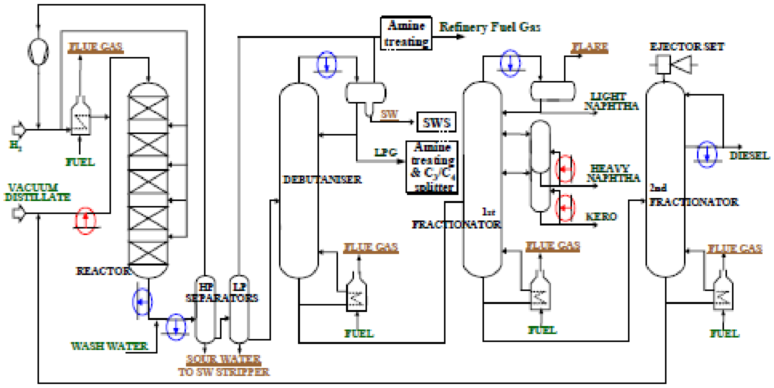


Figure 2.15: Simplified process flow scheme for hydrocracker (single stage with recycling)

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 feed stock 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 xx shows the typical operating conditions of hydrocrackers.

Table 2.4 Typical hydrocracker operating conditions

Operating conditions	Naphtha	Mid distillate	Light gas oil	Heavy gas oil	Residuum
Liquid hourly space velocity	1.0 – 5.0	1.0 – 4.0	1.0 – 5.0	0.75 – 3.0	0.15 – 1
H_2/HC ratio, Nm^3/m^3	50	135	170	337	300
H_2 partial pressure, kg/cm^2	14	28	35	55	55
Reactor temperature, °C	260 – 380	300 – 400	300 – 400	350 – 425	350 – 425

(Further information in BREF section 2.13)

2.12 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 (C_3-C_5) 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 2.7) 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 hydrofluoric acid (HF) or sulphuric acid (H_2SO_4) 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’ january2011.Baku Heydar Aliyev Refinery (Azerbaijan) selected a soli-acid alkylation unit for the basic design.
- 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. There are also techniques to facilitate the retrofitting of a HF plant into a H_2SO_4 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 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 xx), 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 xx), 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. 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 (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. Normal butanes which come in with the unit feed streams are drawn off as a side-stream from the isostripper, treated with KOH and sent to storage.

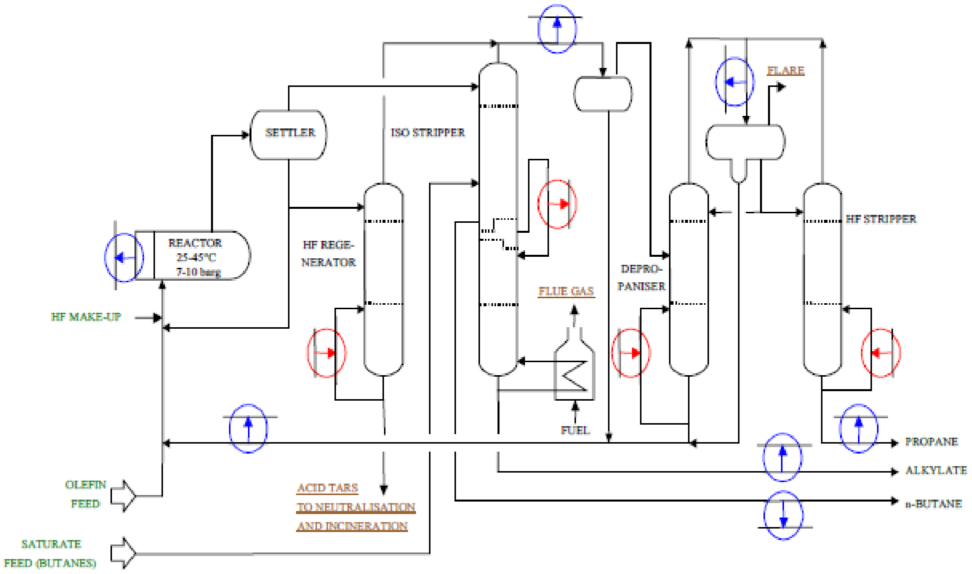


Figure 2.16: Simplified process flow scheme for HF alkylation unit

In the sulphuric acid proces 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 H_2SO_4 in the reactor. The reactor circulation stream enhances a large interfacial area at low temperature (4-15 ºC). Reaction products are first separated in a flash drum and then through a debutaniser. Onsite acid regeneration is also feasible (i.e. WSA technique).

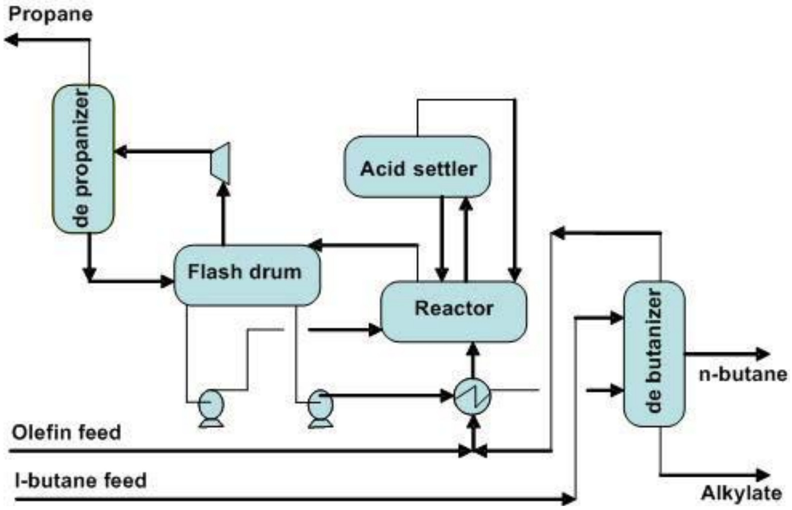


Figure 2.17: Simplified process flow scheme for sulphuric acid alkylation

(Further information in BREF section 2.2)

2.13 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 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) 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

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.

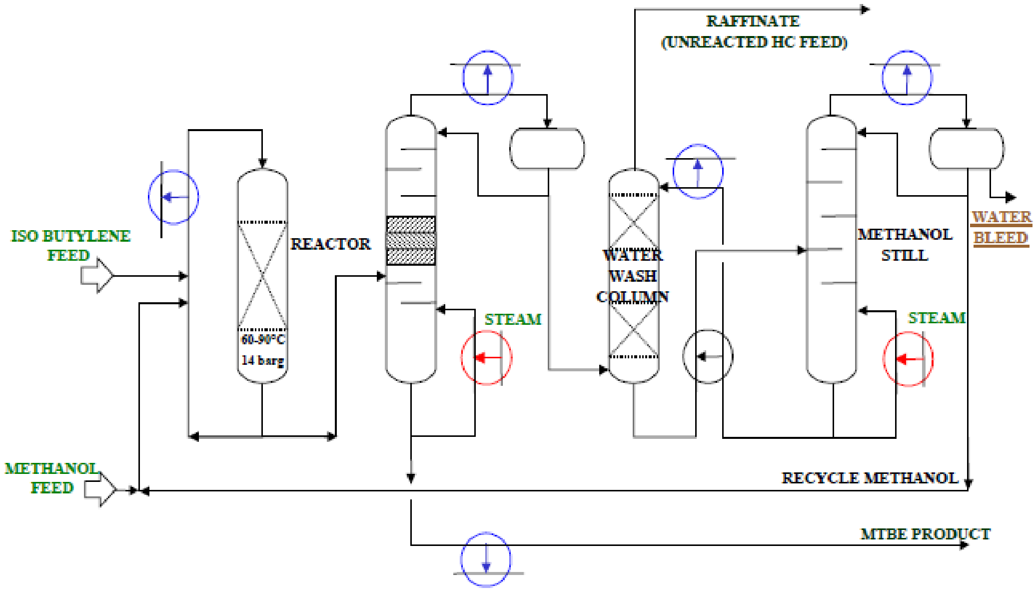


Figure 2.18: Simplified process flow scheme for a MTBE productions process

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_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 xx shows a simplified scheme for the TAME production. C_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_5 side-stream is withdrawn from the column as feed to the TAME unit. Column bottom liquids (C_{6+}) are routed to re-blending with the eventual product from the TAME unit. The C_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_1, C_2, C_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_{6+} stream and passed to storage. The methanol/water fraction is recycled to the methanol recovery plant feed drum.

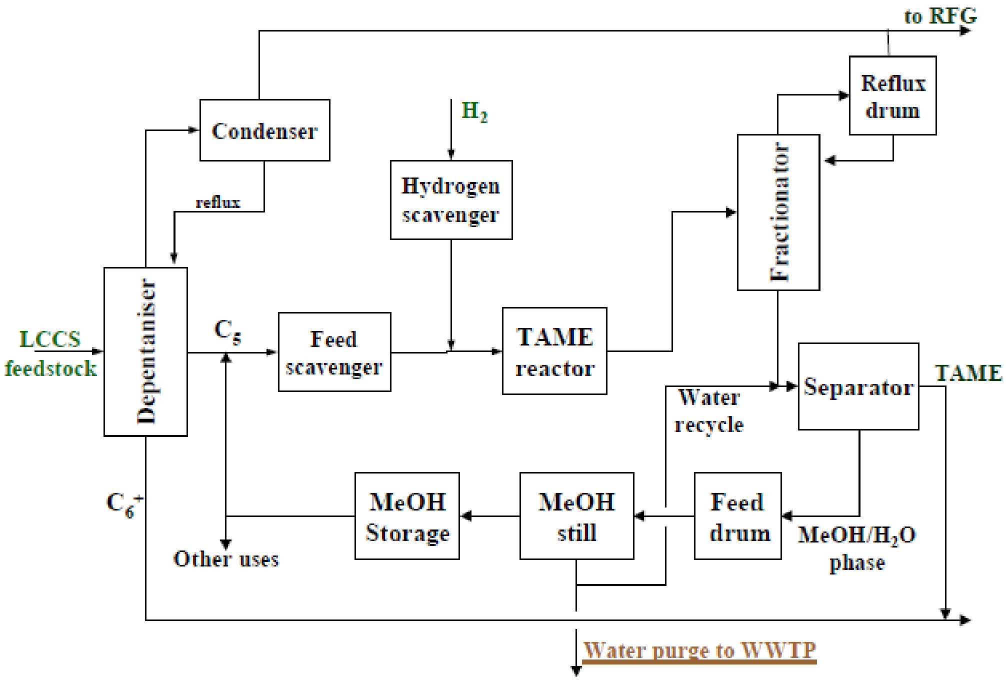


Figure 2.19: Simplified process flow scheme for TAME production

(Further information in BREF section 2.11)

2.14 Base oil production

Although only 20 % of EU refineries produce base oil, some actually specialise in it.

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 2.2); 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:

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;

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

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 2.2), 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.

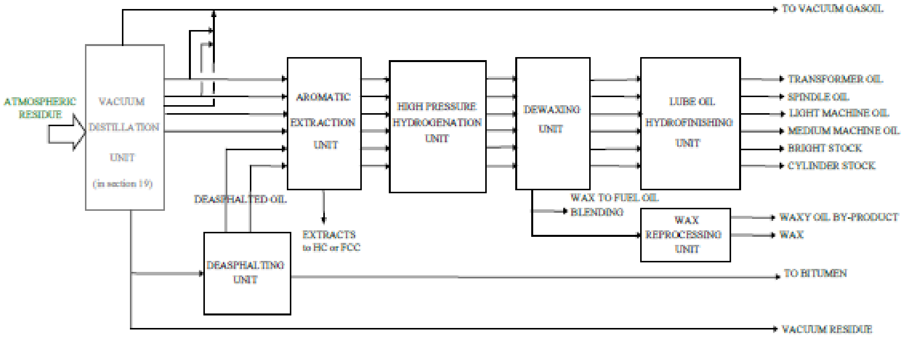


Figure 2.20: Block scheme of a lubricating oil manufacturing plant

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 allhydroprocessing 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 hydroprocessing technologies are available to produce improved base oils of API group II and III quality level oils:

- integrated solvent hydroprocessing;
- catalytic hydroprocessing;
- 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 ºC) 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 ºC.

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 crudes 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 2.4).

In standalone lube oil refineries, the small amounts of H_2S generated due to hydrotreatment are normally incinerated because Claus unit is not available. Instead of hydrotreatment, sulphuric acid and clay treatments may typically be used in old plants.

(Further information in BREF section 2.3)

2.15 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.

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 2.2) and in some instances the residue (extract) from a deasphalting unit (Section 2.14).

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 the most comon in refineries. A simplified process flow diagram of the BBU is shown in Figure xx 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 ºC. With a batch-operated BBU, a feed buffer vessel is usually included to store the hot feedstream from the vacuum unit.

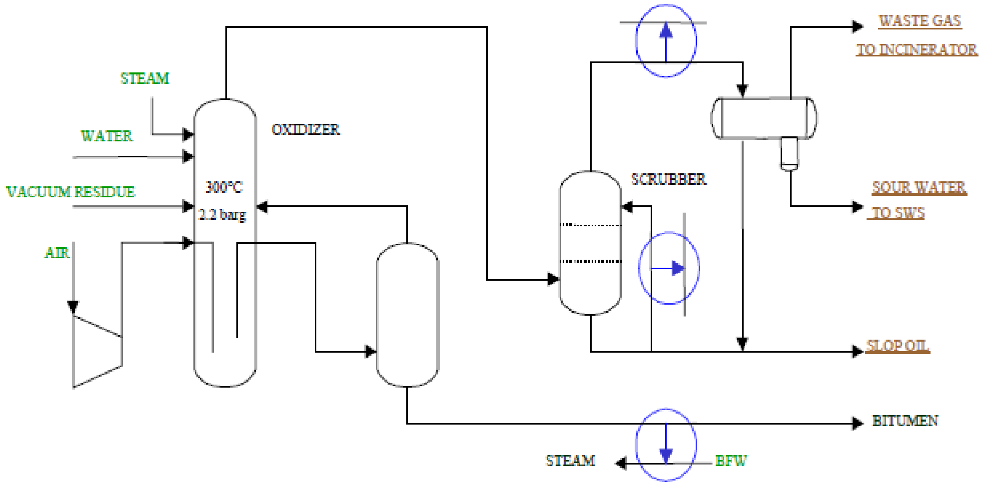


Figure 2.21: Simplified process flow scheme of a bitumen blowing unit

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 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. 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, N_2, O_2, CO_2 and SO_2, is incinerated at high temperatures (~800 °C) to ensure complete destruction of minor components such as H_2S, 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.

(Further information in BREF section 2.4)

2.16 Petrochemicals production: 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:

$2\ C_3H_6 \rightarrow C_6H_{12}$ Dimerisation
$2\ C_4H_8 \rightarrow C_8H_{16}$ Dimerisation
$C_3H_6 + C_4H_8 \rightarrow C_7H_{14}$ Condensation
$3\ C_3H_6 \rightarrow C_9H_{18}$ Polymerisation

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 xx.

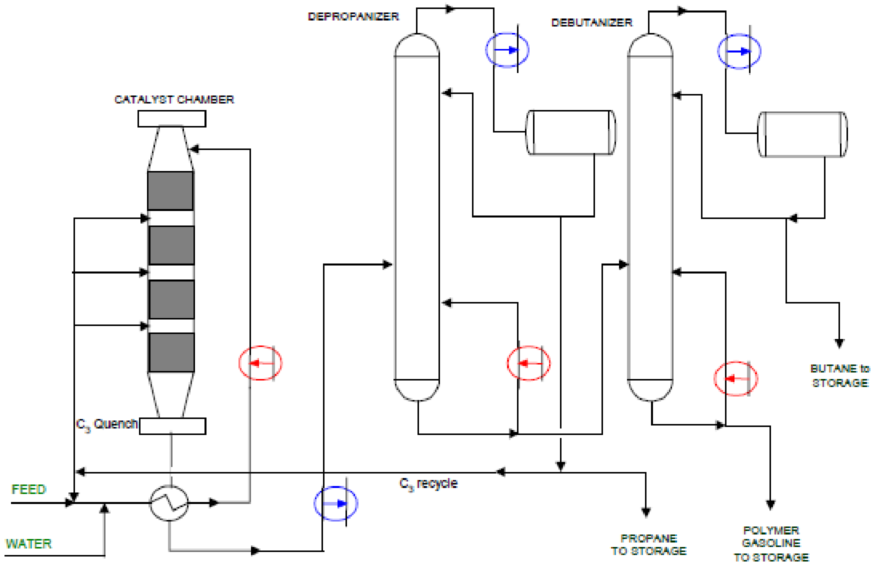


Figure 2.22: Simplified scheme of a polymerisation unit

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.

(Further information in BREF section 2.18)

2.17 Auxiliary and complementary installations

2.17.1 Storage and handling of refinery materials

There is Further information in BREF section on Emisions from Storage. 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.

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. 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. A large part (often 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 xx shows a drawing of the different types of storage systems found in a refinery.

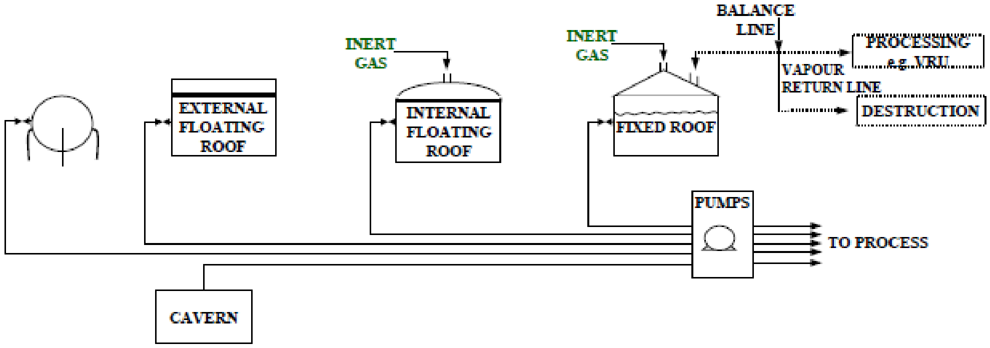


Figure 2.23: Examples of some types of storage tanks

Pressure vessels are normally used to store 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, from 20 mbarg (low pressure) to 60 mbarg (high pressure). In these situations measures to prevent vapour loss and the occurence of flammable atmospheres such as inerting and/or vapour recovery are required Such tanks are necessarily provided with ressure/vacuum relief valves. 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 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.

Odorising plants are 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.

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.

(Further information in BREF section 2.21)

2.17.2 Hydrogen production

Purpose and principle

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 2.4 and 2.11). Hydrogen can be provided by one of the following processes:

- reforming operations (Section 2.3) 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 2.17.4) 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 xx.

Table 2.5: Main chemical reactions occuring in hydrogen production processes

Steam reforming process	
CnHm + n H_2O ===>n CO + (n+m/2) H_2	Generic for steam reforming (endothermic)
CH_4 + H_2O ===>CO + 3 H_2	Steam methane reforming (ΔH = -206kJ/mol at 15°C)
CO + H_2O <===>CO_2 + H_2	Shift (exothermic) (ΔH = + 41.2 kJ/mol at 15°C)
CO + 3 H_2 <===>CH_4 + H_2O CO_2 + 4 H_2 <===>CH_4 + 2 H_2O	Methanation (exothermic)
Partial oxidation	
CnHm + n/2 O_2 ===>n CO + m/2 H_2	Generic for partial oxidation (endothermic)
CO + H_2O ===>CO_2 + H_2	Shift (exothermic) (ΔH = + 41.2 kJ/mol at 15°C)
Gasification	
C + H_2O ===>CO + H_2	Coke gasification (ΔH = -132 kJ/mol at 15°C)
CO + H_2O ===>CO_2 + H_2	Shift (exothermic) (ΔH = + 41.2 kJ/mol at 15°C)

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 (99.9 - 99.999 %

v/v). The partial oxidation process requires oxygen if oxygen-blown gasification is used instead of air-blown gasification.

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 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 useful products are generated as raw synthesis gas containing carbon monoxide and hydrogen (see Table xx). 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. 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. 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, NO_x and SO_x 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. In its simplest form, as shown in Figure xx, 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.

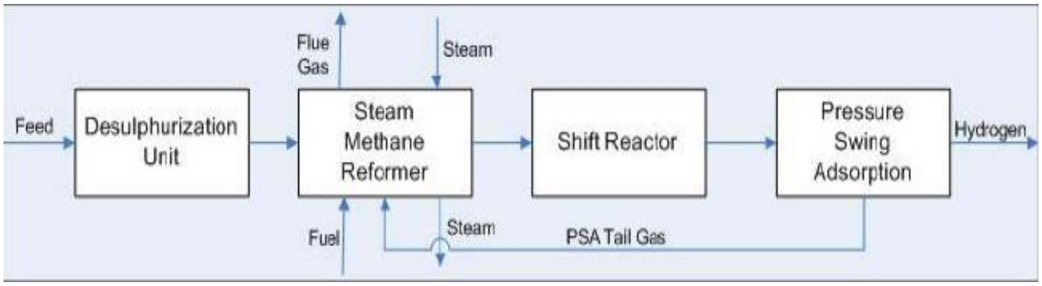


Figure 2.24: The four main steps of H_2 production by steam methane reforming. Source EIGA, Best available techniques for hydrogen production by steam methane reforming, 2009

The reaction is typically carried out at 760 – 840 750 – 1000°C and a pressure of 20 – 30 20 – 40 barg over a fixed catalyst bed 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.

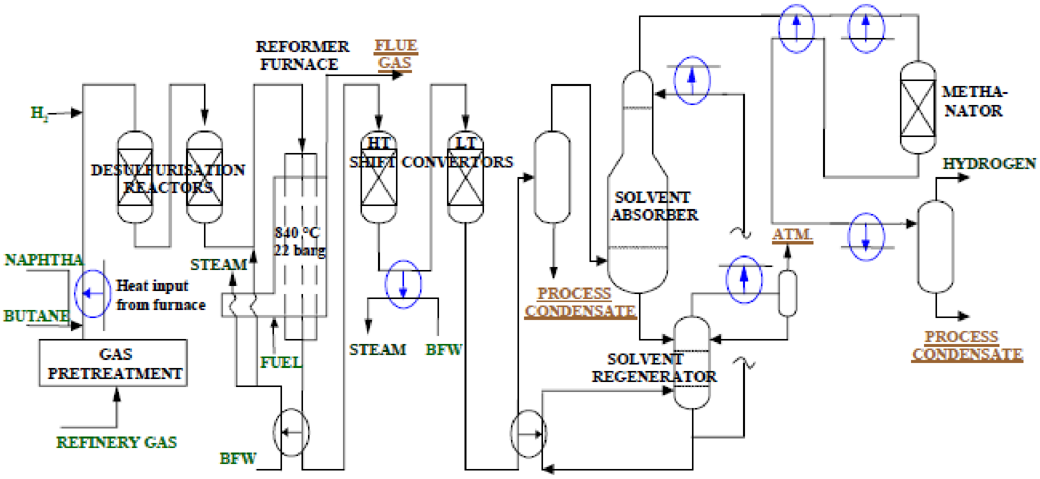


Figure 2.25: Hydrogen production by steam reforming and pressure swing recovery

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 is can be done in a one-step (low, medium or high temperature) converter or, as shown on Figure xx here below, in a two-step highshift (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_2O) after it has passed the cyclones, contains hydrogen sulphide (H_2S) 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 2.6: Example of composition of petroleum coke used and the composition of the syngas produced in a oxygen-blown fluidised-bed gasification process

Analysis of petroleum coke used in gasification		Composition of gas produced by gasification at 980 - 1135 °C	
Ultimate analysis	% w/w		% v/v
Carbon	87.1 – 90.3	CO	34.3 - 45.6
Hydrogen	3.8 – 4.0	CO_2	27.3 - 36.4
Sulphur	2.1 – 2.3	Hydrogen	13.5 - 16.8
Nitrogen	1.6 – 2.5	Water	8.7 - 13.9
Oxygen	1.5 – 2.0	Methane	0.1 - 0.9
Proximate analysis		Nitrogen	0.4 - 0.7
Fixed carbon	80.4 – 89.2	H_2S	0.3 - 0.6
Volatiles	9.0 – 9.7		
Moisture	0.9 – 10.2		
Ash	0.2 – 0.4		

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 2.17.4). 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.

(Further information in BREF section 2.14)

2.17.3 Cooling systems

Under the IPPC process, a horizontal BREF on Industrial Cooling Systems 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 (mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Union, cooperate to protect the marine environment of the North-East Atlantic) and HELCOM (Helsinki Commission to protect the marine environment of the Baltic Sea) working groups. Two of the corresponding studies can be found in the following links:

http://www.helcom.fi/Recommendations/en_GB/rec23_8/

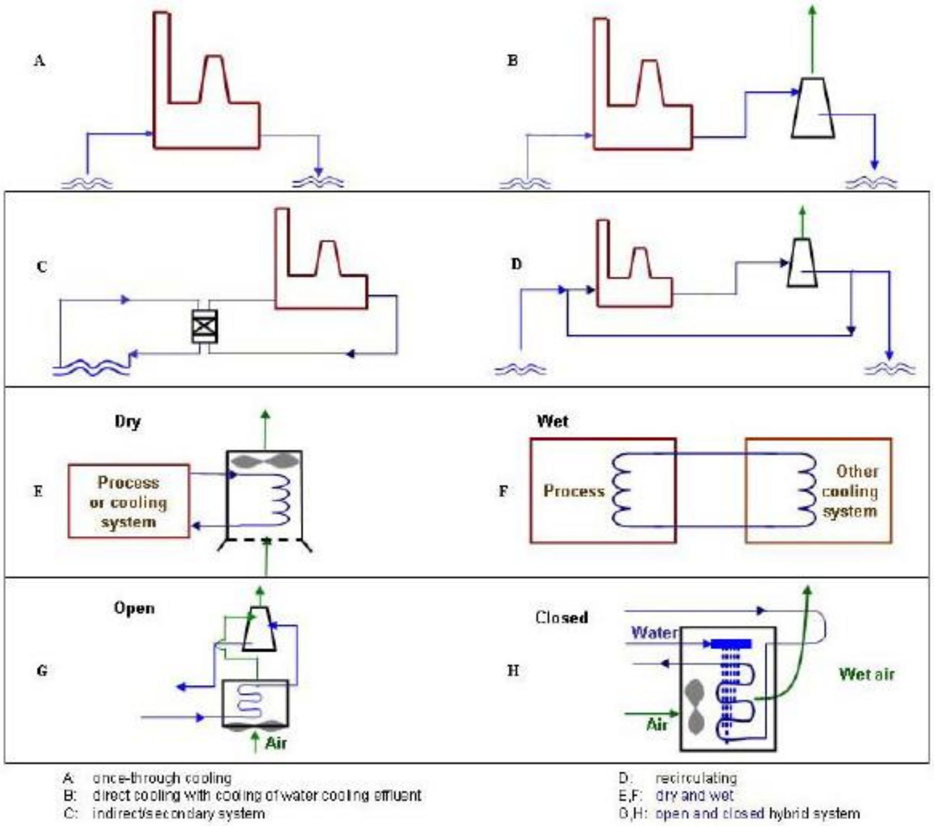
http://www.ospar.org/documents/dbase/decrecs/agreements/80-02e.doc

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 xx and briefly described below:



A: once-through cooling
B: direct cooling with cooling of water cooling effluent
C: indirect/secondary system
D: recirculating
E,F: dry and wet
G,H: open and closed hybrid system

Figure 2.26: Simplified diagrams of the cooling systems used in refineries

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 xx.

Direct water cooling (i.e. quenching)

Because of the high contamination generated by this type of cooling, quenching is only used in cokers (Section 2.10), 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 xx A and B).

Once-through cooling water used for heat exchange with a recirculating water system which then cools the process streams (Figure xx C).

Once-through cooling water is used to cool process streams directly (via heat exchangers) (Figure xx 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 xx 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 xx F).

Hybrid systems

In these 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 xx 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 xx F) using a circulation system (e.g. brine, glycol) where the refrigerant cools the circulating liquid.

(Further information in BREF section 2.8)

2.17.4 Energy systems

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 provided by fuel combustion either directly (by heaters, furnaces) or indirectly via 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).

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). This is a mixture of methane, ethane, ethylene and hydrogen and may contain some CO and small amounts of C_3, C_4, N_2 and H_2S. 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 + H_2) to the RFG system. Most of the refinery fuel gas systems have 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. 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 H_2S before being released to the refinery fuel gas system, and dust removal and COS conversion if necessary. Coke gas forms a main refinery gas source if coking takes place in the refinery. Sulphur content in the form of H_2S is normally below 100 – 220 mg/Nm^3, and will strongly depend on the pressure used in the amine treating units. Levels of 4 – 40 mg/Nm^3 are possible for gas treated at high pressure (20 bars), and lower levels, 2 – 15 mg/Nm^3 can even be reached with very high pressure (50 bars). The nitrogen content is negligible.

Fuel gas system

Figure xx 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.

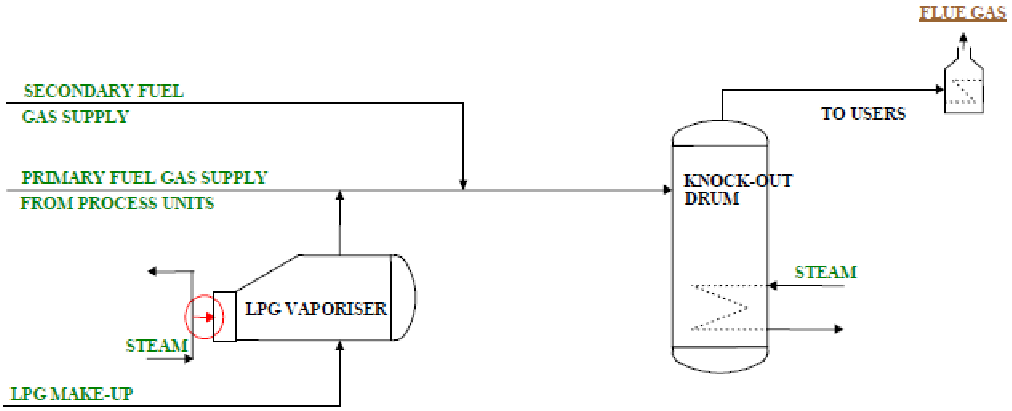


Figure 2.27: Simplified flow diagram of a fuel gas system

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 – 6 %), 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 – 500mg/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. Table xx shows the metal content of residual fuel oil typically used in refineries.

Table 2.7: Metal content of residual oil

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

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 xx) 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 2.10). Coke is burnt in the catalytic cracking regenerator (Section 2.9) and coking process (Section 2.10) and represents a heat production source in the refinery. Coal, as imported fuel, is not applied in European refineries.

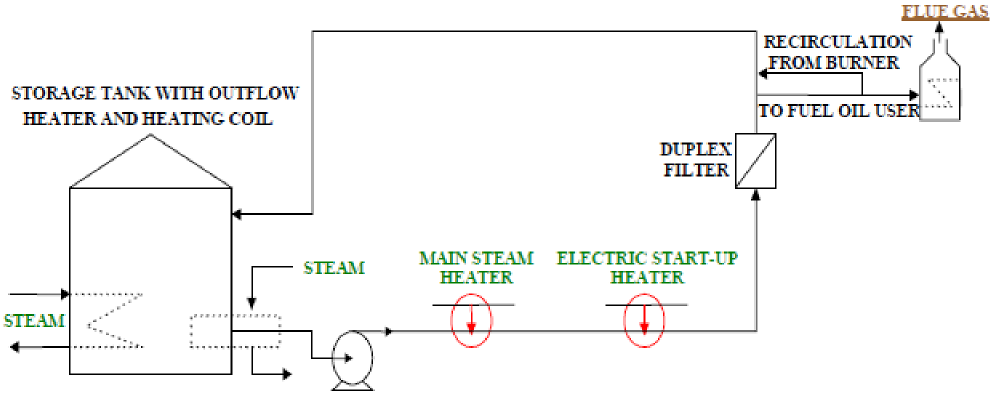


Figure 2.28: Simplified flow diagram of a heavy fuel oil system

Energy production techniques

This section is not intended to include a detailed description of energy production techniques (steam and power), since one can be found in the Large Combustion Plant (LCP) BREF.

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 heatrelease 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 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 hightemperature 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. Combinedcycle 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.

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 2.17.2).

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 ($CO+H_2$). After the combustion chamber, the system contains a number of sophisticated energy recovery systems to produce steam and electricity. Figure xx 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.

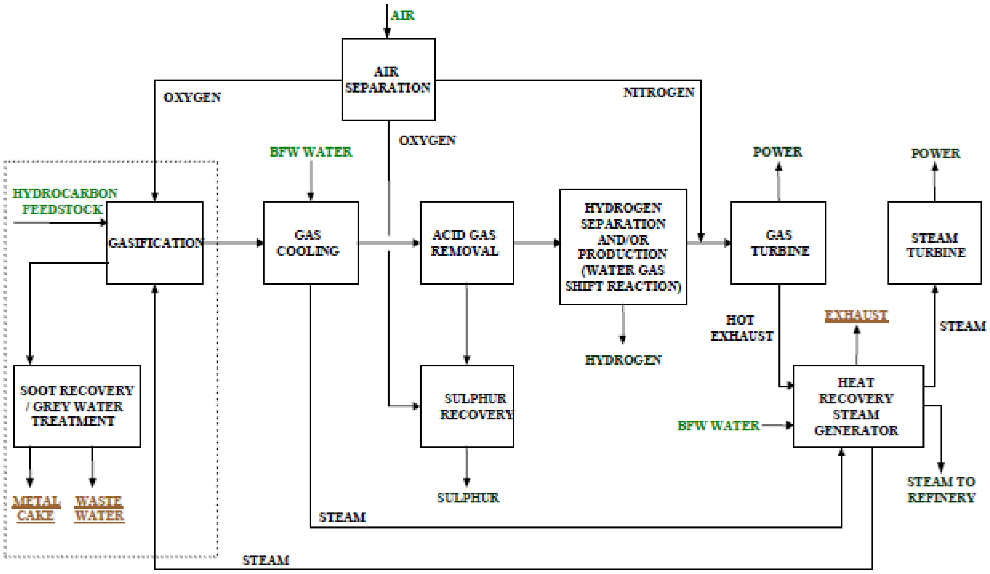


Figure 2.29: Block flow scheme for IGCC

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 gasifiedthrough 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 H_2S. 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 H_2S formed in the gasifier and 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 H_2S 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.

Products from the energy system

As mentioned at the beginning of this section, the energy system of a refinery 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) team 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 xx and to the LCP BREF).

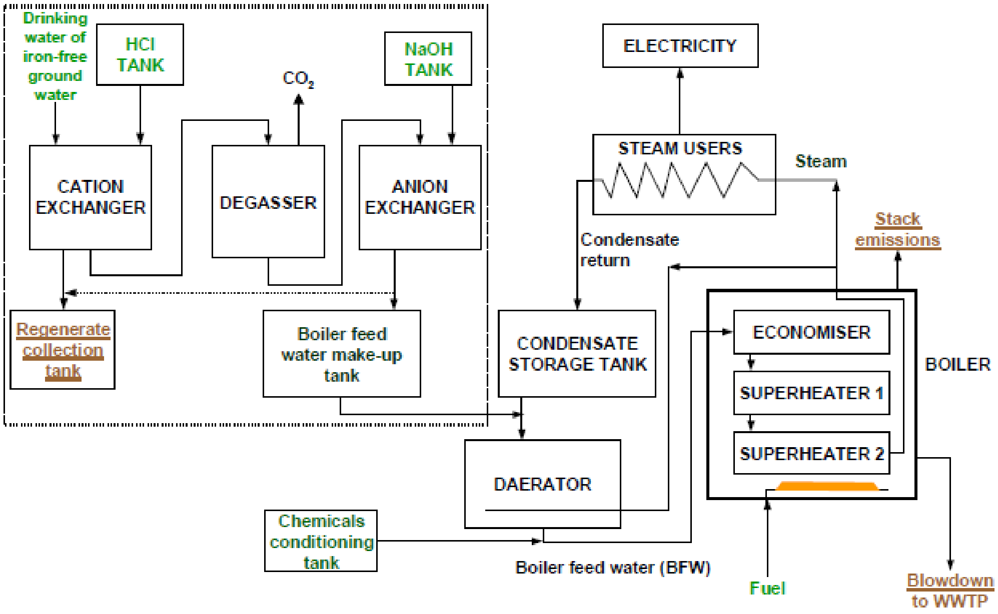


Figure 2.30: Typical layout of a boiler feed water preparation unit and a steam boiler

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 xx). 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. 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 appropiate 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.

(Further information in BREF section 2.10)

2.17.5 Techniques for the abatement of emissions

There are many non-production techniques in use in a refinery. Particularly relevant, for this document are relevant these techniques used to control and abate the emissions to air, water and soil which have been briefly described in section 1.2 of this document, and which will be treated in more detail in Chapter 3. Descriptions of many of these techniques can be found in the BREF Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF), sections 3.3, 3.4 and 3.5, and in Chapter 4 of this guide.

Even if some preventive techniques or primary measures can also be implemented, pollutants such as NO_x, particulates, H_2S, SO_2, 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 H_2S produced on-site. These systems typically contain an amine scrubbing system and a sulphur-recovery unit to convert H_2S 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.

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 onsite 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.

(Further information in the BREF for refining of mineral oil and gas, section 2.25)

3 CURRENT EMISSION LEVELS, ENERGY AND RAW MATERIAL CONSUMPTION

The data and information provided in this Chapter correspond to the year 2012. Currently the evolution of the sector in Turkey is fast, including the construction of a new refinery in Izmir, so updates in the data provided will be needed in following years.

3.1 Air and odour emissions. Air quality and monitoring

Current ranges of emission rates for the refining sector in Turkey are as follows:

Unit *	SO_x	NO_x	Dust	Other pollutants
Combustion units	200-1700 mg/Nm^3	70-800 mg/Nm^3	5-75 mg/Nm^3	

- Table source: TÜPRAŞ

In TÜPRAŞ Refineries, there are continuous emission monitoring systems based on the current national legislation namely Industrial Air Pollution Control and Large Combustion Plant Regulation (03.07.2009/27277, 08.06.2010/27605) With these analysers, values can be obtained for: (NO_x, SO_x, dust, CO) and also data can be obtained for some auxiliary parameters as (T, P, Flow, %O_2).

For TÜPRAŞ Refineries, VOC sampling points are selected based on the Industrial Air Pollution Control Regulation requirements. All VOC measurements are conducted periodically as defined in the Regulation. Emissions of Volatile Organic Compounds (VOCs) have the following limits stated in the national legislation, namely in the By-Law 27277 on Control of Air Pollution Caused by Industrial Installations:

Parameter	Limit Value [µg/m^3]	
	Long term emission limit value	Short term emission limit value
Total organic compounds (carbon equivalent)	500	800
Benzene	75	120
Toluene	75	120

Xcylene	75	120
Olefins	75	120
Ethyl Benzene	75	120
Izopropyle Benzene	5	20
Trimethyl Benzene	5	10
Mercaptanes	1	2
Tetra ethyl-tetra methyl lead	-	1

3.2 Waste water discharges and control

Current ranges of water emission rates for the refining sector in Turkey are shown below:

Point of discharge	Average flow	Pollutants controlled	Range of values for emission
Sea/River	80-1000 m^3/h	pH	6.00-9.00
		COD	30-250 ppm
		Conductivity	140-2800 ppm
		Suspended solids	6-60 ppm
		Total CN^-	0-1 ppm
		Sulfides	0.02-1 ppm
		Oil, Grease	3-10 ppm
		Hydrocarbon	1,5-10 ppm
		NH_4-N	0-20 ppm
		Phenol	0.02-1 ppm
		Cr^{+6}	0-0.1 ppm

In TÜPRAŞ Refineries, wastewater treatment plants consist of physical (e.g. screens, tilted plate separators, grit removals, API basins), equalization basins, chemical (flocculation) and biological treatment units. For sludge treatment, sludge thickening beds and decanters are used. Also, there exists a wastewater reuse system which is advanced physical treatment process.

3.3 Waste generation and disposal

Wastes generated in refineries generally hazardous waste consist of tank bottom sludge, oil sludge from maintenance operations and spent catalysts. In addition, all material which is contaminated with hazardous waste is also considered as hazardous waste. These wastes are either recycled or reused, or sent to disposal via licensed vehicles which are equipped with carrying these type of wastes. Additionally, TÜPRAŞ Refineries have temporary waste storage areas for their hazardous and non-hazardous wastes.

3.4 Noise and vibration

Noise studies: Yes

Number of measurement points: differs from 37 to 357

Years of elaboration of the studies: 2008

According to the current environmental legislation, if a company has the requested certification, there is not an obligation to measure noise. However; during new equipment supply, noise is taken into consideration. In addition, the current equipment is evaluated in order to decrease the noise level.

3.5 Soil and groundwater risks

No information about soil and groundwater pollution risk was provided by the Turkish oil refining sector.

3.6 Raw material consumption

All the data presented below belongs to the year 2011

Crude oil total consumption (x1000 ton) = 20,896

Product obtained (x1000 ton) = 20,209

3.7 Energy consumption

No information about energy consumption was provided by the Turkish oil refining sector.

4 BEST AVAILABLE TECHNIQUES (BATs) IN THE REFINERY SECTOR

The BAT Conclusions for Refining of Mineral Oil and Gas have not been approved at the moment of writing this Guide, so there may be some significant modifications when the last version of the Draft BREF document (published on May 2013, and which has been the reference for this guide) is approved within the Forum created by the European Commission. That Draft has to be submitted and assessed by the Forum mentioned in the article 13 of the Industrial Emissions Directive 2010/75/EU, and afterwards the BAT Conclusions will be submitted for formal approval following the Committee procedure defined in the EC Implementing Decision 2012/119/EU. The main aspects which may be subject to change are those which have generated dissenting views in the Final Meeting of the Technical Working Group in April 2013. These aspects will be mentioned along this chapter and will be explained in detail in Section 4.7.

In order to correctly understand the different techniques applicable in the refinery sector, it must be clear that the definition of *techniques* in the IED refers, not only to the technology used, but also to the way in which the installation is designed, built, maintained, operated and decommissioned. This chapter covers environmental management systems, process-integrated techniques and end-of-pipe techniques applicable for the prevention and control of pollution from refining processes. Waste prevention and management is also included, as well as techniques that reduce the consumption of raw materials, water and energy. Some techniques also cover measures to prevent or reduce emissions when not normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions and momentary stoppages). The BREF for Refining of Mineral Oil and Gas (REF BREF) 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 should be considered by the Competent Authority for the determination of BAT for an individual installation.

The sections in this chapter are structured covering the main environmental aspects associated to the different refinery processes. The process and abatement techniques considered in the determination of BAT are presented for each one of these environmental aspects (i.e. emissions to air, water discharges, waste generation, etc.) as well as for the main pollutants from refineries, according to the list of polluting substances in Annex II of IED. BAT conclusions and BAT associated emission levels (BAT-AELs) are listed along the different sections following this structure. Additional information on the description, operational data, applicability, economical aspects and cross-media effects of the techniques can be found in Chapter 4 of REF BREF. Furthermore, general description and principles of the functioning of these techniques can be consulted in the BREF Reference Document on Common Waste Water and Waste Gas Treatment/Management Systems in Chemical Sector (CWW BREF) where individual treatment techniques, generally applicable in different sectors, are presented as waste water treatment techniques (CWW BREF, Section 3.2.3), sludge treatment techniques (CWW BREF, Section 3.2.4) and gas end-of-pipe treatment techniques (CWW BREF, Section 3.2.5). Many references are made along this Guide to the Sections in the REF BREF where more information can be found. The REF BREF sets out the BATs specific to this industrial sector. Nevertheless, other BREFs contain as well BATs and other relevant information that may be considered and may help in the assessment of the environmental impacts of this sector and the techniques to reduce them. For further information related to the environmental impact of cooling systems used in combustion plants, techniques can be found in the BREF on industrial cooling systems. Regarding general information on the monitoring and reporting of emissions from the combustion of fossil fuels, the methods and instruments used for the monitoring of emissions should be the applicable national or international methods; for more detailed information on general monitoring issues, reference is made to the BREF on the General Principles of Monitoring (Monitoring BREF). This BREF does not establish BATs but contains a lot of relevant information related to the measurements and data management. At the moment of drafting this guide, the Monitoring BREF is being reviewed, in addition, its status has been changed from “BREF” into “Reference Report” by the European Commision due to the fact that it is not possible to derive BAT Conclusions as defined in the Industrial Emission Directive. For more information on the techniques applicable for the prevention and reduction of emissions from storage and handling activities, the description of techniques applicable can be found in the BREF on Emissions from Storage.

How to proceed in case that the BAT associated emission levels and conditions imply a disproportionate investment for the corresponding installation:

Frequently, depending on local conditions of the sector in a country, difficulties to fulfill some emission level values and conditions considered as BAT are found. According to the feedback of representatives of TÜPRAŞ that will probably be the case of Turkish refining sector, as in some cases it will be technically and/or economically impossible to reach ELVs and conditions of the BREF starting from their current technologies and levels of emissions, described in chapter 3. This situation may happen not only in very old installations but also in those that were designed only a few years ago but without taking into account the new techniques and levels stated in the reviewed version of the REF BREF, because it was not applicable or existing at the moment of the design of those installations.

Regarding these problematic cases, first it is important to know that BREF values and conditions will not be applicable immediately after the publication of this guide, as there will be a transition period to pass from present legal conditions (current applicable Turkish legislation) to BAT values and conditions that will be applicable in a future. More specifically, 3 years after the By-Law on Integrated Environmental Permits is published in the Official Bulletin, it will enter into force for new installations, while in the case of existing installations a longer transition calendar to obtain the new integrated environmental permits for the different sectors under the scope of the By-Law will be defined by the Ministry of Environment and Urbanism (MoEU). This transition period for existing installations will start 3 years after the By-Law on Integrated Environmental Permits is published in the Official Bulletin, and will last for 10 years, but as said, the MoEU will define, within that period of 10 years, what are the deadlines for the different kinds of installations under the scope of the By-Law.

Secondly, when a given installation applies to get an integrated environmental permit, and always depending on the final decision of the permitting competent authority, in very special cases it may be given an extra adaptation period or even emission limit values or conditions less restrictive than the ones stated in the BAT conclusions documents. This can happen only when the operator provides an assessment showing that the achievement of emission levels associated with the best available techniques as described in BAT conclusions would lead to disproportionately higher costs compared to the environmental benefits due to: a) the geographical location or the local environmental conditions of the installation concerned, b) the technical characteristics of the installation concerned.

Thirdly, it must be always kept in mind by both the operators and the permitting competent authority that in general the implementation of a given BAT mentioned in the corresponding BAT Conclusions document is not obligatory. What has a more binding character, with the exceptions mentioned in the previous paragraph, are the BAT associated emission levels (BAT-AELs) which appear in those documents.

Definitions

For the purpose of the BAT conclusions in this chapter, the following definitions apply:

a. '**Unit**' means a segment/subpart of the installation in which a specific processing operation is conducted

b. **'New unit'** means a unit first permitted on the site of the installation after the date of entry into force for new installations of the By-Law on Integrated Environmental Permits currently drafted by the Ministry of Environment and Urbanism, or a complete replacement of a unit on the existing foundations of the installation after the date of entry into force for new installations of the By-Law on Integrated Environmental Permits.

c. **'Existing unit'** means a unit which is not a new unit

d. **'Process off-gas'** means the collected gas generated by a process which must be treated e.g. in an acid gas removal unit and SRU

e. **'Flue-gas'** means the exhaust gas exiting a unit after an oxidation step, generally combustion (e.g. regenerator, Claus unit)

f. **'Tail gas'** means a common name of the exhaust gas from an SRU (generally Claus process)

g. **'VOC'** means volatile organic compounds as defined under Directive 2010/75/EU

h. **'Diffuse VOC emission'** means 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)

i. **'Fugitive VOC emission'** means diffuse VOC emissions from 'point' sources

j. **'NO_x expressed as NO_2'** means the sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2) expressed as NO_2

k. **'SO_x expressed as SO_2'** means the sum of sulphur dioxide (SO_2) and sulphur trioxide (SO_3) expressed as SO_2

l. **'H_2S'** means hydrogen sulphides. Carbonyl sulphide and mercaptan are not included

m. **'Hydrogen chloride expressed as HCl'** means all gaseous chlorides expressed as HCl

n. **'Hydrogen fluoride expressed as HF'** means all gaseous fluorides expressed as HF

o. **'FCC unit'** means 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

p. **'SR unit'** means sulphur recovery unit (see technique definition in Section 4.2.2)

q. **'Combustion unit'** means liquid, gas, solid or multi-fuel fired unit burning refinery fuels alone or with other fuels for the production of energy at the refinery site. Combustion units include e.g. boilers (except CO boilers), furnaces and gas turbines. (NB: combustion plant running exclusively on commercial fuels are covered by the LCP BREF)

r. **'Refinery fuel'** means solid, liquid or gaseous combustible material from the distillation and conversion steps of the refining of crude oil'. Examples of commonly used refinery fuels are refinery fuel gas (off-gases from distillation or conversion), syngas, and refinery oils. Pet coke may also be used.

s. **'Volatile liquid hydrocarbon compounds'** are petroleum derivatives with a Reid vapour pressure (RVP) of more than 4 kPa. This is particularly meant for e.g. Naphtha, crudes and aromatics.

t. **'NMVOC'** means Non methane volatile organic compounds (VOC)

u. **'Recovery rate'** means the percentage of non-methane volatile organic compounds (NMVOC) recovered from the streams conveyed into a vapour recovery unit (VRU)

v. **'Continuous measurement'** means a measurement using an 'automated measuring system' (AMS) or a 'continuous emission monitoring system' (CEMS) permanently installed on site

w. **'Periodic measurement'** means a determination of a measurement (particular quantity subject to measurement) at specified time intervals using manual or automated reference methods

x. **'Indirect Monitoring of emissions to air'** means an estimation of the emissions concentration in the flue-gas of a pollutant obtained through an appropriate combination of measurements of surrogate parameters (such as O_2 content, sulphur or nitrogen content in the feed/fuel), calculations and periodic stack measurements. The use of emission ratios based on S content in the fuel is one example of indirect monitoring. Another example of indirect monitoring is the use of PEMS

y. **Predictive Emissions monitoring systems (PEMS)** means a system to determine the emissions concentration of a pollutant based on its relationship with a number of characteristic continuously monitored process parameters (e.g. fuel gas consumption, air/fuel ratio) and fuel of feed quality data (e.g. the Sulphur content) of an emission source

4.1 Fuel consumption reduction and thermal/energetic optimization

For the correct interpretation of the information in this Section, it is necessary to clarify that REF BREF only analyzes the refinery fuels produced within the facility. In this respect, emission levels, consumption data, cross-media effects, etc. related to commercial fuels (natural gas, fuel oil, etc.) can be found in the BREF for Large Combustion Plants (LCP BREF). Furthermore, the techniques applicable on energy efficiency are addressed as general matter in the BREF for Energy Efficiency (ENE BREF).

All measures to reduce energy consumption will result in a reduction of emissions to air, including CO_2. Among the techniques to consider in the determination of BAT, the execution of campaigns on combustion improvement, the installation of alternative concepts (gas turbines, CHP, expanders, improved heat integration) and the switch to cleaner-burning fuels are some of the examples that can be applied for the energy optimization. Cross-media effects will result as consequence of the application of end of pipe techniques to abate emissions, as it will lead to higher energy consumption and increase of CO_2.

An increase in the energy efficiency has a direct impact on reducing air emissions, and indirectly on the generation of waste water and waste. Lower consumption of fuels or more energy conservation increase the possibility that the refinery gas supply will be sufficient for the whole refinery. The reduction in the energy consumption or the increase in the energy efficiency will also result in the reduction of the total operating cost.

Energy management may be included in the refinery’s management system. The optimization of the design and management of energy systems is focused on the harmonization of the variable fuels production and consumption in processes and utilities at the lowest economic and environmental cost. In principle, the ISO 14000 system series or EMAS and EN 16001 on energy management systems provide an adequate framework to develop a satisfactory energy management system. Some actions such as reporting of energy consumption data to the authorities, energy audits, participation in ranking/benchmarking activities or investment plans on energy consumption reduction are considered good practices to ensure a continuous improvement. Another measure to adapt production and consumption of fuels is to try to improve the energy intensity within the refinery. There are several methodologies that allow the evaluation of the energy efficiency in a refinery, including the Solomon energy efficiency index, specific energy consumption and the index relating the energy consumption to the amount of feedstock processed.

Design techniques such as the optimization of heat integration and the use of improved furnace efficiency combined with computer-controlled combustion are general measures applicable. Heat integration/recovery techniques directly result in lower emissions of CO_2, NO_x, particulates and SO_2 (REF BREF, Section 3.10). Also, cost savings by reduction of the fuel consumption are achieved. Nevertheless, the exchange of heat between processes implies transference on disturbances from one process to another that can affect safety, so stability control systems may be required. Other design techniques are:

- Installation of waste heat boilers in heaters
- Installation of expanders/power recovery (e.g. in FCC unit)
- Expanded heat exchanger areas in which cold streams are preheated by war product streams directly from processes
- Direct feed of semi-products to process without cooling and storage
- Balancing of vapour and refinery fuel gas systems

Process control and maintenance techniques, such as steam consumption reduction, decrease the overall energy consumption and minimize 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. Information on process control and maintenance techniques that can be implemented is given in REF BREF, Section 4.10.1.2.2.

Techniques to consider in the determination of BAT for energy production include:

a) Techniques applicable in furnaces and boilers: In the case of furnaces and boilers, the application of primary techniques will lead to reduction of energy consumption and related emissions from processes requiring heat or steam production. The implementation of these techniques will also decrease CO, NO_x, SO_x and particulate emissions. Some specific techniques for reducing air pollutants, such as low-NO_x, flue-gas desulphurization and others will be explained later in this chapter. General primary techniques are summarized below (see also LCP BREF):

- Installation of combustion air preheaters to increase the furnace efficiency significantly
- Optimization of furnace operations, and hence combustion efficiency, by an advanced control of the operations variables
- High thermal efficiency heater/boiler designs with good control systems
- Minimization of heat losses via exhaust gas

- Continuous monitoring of temperature and O_2 concentration of flue-gas for combustion optimization
- Maintain a high boiler pressure
- Preheating of fuel charged to the boilers
- Preheating of boiler feed water with steam
- Prevention of the condensation of exhaust gas on surfaces
- Minimization of own requirements by high efficiency pumps, vents, etc
- Optimization of combustion conditions
- Techniques to control CO emissions (good operational control, constant delivery of liquid fuel in the secondary heating, good mixing of exhaust gases or 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

b) Techniques applicable in gas turbines: In the case of gas turbines, the following techniques can be applied in order to increase efficiency and reduce NO_x, SO_x, CO and particulates emissions to air:

- 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-NO_x burners
- 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

Steam injection typically produces higher emissions of CO and hydrocarbons. Steam should be produced if it is not available in the refinery.

c) Cogeneration Plants: For the combination refinery/other power generators (OPG), the energy consumption and CO_2 emissions will be reduced by the application of the cogeneration plant (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 cogeneration, reducing fuel use and its related emissions. 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.

d) Gasification of heavy oils or coke: Integrated Gasification Combined Cycle (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. Hot gas cleanup systems have the potential to increase system efficiency and lower system costs. The purpose of this technique is to produce steam, hydrogen (optional) and electric power from a variety of low-grade fuel types with the highest conversion efficiency possible. The emissions from the IGCC show a significant decrease compared with conventional power/steam plants. The SO_2 concentration in the refinery exhaust is reduced by 80 % but CO_2 emissions increase. This technique can be seen as an alternative approach to removing sulphur using feed hydrotreatment (REF BREF, 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 high sulphur content. 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. More information can be found in REF BREF, Section 2.10.

BAT 1: Energy Efficiency improvement

In order to use energy efficiently, **BAT is to** use an appropriate combination of the following techniques (REF BREF, Section 5.1.2):

Technique	**Description**
1. Design Techniques	
a. Pinch analysis	Methodology based on a systematic calculation of thermodynamic targets for minimizing energy

	consumption of processes. Used as a tool for the evaluation of total systems designs
b. Heat integration	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.
c. Heat and power recovery	Use of energy recovery devices e.g.: • Waste heat boilers • Expanders/power recovery in the FCC unit • Use of waste heat in district heating
2. Process control and maintenance techniques	
a. Process optimization	Automated controlled combustion in order to lower fuel consumption per tonne of feed processed often combined with heat integration for improving furnace efficiency
b. Management and reduction of steam consumption	Systematic mapping of drain valve systems in order to reduce steam consumption and optimize its use
c. Use of energy benchmark	Participation in ranking and benchmarking activities in order to pursue a continuous improvement by learning from best practice
3. Energy efficient production techniques	
a. Use of combined heat and power	System designed for the co-production (or the cogeneration) of heat (e.g. steam) and electric power from the same fuel
b. Integrated gasification combined cycle (IGCC)	Technique whose purpose is to produce steam, hydrogen (optional) and electric power from a variety of fuel types (e.g. heave fuel oil or coke) with a high conversion efficiency

This BAT conclusion is based on information given in REF BREF, Section 4.10.1

4.2 BAT to reduce emissions to air

The main air emissions from refineries are CO_2, SO_x, NO_x, VOC and particulates (dust, soot and associated heavy metals). Noise, odour, H_2S, NH_3, CO, CS_2, benzene, toluene, dioxins, HF and HCl also contribute to the atmospheric emissions. They emerge typically from sources such as stacks of process furnaces and boilers, regenerators (FCC), individual items as valves and pump seals and, to a lesser extent, from flares and incinerator stacks.

In this Section, the techniques for preventing and controlling air emissions are structured according to the main pollutants emitted. However, BAT conclusions for the minimization of combined pollutants emissions are also described. Some techniques identified for specific pollutants may have a direct/indirect effect on other pollutants and parameters associated. These cross-media effects resulting from the implementation of certain techniques are described in major detail in the REF BREF sections referenced along this chapter.

Some techniques may have a positive and/or negative impact on other environmental media or on raw material and energy consumption. For example, as it has been explained in the previous section, the implementation of techniques that increase the energy efficiency will have a direct impact on the reduction of air emissions (NO_x, SO_x, CO, CO_2 and particles). Nevertheless, the application of some of these techniques may also have a negative effect on the control of certain pollutants and parameters as, for instance, the technique of air preheating which typically increases the production of NO_x. In this case, in order to address the increase in thermal NO_x for units fired with fuel gas, it is necessary to apply adjustment factors for NO_x emissions as a function of preheated air temperature (REF BREF Section 4.10.3.1, Figure 4.27). 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 (Section 4.10.2.3, Figure 4.26) in order to avoid double counting the NO_x increase due to the fuel nitrogen conversion.

Selection and treatment of fuel

An alternative to reduce SO_2, NO_x, CO_2 and metals emissions from a refinery is 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). The move from liquid to gas fuel would require process upgrades and gas grid connections and the surplus residue that results from replacing the residual fuel by gas would have to be considered in the integrated solution for the fuel system of the refinery.

Gaseous fuels typically release less NO_x per unit of energy compared to liquid fuels, especially liquid refinery fuels. For gaseous fuels, usually only thermal NO_x is relevant; however NO_x emissions will depend on the gaseous fuel composition. Oil burning normally leads to higher levels of NO_x releases for several reasons, especially due to fuel NO_x arising from the nitrogen content (REF BREF, Section 4.10.2.3), the need to balance NO_x and particulate releases and the design requirements for firing in combination with gas.

Gas-fired boilers generate lower particulate emissions (including heavy metals) and SO_2 emissions when the refinery gases are cleaned in amine scrubbers. CO_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). When refinery fuel gases are sulphur-containing at source (i.e. from crude distillation, cracking and all hydrodesulphurising processes) the gas streams are normally treated by amine scrubbing to remove H_2S before being released to the refinery fuel gas system.

For liquid refinery fuels, the content of the fuel used is determined by the crude used and by the process units that it has passes through. Feed hydrotreating of fuels will reduce the feed nitrogen, sulphur and metals content, which in turn reduces de SO_2, NO_2 and particulate emissions. However, the hydrotreatment of fuels is a very energy-intensive process, consuming hydrogen with a consequent increase in CO_2 emissions and effluent water and waste (used catalyst) are generated.

An alternative method for the gasification of heavy residual oils or petroleum coke is the combustion in a fluidised boiler with limestone injection for sulphur capture. With the application of fluidised-bed boilers, 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. 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.

General considerations

Unless stated otherwise, emission levels associated with the best available techniques (BAT-AELs) for emissions to air given in this Section refer to monthly average values of concentration, expressed as mass of emitted substance per volume of waste gas, under the following standard conditions: dry gas, temperature 273.15 K, pressure 101.3 kPa.

Averaging period for emissions to air

For continuous measurements	Unless stated otherwise, BAT-AELs refer to daily monthly average values
	Monthly average: average over a period of one month based on valid hourly averages measured by continuous measurements
	Daily average: average over a period of one day based on valid hourly averages measured by continuous measurements
For periodic measurements	BAT-AELs refer to the average value of three spot samples of at least 30 minutes each

Activities	Unit	Oxygen reference conditions
Combustion process using solid, liquid or gaseous fuels with the exception of gas turbines and engines	mg/Nm^3	3 % oxygen by volume
Catalytic cracking (regeneration of catalyst)	mg/Nm^3	3 % oxygen by volume
Gas turbines (including combined cycle gas turbines – CCGT) and engines	mg/Nm^3	15 % oxygen by volume
Sulphur recovery unit (SRU)	mg/Nm^3	3 % oxygen by volume

The formula for calculating the emissions concentration at a reference oxygen level is shown below:

$$E_R = (21 - O_R / 21 - O_M) \times E_M$$

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

Preliminary note regarding the monitoring of emissions

Regarding monitoring requirements, what has a binding character, with the exceptions mentioned in the explanations at the beginning of this chapter, are the **monitoring frequencies associated to the BAT-AELs**. There may exist some particular installations in Turkey where it could be technically and/or economically difficult to implement some of the monitoring devices required to fulfill the conditions of the table of BAT 2 about monitoring (see below). According to the explanations at the beginning of this chapter, if this happens, the permitting competent authority will set in the permit alternative strategies to monitor the contaminants, in a way that could provide a similar level of pollution control.

BAT 2: Monitoring of emissions to air

BAT is to monitor emissions to air by using the monitoring techniques with at least the minimum frequency given below and in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality (REF BREF, Section 5.1.4).

Description	**Process unit**	**Minimum frequency**	**Monitoring technique**
Monitoring of emissions to air			
1 Monitoring of SO_x, NO_x, and dust	Catalytic cracking	Continuous (2, 4)	Direct measurement
	Combustion units ≥100 MW(6) and calcining units	Continuous (2, 4)	Direct measurement (5)
	Other combustion units of 50 up to 100 MW (6)	Continuous	Direct measurement of indirect monitoring (2)

	Other combustion units	Once a year and after significant fuel changes (1)	Direct measurement of indirect monitoring (2)
	Sulphur recovery units (SRU)	Continuous for SO_2 only (4)	Direct measurement of indirect monitoring (3)
2 Monitoring of NH_3 emissions	All units equipped with SCR or SNCR	Continuous	Direct measurement
3 Monitoring of CO	Catalytic cracking and combustion units ≥ 100 MW	Continuous	Direct measurement
	Other combustion units	Once every 6 months (1)	Direct measurement
4 Monitoring of emissions of metals (Ni, Sb, V),	Catalytic cracking	Once every 6 months and after significant changes to the unit (1)	Direct measurement or analysis based on metals content in the catalyst fines and in the fuel
	Combustion units (8)		
5 Monitoring of PCDD/F	Catalytic reformer	Once a year or once a regeneration whichever the longer	Direct measurement

(1) Continuous SO_x emissions from SRU may replaced by a material balance provided appropriate measurements of SRU efficiency are based on regular plant performance tests

(1) Monitoring frequencies may be adapted if, after a period of one year, the data series clearly demonstrate a sufficient stability

(2) Continuous measurement of SO_2 emissions may be replaced by calculations based on measurements of the sulphur content of the fuel or the feed where it can be demonstrated that this leads to an equivalent level of accuracy

(3) SO_2 emissions measurements from SRU may be replaced by a continuous material balance or other relevant process parameter monitoring provided appropriate measurements of SRU efficiency are based on periodic (e.g. once every 2 years) plant performance tests

(4) Only SO_2 is continuously measured, SO_3 is only periodically measured (e.g. during calibration of the SO_2 monitoring system).

5) Or indirect monitoring of SO_x

(6) Refers to the capacity connected to the stack where emissions occur

(7) Sb is to be monitored only in catalytic cracking units when Sb injection is used in the process (e.g. for metals passivation)

(8) With the exception of combustion units firing only refinery fuel gas

BAT 3: Monitoring of process parameters

BAT is to monitor the relevant process parameters by using the monitoring techniques and the minimum frequency given below.

Description	**Process unit**	**Minimum frequency**	**Monitoring technique**
2.1 Monitoring of parameters linked to pollutant emissions, e.g. O_2 content in flue-gas, N and S content in fuel or feed (1)	Catalytic cracking and combustion units > 50 MW_{th}	Continuous for O_2 content. For N and S content, periodic at a frequency based on significant fuel/feed changes	Specific to each relevant paramenter
(1) N and S monitoring in fuel or feed is not applicable when continuous measurements of NOx and SOx are carried out at the stack			

BAT 4: Monitoring of diffuse emissions of VOC

BAT is to monitor VOC diffuse emissions to air from the entire site by using all of the following techniques (See *Technique f,* in Section 4.2.5):

1. Sniffing methods associated with correlation curves for key equipment;
2. Optical gas imaging techniques;
3. Calculations of chronic emissions based on emissions factors periodically (e.g. once every 2 years) validated by measurements;

The screening and quantification of site emissions by periodic campaigns of measurements with optical absorption based techniques, such as differential absorption light detection and ranging (DIAL) or solar occultation flux (SOF) is a useful complementary technique.

BAT 5: Optimal operation of waste gas treatment systems

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 (REF BREF, Section 5.1.5). Special procedures can be defined for specific operating conditions, in particular:

- During start-up and shutdown operations
- 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)
- In case of insufficient waste gas flow or temperature which prevents the use of the system at full capacity

BAT 6: Prevention of air emissions from flares

In order to prevent emissions to air from flares (REF BREF, Section 5.20), **BAT is to** use flaring only for safety reasons or non-routine operational conditions (e.g. start-ups, shutdown).

Flares emit at least CO, CO_2, SO_2 and NO_x (REF BREF, Section 4.25.7). Under specific conditions, flaring activities lead to soot formation and VOC emissions. Small amounts of complex hydrocarbons (e.g PAH), may also be released. The composition depends on a number of factors including the composition of flare gas, flaring rate, flare system, wind and combustion efficiency at the flare tip.

BAT 7: Reduction of air emissions from flares

In order to reduce emissions to air from flares when flaring is unavoidable (REF BREF, Section 5.20), **BAT is to** use the techniques given below.

Technique	**Description**	**Applicability**
1. Correct plant design	Correct plant design includes sufficient flare gas 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 (star-up, shut down, emergency)	Applicable to new units. Flare gas recovery system may be retrofitted in existing units
2. Plant management	Plant management includes organizational and control measures to reduce the case of flaring by, for example, balancing RFG system, using advanced process control	Generally applicable
3. Correct flaring devices design	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	Applicable to new units
4. Monitoring and reporting	Continuous monitoring (measurements of gas flow and estimations of other parameters) of gas sent to flaring and associated parameters of combustion (e.g. mixture flow gas and heat content, ratio of assistance, velocity, purge gas flowrate, 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. Visual remote monitoring of the flare can also be carried out by using colour TV monitors during flare events.	Generally applicable

BAT 8: Minimization of noise

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

In order to prevent or reduce noise **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.1.9):

- Make an environmental noise assessment and formulate a noise management plan as appropriate to the local environment
- Enclose noisy equipment/operation in a separate structure/unit
- Use embankments to screen the source of noise
- Use noise protection walls

4.2.1 Techniques to reduce dust emissions and BAT-AELs

The concern with dust emissions (including heavy metals) stems from health effects. The main dust emission sources are process furnaces/boilers (mainly fired with liquid heavy fuel oil), catalytic cracker regenerators, coke plants, incinerators, decoking and sootblowing of furnaces and the flare.

Techniques to consider as BAT for the prevention and control of dust emissions include:

a) Electrostatic precipitators (ESP): 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 number of fields, residence time (size), catalyst properties and upstream particles removal devices (REF BREF, Section 4.5.9.2). The refinery may need extra facilities to manage the fine particulates (catalyst) recovered that require disposal. As a consequence of the particulate reduction, metals (Ni, Sb, V and their components) can also be reduced. At FCC units, 3-fields ESP and 4-fields ESP are commonly used. ESP may be used on a dry mode or with ammonia injection to improve the particles collection.

For the calcining of green coke, the ESP capture efficiency may be reduced due to the difficulty for coke particles to be electrically charged.

b) Bag filters: 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 (REF BREF, Section 4.5.9.3).

c) Multistage cyclone separators: Cyclonic collection device or system installed following the two stages of cyclones. Generally known as a third stage separator (TSS), 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 (REF BREF, Section 4.5.9.1).

These 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. Catalyst fines recovered containing some hazardous metals are hazardous industrial waste which has to be properly handled and eliminated in order to avoid any pollution transfer from air to water and soil.

d) Centrifugal washers: Centrifugal washers combine the cyclone principle and an intensive contact with water as, for example, Venturi washers. (REF BREF, Section 4.25.4.5).

e) Third stage blowback filter: Hot ceramic filters can be retrofitted to the underflow of third stage cyclones. 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 (REF BREF, Section 4.5.9.3).

Reverse flow (blowback) and fabric filters are both able to achieve higher performance figures 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.

BAT 9: Reduction of dust emissions from storage and handling activities

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 (REF BREF, Section 5.1.3):

- Store bulk powder materials in enclosed silos equipped with a dust abatement system (e.g. fabric filter)
- Store fine materials in enclosed containers or sealed bags
- Keep stockpiles of coarse dusty material wetted, stabilise the surface with crusting agents, or store under cover stockpiles of coarse dusty materials
- Use road cleaning vehicles.

This BAT conclusion in based on information given in REF BREF, Section 4.21

BAT 10: Reduction of dust and metals emissions from the regenerator of the catalyst (catalytic cracking process)

In order to reduce dust and metals emissions to air from the regenerator of the catalytic cracking process, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.5):

1. Primary or process related techniques, such as:

Technique	**Description**	**Applicability**
1 Use of an attrition-resistant catalyst	Selection of catalyst substance which is able to resist abrasion and fragmentation in order to reduce dust emissions	Generally applicable, provided the activity and selectivity of the catalyst are sufficient
2 Use of low sulphur feedstock (e.g. by feedstock selection or by hydrotreatment of feed)	Feedstock selection favours low sulphurfeedstocks among the possible sources to be processed at the unit. Hydrotreatment aims at reducing sulphur, nitrogen and metal content of the feed	Requires sufficient availability of low sulphur stocks, hydrogen production and hydrogen sulphide (H_2S) treatment capacity (e.g. amine and Claus units)

2. Secondary or end of pipe techniques, such as:

Technique	**Description**	**Applicability**
1 Electrostatic precipitator (ESP)	See technique a)	Generally applicable. The implementation of the technique may require significant space availability.
2 Multistage cyclone separator	See technique c)	Generally applicable
3 Third stage blowback filter	See technique e)	Applicability may be restricted due to limited full scale examples
4 Wet scrubbing	Gaseous compounds are dissolved in a suitable liquid Simultaneous removal of solid and gaseous compounds may be achieved (REF BREF, Section 4.5.10.2)	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability

Table 4.1 BAT-AELs for dust and metals emissions from the catalytic cracking process (regenerator)

Parameter	**Type of unit**	**BAT-AEL (monthly average) (1) mg/Nm^3**
Dust	New units	< 10– 25
	Existing units	10 – 50 (2)
(1) Soot blowing in CO boiler and trough the gas cooler are excluded (2) The lower end of the range can be achieved with a 4-fields ESP		

The associated monitoring is described in BAT 2

This BAT conclusion is based on information given in REF BREF Section 4.5.9

Note: A dissenting view between some members of the Technical Working Group (TWG) had to be assessed by the EIPPCB for this BAT Conclusion (See Section 4.7)

BAT 11: Reduction of dust and metals emissions from the coking process

In order to reduce emissions to air from coking production processes, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.7):

1. Primary or process related techniques, such as:

Technique	**Description**	**Applicability**
1 Collection and recycling of coke fines	Systematic collection and recycling of coke fines generated during the whole process coking (drilling, handling, crushing, calcining, cooling, etc.)	Generally applicable
2 Handling and storing coke according to BAT 8	See BAT 8	Generally applicable
3 Use a closed blowdown system	Arrestment system for pressure relief from the coke drums	Generally applicable
4 Recovering gas (including final venting) as a component of refinery fuel gas (RFG)	Carrying final venting from coke drum to gas compressor to recover as RFG, rather than flaring. For the flexi-coking process a conversion step (to convert the carbonyl sulphide (COS) into H_2S) is needed prior to treating the gas from the coking unit	For existing units, the applicability of the techniques may be limited by space availability

This BAT conclusion is based on information given in REF BREF Section 4.7

Explanatory note: During the coke production stage, coke particulates (including metals) are emitted in flexicokers, fluid cokers and calciners. In the case of delayed coker process there are only emissions of dust (but not coke particulates) related with the heat production necessary in the furnaces to pre-heat the charge.

During the produced coke handling and storage stages, emission of coke particles may as well happen (in any coking process) except for completely enclosed systems.

BAT 12: Reduction of dust emissions from the calcining of green coke

In order to reduce dust emissions to air from the calcining of green coke process, **BAT is to** use a combination of the techniques given below:

Technique	**Description**	**Applicability**
1. Electrostatic precipitator (ESP)	See technique a)	For existing units, the applicability may be limited by space availability. For graphite and anode coke calcining production, the applicability may be restricted due to the high resistivity of the coke particles
2. Multi-stage cyclone separator	See technique c)	Generally applicable

Table 4.2: BAT-AELs for dust and metals from the calcining of green coke process

Parameter	**BAT-AEL (monthly average)**
	mg/Nm^3
Dust	10 – 50 (1)(2)(3)

(1) For existing units equipped with a 3-fields ESP the upper end of the range is 50 mg/Nm^3

(2) The lower end of the range can be achieved with a 4-fields ESP

(3) When an ESP is not applicable, values of up to 150 mg/Nm3 may occur

The associated monitoring is described in BAT 2

BAT 13: Reduction of dust and metal emissions from the combustion units

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 (REF BREF, Section 5.9):

1. Primary or process related techniques, such as:

Technique	**Description**	**Applicability**
1. Selection or treatment of fuel		
a. Use of gas to replace liquid fuel	Gas instead of liquid combustion leads also to lower level of dust emissions	The applicability may be limited by the constraints associated with the availability of low sulphur fuels such as natural gas, which may be impacted by the energy policy of the Member State
b. Use of low sulphur refinery fuel oil (RFO) e.g. by selection or hydrotreatment of RFO	Refinery fuel oil selection favours low sulphur liquid fuels among the possible sources to be used at the unit. Based on hydrogenation reactions, hydrotreatment aims mainly at producing low-sulphur fuels and optimising the process configuration. It reduces sulphur, nitrogen and metal content of the fuel	Applicability is limited by availability of low sulphur liquid fuels, hydrogen production and hydrogen sulphide (H_2S) treatment capacity (e.g. amine and Claus units)
2. Combustion modifications		
a. 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	Generally applicable to all type of combustion

	conditions	
b. Atomisation of liquid fuel	Use of high pressure to reduce the droplet size of liquid fuel. Recent optimal burner design generally includes steam atomization	Generally applicable to liquid fuel firing

2. Secondary or end of pipe techniques, such as:

Techniques	**Description**	**Applicability**
1. Electrostatic precipitator (ESP)	See technique a)	Generally applicable
2. Third stage blowback filter	See technique e)	Generally applicable
3. Fabric filter	See technique b)	Generally applicable
4. Wet scrubbing	Process gaseous compounds are dissolved in a suitable liquid. Simultaneous removal of solid and gaseous compounds may be achieved.	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with a high level of salt) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability.
5. Centrifugal washers	See technique d)	Generally applicable

Table 4.3 BAT-AELs for dust and metals emissions from the combustion units

Parameter	**Type of combustion**	**BAT-AEL (monthly average)** **At 3% O_2** mg/Nm^3
Dust(3)	Multi-fuel firing	5 – 50

		for existing units > 50 MW_{th} (1) (2)
		5 – 25 for new units > 50 MW_{th}
[1] The lower end of the range is achievable for units with the use of end-of-pipe techniques. [2] The upper end of the range refers to the use of a high percentage of oil burning and where only primary techniques are applicable. [3] It must be reminded that for existing units the ELVs in the annexes 6 and 7 of the by-law 27605, and for new units the ELVs in the annexes 2 and 3 of the by-law 27605 will have to be respected (always for $\geq$ 50MW_{th}).		

The associated monitoring is described in BAT 2

This BAT conclusion is based on information given in REF BREF Sections 4.5.9 and 4.10.5

4.2.2 Techniques to reduce the SO_2 emissions and BAT-AELs

The principal emission sources of SO_2 are process furnaces/boilers, sulphur recovery units, FCC regenerators, flare system, waste water stripping and incondensable off-gas incinerators, decoking operations and coke calcination. 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.

There is a direct relation between the sulphur content of the fuel and the amount of SO_x emitted (for example, a fuel with 1 % sulphur generates a flue-gas with around 1700 mg/Nm^3).

Odours in a refinery are mainly created by sulphur compounds as H_2S, mercaptanes but also by some hydrocarbons (e.g. aromatics). The main focus sources of odour in refineries are storage (e.g. sour crudes), bitumen production, desalter water, sewers, dissolved air flotation and biotreatment and flaring.

Techniques to consider as BAT for the prevention and control of SO_x emissions are:

a) Treatment of refinery fuel gas (RFG): Some refinery fuel gases may be sulphur-free at source (e.g. from catalytic reforming and isomerisation processes) but most other processes produce sulphur-containing gases (e.g. off gases from visbreaker, hydrotreater or catalytic cracking units).

These gas streams require an appropriate treatment for gas desulphurisation (e.g. by amine gas removal to remove H_2S) before being released to the refinery fuel gas system.

b) Liquid fuel desulphurisation: In addition to low sulphur crude selection, fuel desulphurisation is made by hydrotreatment process where hydrogenation reactions take place and lead to reducing sulphur content (REF BREF, Section 4.13.2).

c) Use of gas to replace liquid fuel: Decrease the use of liquid refinery fuel (generally heavy fuel oil containing sulphur, nitrogen, metals, etc.) 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 (REF BREF, Section 4.10.2.1).

d) Use of SO_x reducing catalysts additives: 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.

SO_x reducing catalysts additives might have a detrimental effect on dust emissions by increasing catalyst losses due to attrition and on NO_x emissions by participating to the CO promotion together with the oxidation of SO_2 to SO_3 (REF BREF, Section 4.5.10.1).

e) Hydrotreatment: 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 transfers 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.

Feed hydrotreating of fuels reduces the feed sulphur, nitrogen and metals content, which in turn reduces the SO_2, NO_x and particulate emissions. 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 (REF BREF, Section 4.10.2.3).

The hydrotreatment of fuels is a very energy-intensive process consuming hydrogen with a consequent increase in CO_2 emissions. Moreover, effluent water and waste (used catalyst) are generated.

f) Acid gas removal (e.g. by amine treating): Separation of acid gas (mainly hydrogen sulphide H_2S) from the fuel gases by dissolving it in a chemical solvent (absorption). The commonly used solvents are amines. One important issue concerning the selection of the type of amine is the selectivity concerning H_2S and CO_2. It is generally the first step treatment needed before elemental sulphur can be recovered in the SRU (REF BREF, Section 4.25.5.1).

Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from hydrogen sulphide. 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, with a residual H_2S content, and the concentrated H_2S/acid stream, which is routed to the SRU for sulphur recovery.

g) Sulphur recovery units (SRU): Specific unit which most often consists of a Claus process for sulphur removal of hydrogen sulphide-rich gas streams from amine treating units and sour water strippers. SRU is generally followed by a tail gas treatment unit (TGTU) for remaining H_2S removal. (REF BREF, Section 4.25).

The Claus process consists of the partial combustion of the H_2S -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. 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_2S which must be removed from the liquid sulphur at a later stage of the process. 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.

The reduction of SO_2 leads to an increase of the CO_2 emission. Other components entering the SRU may include NH_3, CO_2 and, to a minor extent, various hydrocarbons.

h) Tail gas treatment unit (TGTU): A family of techniques, additional to SRU in order to enhance the removal of sulphur compounds (REF BREF, Section 4.25.5.2.2). 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 SO_2 and recovering sulphur from SO_2
- Reduction to H_2S and recovering sulphur from this H_2S (e.g. amine process)

Tail gas treatment units increase the overall recovery of H_2S and decrease the sulphur emissions from the refinery. As already mentioned, the reduction of SO_2 leads to an increase in the CO_2 emissions

i) 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 SO_2 and transforming it into solid sulphur. Various FGD methods exist with varying SO_2 removal efficiencies.

Systems either of the regenerative type or the non-regenerative type exist for SO_x removal only, and also for the simultaneous removal of dust and NO_x. These are competitive with systems consisting of separate units for SO_2 elimination (i.e. wet scrubbers) and NO_x removal (i.e. SCR). Information on the various regenerative and non-regenerative processes is given in REF BREF, Section 4.25.5.4.

j) 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 (REF BREF, Section 4.5.10.2). The SO_x removal efficiency is in the range of 85-98%

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, for example:

- Venturi using the energy from inlet gas by spraying it with the liquid;
- Packed towers, plate towers, spray chambers.

Where scrubbers mainly aim at SO_x removal (SO_3 abatement is typically not as high as SO_2), suitable design is needed to remove also dust. With the inclusion of an extra treatment tower to oxidise the NO to NO_2, NO_x can also be removed efficiently.

k) Non-regenerative scrubbing: Sodium or magnesium based solution is used as alkaline reagent to absorb SO_x generally as sulphates (REF BREF, Section 4.5.10.2). These techniques are based on, for example:

- Wet limestone
- Aqueous ammonia
- Seawater

Non-regenerative wet scrubbing systems create secondary problems of aqueous slurry waste disposal and increase the refinery energy consumption.

l) Seawater scrubbing: A specific non regenerative type of scrubbing using alkalinity of the seawater as solvent where large amount of seawater is available. Seawater scrubbing transfers sulphur emissions from air as SO_2 to the sea as SO_4, with a significant reduction in the overall environmental impact. The sulphur content of the effluent seawater from the process itself is increased by only approximately 3%. Particulates containing metals (e.g. V, Ni, Sb) and other pollutants from the flue-gas are also transferred to the seawater. 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 (REF BREF, Section 4.5.10.5).

m) Regenerative scrubbing: Use of specific SO_x 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. The main additional benefit is the possibility to regenerate the SO_x absorbing reagent and to recover concentrated SO_2 streams which can be converted and sold/recycled as liquid SO_2, sulphuric acid or elemental sulphur. In correlation to this, a much lower amount of solid residue must be recovered and eliminated. Typical impacts of regenerative systems are the possible debottlenecking of H_2S handling facilities (e.g. SRU, amine scrubbers) or the production of other eventual by-products (REF BREF, Section 4.5.10.2).

n) 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. The sulphur efficiency removal is higher in the semi-dry process (REF BREF, Section 4.5.10.4).

BAT 14: Reduction of SO_x emissions from the regenerator of the catalytic cracking process

In order to prevent or reduce SO_x emissions to air from the regenerator of the catalytic cracking process, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.5):

1. Primary or process related techniques, such as:

Technique	Description	Applicability
1. SO_x reducing catalysts additives	Use of a substance which transfers sulphur associated to coke from the regenerator back to the reactor. See technique d)	Applicability may be restricted by regenerator conditions design. Requires appropriate hydrogen sulphide abatement capacity (e.g. SRU)
2. Use of low sulphur feedstock (e.g.by feedstock selection or by hydrotreatment of feed	Feedstock selection favours low sulphur feedstocks among the possible sources to beprocessed at the unit. Hydrotreatment aims at	Requires sufficient availability of low sulphur feedstocks, hydrogen production and hydrogen sulphide (H_2S) treatment

	reducing sulphur, nitrogen and metal content of the feed. See technique e)	capacity (e.g. amine and Claus units)

2. Secondary or end of pipe techniques, such as:

Technique	**Description**	**Applicability**
1. Non-regenerative scrubbing	Wet scrubbing or seawater scrubbing	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability.
2. Regenerative scrubbing	Use specific SOx absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as by-product during a regenerating cycle where the reagent is reused. (see Section 5.21.3 of REF BREF)	The applicability is limited to the case where regenerated by-products can be sold. Retrofitting existing units may be limited by the existing sulphur recovery capacity. The applicability of the technique may require significant space availability

Table 4.4 BAT-AELs for SO_x emissions from catalytic cracking process (regenerator)

Parameter	**Type of unit/moe**	**BAT-AEL (monthlyaverage)** mg/Nm^3

SO_x expressed as SO_2	New units	≤ 300
	Existing units / full combustion	< 100- 800 (*)
	Existing units / partial combustion	100 – 1200 (*)
(*) Where selection of low sulphur (e.g. <0.5% w/w) feed (or hydrotreatment) and/or scrubbing is applicable, for all combustion modes: ≤600 mg/Nm3 can be achieved.		

The associated monitoring is described in BAT 2

This BAT conclusion is based on information given in REF BREF Sections 4.5.10 and 4.25.5

Note: A dissenting view between some members of the Technical Working Group (TWG) had to be assessed by the EIPPCB for this BAT Conclusion (See Section 4.7)

BAT 15: Reduction of SO_x emissions from the coking process

In order to reduce SO_x emissions to air from the calcining of green coke, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.7):

Technique	**Description**	**Applicability**
1. Non-regenerative scrubbing	Wet scrubbing or seawater scrubbing	The applicability may be limited in arid areas and in the case where the by-products from treatment) including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability
2. Regenerative scrubbing	Use of a specific SO_x absorbing reagent (e.g. absorbing solution) which generally enables the recovery of sulphur as a by-	The applicability is limited to the case where regenerated by-products

	product during a regenerating cycle where the reagent is reused.	can be sold. Retrofitting existing units may be limited by the existing sulphur recovery capacity. The applicability of the technique may require significant space availability

This BAT conclusion is based on information given in REF BREF Section 4.7

Explanatory note: During the coke production stage, SO_x are emitted in flexicokers, fluid cokers and calciners. In the case of delayed coker process there are only emissions of SO_x related with the heat production necessary in the furnaces to pre-heat the charge.

BAT 16: Reduction of SO_x emissions from the combustion units

In order to prevent or reduce SO_x emissions to air from the combustion units, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.9):

1. Primary or process related techniques, such as:

Technique	Description	Applicability
Use of gas to replace liquid fuel	See technique c)	The applicability may be limited by the constraints associated with the availability of low sulphur fuels, such as natural gas, which may be impacted by the energy policy of the Member State
Treatment of refinery fuel gas (RFG)	Residual H2S concentration in RFG depends on treatment process parameter, e.g. the amine scrubbing pressure.	For low calorific gas containing carbonyl sulphide (COS), e.g. from coking units, a converter may be required prior to H_2S

	See technique a)	removal
Use of low sulphur refinery fuel oil (RFO) e.g. by the hydrotreatment of RFO	Refinery fuel oil selection favours low sulphur liquid fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing sulphur, nitrogen and metal content of the fuel. See technique e)	Applicability is limited by availability of low sulphur liquid fuels, hydrogen production and hydrogen sulphide (H_2S) treatment capacity (e.g. amine and Claus units)

2. Secondary or end of pipe techniques, such as:

Technique	**Description**	**Applicability**
Non-regenerative scrubbing	Wet scrubbing or seawater scrubbing	The applicability may be limited in arid areas and in the case where the by-products from treatment (including e.g. waste water with high level of salts) cannot be reused or appropriately disposed of. The applicability of the technique may require significant space availability
Regenerative scrubbing	Use of a specific SO_x 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. The	Applicability is limited to the case where the regenerated by-products can be sold. Retrofitting existing units may be limited by the existing sulphur recovery capacity. The applicability of the technique

		may require significant space availability
SNO_x combined technique	Combined technique to remove SO_x, NO_x and dust where a first dustremoval stage (ESP) takes place followed by some specific catalytic processes. The sulphur compounds are recovered as commercial-grade concentrated sulphuric acid, while NO_x is reduced to N_2. Overall SO_x removal is in the range: 94 - 96.6 %.	Applicable for high flue-gas (e.g. *>800.000 Nm^3/h*) flow and when combined NO_x and SO_x abatements are required.

Table 4.6 BAT-AELs for SO_x emissions from RFG gas firing in combustion units, with the exception of gas turbines::

Parameter	**BAT-AEL (monthly average)** **mg/Nm^3** **at 3% O_2**
SO_2(1)	5 – 35 (*)
(*) In specific configuration of RFG treatment with low scrubber operative pressure and with a refinery fuel gas with an H/C ratio above 5 H_2 content >45 %, the upper end of the range can be as high as 45 mg /Nm3 (1) It must be reminded that for existing units there are ELVs in the annexes 6 and 7 of the by-law 27605, and for new units there are ELVs in the annexes 2 and 3 of the by-law 27605 (applicable only for ≥ $50MW_{th}$).	

Table 4.7 BAT-AELs for SO_x emissions from multi-fuel firing in combustion units, with the exception of gas turbines and stationary gas engines:

Parameter	**BAT-AEL (monthly average) (*)** **mg/Nm^3** **at 3% O_2**

SO_2 (1)(2)	35 –600 (*) for existing units > 50 MW_{th}
(*) Refers to the weighted average emissions from multi-fuel firing in combustion units with the exception of gas turbines and stationary gas engines (1) It must be reminded that for existing units the ELVs in the annexes 6 and 7 of the by-law 27605, and for new units the ELVs in the annexes 2 and 3 of the by-law 27605 will have to be respected (always for $\geq$ 50MW_{th}). (2) The ELVs stated in the by-law 27605 are calculated, in this case, according to the methodology stated in its articles 14.2 and 14.3.	

The associated monitoring is described in BAT 2

This BAT conclusion is based on information given in Sections 4.5.10, 4.10.2 and 4.10.3.

What happens in the case of installations using only liquid fuel?

During the preparation of this guide appeared some questions about what could happen when only liquid fuel is used. In the REF BREF this case is not covered. The reason is that the REF BREF considers always multi-fuel because the substitution of liquid fuels by gas fuels is a BAT, and therefore it is implicitly assumed that installations will progressively abandon the only liquid fuel option. Independently of this approach of the REF BREF, the fact is that currently there are still several installations using only liquid fuel in Turkey. In order to include some considerations for only liquid fuel using installations, the following explanation has been prepared including references to European and Turkish legislation.

For the EU refining sector the Directive 2010/75/EU on industrial emissions (Annex V, Part 7) sets the emission limit values for multi-fuel firing combustion plants. According to this Annex V, multi-fuel firing combustion plants within a refinery, with the exception of gas turbines and gas engines, which use the distillation and conversion residues from the refining of crude-oil for own consumption, alone or with other fuels, have to comply with the following average emission limit values for SO_2:

a) For combustion plants which were granted a permit before 27 November 2002 or the operators of which had submitted a complete application for a permit before that date, provided that the plant was put into operation no later than 27 November 2003: 1000 mg/Nm^3;

b) For other combustion plants: 600 mg/Nm^3.

However, this Directive also states that, on the basis of the best available techniques, the European Commission shall review the need to establish EU-wide emission limit values and to amend these emission limit values. It would be expectable that this review would lead to the establishment of similar values to those in REF BREF.

In addition to this, the national legislation in Turkey establishes, through the 27277 By-Law on Control of Air Pollution caused by Industry, the emission limit values for combustion facilities using liquid fuels. As it has been explained in the beginning of this chapter, the refining industry in Turkey may have certain units that have not been designed according to the new European legislation and which still have an operation lifetime that can last for many years, and it could be the case of the combustion units that operate only with liquid fuels. For these units, a transition period can be regulated by the competent authorities taking into account the emission limit values set in Annex 5 paragraph 4.4 of the above mentioned 27277 By-Law.

BAT 17: Reduction of sulphur emissions to air from off-gases (waste gas sulphur treatment)

In order to reduce sulphur emissions to air from off-gases containing hydrogen sulphides (H_2S) **BAT is to** use all of the following sulphur removal techniques (REF BREF, Section 5.19):

Technique	Description	Applicability
1. Acid gas removal (e.g. by amine treatment)	See technique f)	May not be applicable for stand-alone lubricant or bitumen refineries with a release of sulphur compounds of less than 1 t/d
2. Sulphur recovery units (SRU) e.g. by Claus process	See technique g)	May not be applicable for stand-alone lubricant or bitumen refineries with a release of sulphur compounds of less than 1 t/d
3. Tail gas treatment unit (TGTU)	See technique h)	May not be applicable for stand-alone lubricant or bitumen refineries with a release of sulphur compounds of less than 1 t/d. For retrofitting existing SRU, the applicability of the technique may be limited by the SRU size and configuration of the units and the type of sulphur recovery process already in place.

Table 4.9 BAT-associated sulphur recovery efficiency for waste gas sulphur (H_2S form) removal techniques

Parameter	**BAT-associated environmental performance level** **(monthly average)**
Acid gas removal	Achieve hydrogen sulphide (H_2S) removal in the treated RFG in order to meet gas firing BAT-AEL for BAT 16
Sulphur recovery efficiency (*)	New units: 99.5 - >99.9 %
	Existing units: ≥ 98.5 %
(*) Sulphur recovery efficiency of the whole treatment chain (e.g. including SRU and TGTU) is calculated as the fraction of sulphur in the feed which is recovered in the sulphur stream routed to the collection pits When the applied technique does not include a recovery of sulphur (e.g. seawater scrubber), it refers to the sulphur removal efficiency, as the % of sulphur removed by the whole treatment chain	

The BAT associated monitoring is described in BAT 2

This BAT conclusion is based on information given in REF BREF Section 4.25.5

Note: A dissenting view between some members of the Technical Working Group (TWG) had to be assessed by the EIPPCB for this BAT Conclusion (See Section 4.7)

BAT 18: Reduction of SO_x emissions from the natural gas refinery

In order to reduce sulphur emission to air from the natural gas plant, **BAT is to** apply BAT 17 (REF BREF, Section 5.13).

BAT 19: Reduction of SO_x emissions form sour water stripping units

In order to prevent and reduce emissions to air when using a sour water steam 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 untreated sour water stripping and incondensable untreated gases (REF BREF, Section 5.1.5).

Sour water from the various refinery units is, for the main part, stripped in a sour water stripping (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. Sour off-gases from a stripper unit can be routed to either 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 SO_2 (up to 40 %) and NO_x, routing to an SRU unit should be preferred and is now commonly practised (REF BREF, Section 4.26.4).

BAT 20: Minimization of air emissions from the bitumen production process

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 (REF BREF, Section 5.4):

Technique	Description	Applicability
1. Thermal oxidation of gaseous overhead over 800ºC	The water vapour (sometimes after fully condensation) is left in the air stream to incineration at a temperature of approximately 800ºC	Generally applicable for the bitumen blowing unit
2. Wet scrubbing for gaseous overhead	The off-gases are condensed in a scrubber where most of the hydrocarbons are eliminated	Generally applicable for bitumen blowing unit

This BAT conclusion is based on information given in REF BREF Section 4.4

In addition to the reduction of H_2S, SO_2, SO_3 and odour emissions, also reduction of CO, VOC, particulates and smoke emissions are achievable whit the application of these techniques. Additional contaminated water will be a cross-media effect as 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.

BAT 21: Reduction of air emissions from the etherification process

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 the refinery fuel gas system (REF BREF, Section 5.10)

BAT 22: Reduction of air emissions from the products treatment process

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 destruction by e.g. incineration (REF BREF, Section 5.16)

Applicability: Generally applicable to products treatment processes where the gas streams can be safely processed to the destruction units. May not be applicable to sweetening units due to safety reasons.

BAT 23: Minimization of air emissions from the distillation process

In order to prevent or reduce emissions to air from distillation units, **BAT is to** ensure the appropriate treatment of process off-gases, especially incondensable, by acid gas removal prior to further use (REF BREF, Section 5.15)

Applicability: Generally applicable for crude and vacuum distillation units. May not be applicable for stand-alone lubricant and bitumen refineries with emissions of less than 1 t/d of sulphur compounds. In specific refinery configurations, applicability may be restricted, due to the need of e.g. large piping, compressors or additional amine treating capacity.

4.2.3 Techniques to reduce the NO_x emissions and BAT-AELs

The term NO_x only refers to NO (nitrogen monoxide) and NO_2 (nitrogen dioxide). N_2O can be also found in flue-gases from FCCs and some SCR. In most combustion processes NO contributes to over 90 % of the total NO_x. However, as it is rapidly oxidised to NO_2 in the atmosphere, emissions of NO are expressed as NO_2. The main emission sources for NO_x are combustion processes (i.e.: process furnaces and boilers, CHP and gas turbines), FCC regenerators, coking, and to a lesser extent, eventual waste gas incinerators and the flare system. NO_X emissions from refineries depend on the fuel type, nitrogen or hydrogen content, combustor equipment design, and operating conditions

Techniques to consider in the determination of BAT for the prevention and control NO_x emissions include:

a) Reduction of air/fuel ratio: 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

b) Staged combustion:

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. This technique, also called reburning, is based on the creation of different zones in the furnace by staged injection of fuel and air to reduce NO_x emissions, which have already been formed back into nitrogen (REF BREF, Section 4.10.4.5).

c) Flue-gas recirculation: 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 (REF BREF, Section 4.10.4.3).

d) Low-NO_x burners: The technique (including ultra-Low-NO_x 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). The reduction of peak temperatures leads to the reduction of the oxygen concentration in the primary combustion zone and the residence time at high temperatures, decreasing thereby the thermally formed NO_x. Ultra low-NO_x burners add the internal or external recirculation of flue-gases to the basic low-NO_x burner design, enabling the decrease of the oxygen concentration in the combustion area and a further abatement of NO_x. The application of this technique may be associated with a modified design of the furnace combustion chamber (REF BREF, Section 4.10.4.1).

The design of ultra-low-NOx burners (ULNB) includes combustion staging (air/fuel) and flue-gas recirculation. Dry low-NOx- burners (DLNB) are used for gas turbines

e) Optimization 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

f) Diluents injection: Inert diluents, as flue-gas, steam, water or nitrogen added to combustion equipment reduce the flame temperature and consequently the concentration of NO_x in the flue-gases (REF BREF, Section 4.10.4.4).

g) Selective catalytic reduction (SCR): The technique, also known as catalytic $DeNO_x$, is based on the reduction of NO_x 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. Various catalyst formulations are available for different temperature ranges. A higher NO_x reduction is achieved with the use of higher amounts of catalyst. (REF BREF, Section 4.25.3.3).

As with SNCR, an intrinsic limitation of the SCR technique is the emission of a small amount of unreacted NH_3 (ammonia slip) in the flue-gas stream. The ammonia slip is dependent on many factors, including NH_3 injection rate, catalyst activity, fluegas distribution or process controllability.

Combined techniques for both SO_2 and NO_x removal has use also such a catalyst as, for example, the $DesoNO_x$ process.

h) Selective non-catalytic Reduction (SNCR): The technique is based on the reduction of NO_x 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. This technique, also called thermal $DeNO_x$, reduces NO_x 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. (REF BREF, Section 4.25.3.2).

i) Low temperature NO_x oxidation: The low temperature oxidation process injects ozone into a flue-gas stream at optimal temperatures below 150 ºC, to oxidise insoluble NO and NO_2 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 and may need additional nitrogen removal (REF BREF, Section 4.25.3.1).

There is the risk of ozone slip and the system can increase nitrate concentration in the waste water.

j) Specific additives for NO_x reduction: As a complementary or substitutional approach to non-Pt low-NO_x 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. 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-NO_x CO promoters, depending of the operational conditions of the unit (REF BREF, Section 4.5.8.4)

BAT 24: Reduction of NO_x emissions from the regeneration of the catalyst (catalytic cracking process)

In order to prevent or reduce NO_x emissions to air from the regeneration of the catalyst, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.5):

1. Primary or process related techniques, such as:

Technique	**Description**	**Applicability**
1 Process optimization and use of promoters or additives		
a) a) Process optimization	A combination of operating conditions or practices aimed at reducing NO_x formation e.g. lowering the excess oxygen in the flue-gas in full combustion mode, air staging of the CO boiler in partial combustion mode provided that CO boiler is appropriately designed.	Generally applicable
b) Low NO_x CO oxidation promoters	Use of a substance which selectively promotes the	Applicable only in full combustion mode for the

	combustion of CO only and prevents the oxidation of the nitrogen which contains intermediates to NO_x: e.g. non-platinum promoters	substitution of platinum based on CO promoters. Appropriate distribution of air in the regenerator may be required to obtain the maximum benefit
c) Specific additives for NO_x reduction	Use of specific catalytic additives for enhancing the reduction of NO by CO	Applicable only in full combustion mode in appropriate design and with

2. Secondary or end of pipe techniques, such as:

Technique	**Description**	**Applicability**
1 Selective catalytic reduction (SCR)	See technique g)	To avoid potential fouling downstream, additional filtering might be required upstream the SCR. Applying the technique in existing units may require significant space availability
2 Selective non-catalytic reduction (SNCR)	See technique h)	For partial combustion FCCs with CO boilers, a sufficient residence time at the appropriate temperature is required. For full combustion FCC without auxiliary boilers, additional fuel injection (e.g. hydrogen) may be required to match a lower temperature window
3 Low temperature oxidation	See technique i)	Need for additional scrubbing capacity Ozone generation and the associated risk management need to be properly addressed. The applicability may be limited by the need for additional waste water treatment and related cross-media effects (e.g. nitrate emissions) and by an insufficient supply of liquid oxygen (for ozone generation). The applicability of the technique may

		require significant space availability

Table 4.10 BAT-AELs for NO_x emissions from catalytic cracking process (regenerator)

Parameter	**Type of unit / mode**	**BAT-AEL** **(monthly average values)** mg/Nm^3 at 3% O_2
NO_x expressed as NO_2	New units / all modes	< 30 – 100
	Existing units / full combustion mode	< 100 – 300 (1)
	Existing units / partial combustion mode	100 – 400 (1)
(1) When Sb injection is used for metal passivation, NO_x levels up to 700 mg/Nm^3 may occur. The lower end of the range can be achieved by using SCR		

The associated monitoring is described in BAT 2

This BAT conclusion is based on information given in REF BREF Section 4.5.8

Note: A dissenting view between some members of the Technical Working Group (TWG) had to be assessed by the EIPPCB for this BAT Conclusion (See Section 4.7)

BAT 25: Reduction of NO_x emissions from the coking process

In order to reduce NO_x emissions to air from the calcining of green cocking process, **BAT is to** use SNCR.

Specific applicability for calcining process: The applicability of the technique may be restricted due to the specificity of the calcining process (e.g. residence time, temperature window).

BAT 26: Reduction of NO_x emissions from the combustion units

In order to prevent or reduce NO_x emissions to air from the combustion units, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.9).:

1. Primary or process related techniques, such as:

Technique	**Description**	**Applicability**
1. Selection or treatment of fuel		
a. Use of gas to replace liquid fuel	Gas generally contains less nitrogen than liquid and its combustion leads to lower level of NO_x emissions (1)	The applicability may be limited by the constraints associated with the availability of low sulphur gas fuels, which may be impacted by the energy policy of the Member State
b. Use of low nitrogen refinery fuel oil (RFO) e.g. by RFO selection or hydrotreatment of RFO	Refinery fuel oil selection favours low nitrogen fuels among the possible sources to be used at the unit. Hydrotreatment aims at reducing sulphur, nitrogen and metal content of the fuel.	Applicability is limited by availability of low nitrogen liquid fuels, hydrogen production and hydrogen sulphide (H_2S) treatment capacity (e.g. amine and Claus units)
2. Combustion modifications		
a. Staged combustion **Air staging** **Fuel staging**	See technique b)	Fuel staging for mixed or liquid firing may require specific burner design
b. Optimization of combustion	See technique e)	Generally applicable
c. Flue-gas recirculation	See technique c)	Applicable through the use of specific burners with internal recirculation of flue gas Applicability may be restricted to retrofitting external flue-gas recirculation

		to units with forced induced draught mode of operation
d. Diluent injection	See technique f)	Generally applicable for gas turbines where appropriate inert diluents are available.
e. Use of Low-NO_x burners (LNB)	See technique d)	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. The applicability of low-NO_x burners may be restricted for furnaces in the delay coker process due to possible coke generation in the furnaces. In gas turbines, the applicability of dry low-NO_x burners is restricted to low hydrogen content fuels (generally < 10 %).
(1) Gaseous fuels typically release less NO_x per unit of energy compared to liquid fuels, especially liquid refinery fuels. For gaseous fuels, usually only thermal NO_x is relevant; however NO_x emissions will depend on the gaseous fuel consumption.		

2. Secondary or end of pipe techniques, such as:

Technique	**Description**	**Applicability**
1. Selective catalytic reduction (SCR)	See technique g)	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 reactant injection
2. Selective non-catalytic reduction (SNCR)	See technique h)	Generally applicable for a new unit The applicability for retrofitting existing unit may be constrained by requirement for the temperature window and the residence time to be reached by reactant injection
3. Low temperature oxidation	See technique i)	Applicability may be restricted due to the need for additional scrubbing capacity Ozone generation and risk management associated to be properly addressed
4. SNO_x combined technique	Combined technique to remove SO_x, NO_x 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. Overall NO_x removal is in the range: 87- 90 %	Applicable only for high flue gas flow and when combined NO_x and SO_x abatements are needed

Table 4.11 BAT-AELs for NO_x emissions from combustion gas turbines

Parameter	**Type of equipment**	**BAT-AEL** (1) **(monthly average) (*)** mg/Nm^3 at 15% O_2
NO_x expressed as NO_2(3)	Gas turbine (including combined cycle gas turbines -CCGT) and integrated gasification gas cycle (IGCC)	40 – 120 existing turbines
		20 – 50 (2) new turbines

(1) BAT-AEL refers to emissions from the common stack for the gas turbine and, if present, the supplementary firing recovery boiler.

(2) For high H2 content fuel (i.e. above 10 %), the upper end of the range is 75 mg/Nm3

(3) It must be reminded that for existing units there are ELVs in the annex 8 of the by-law 27605, and for new units there are ELVs in the annex 4 of the by-law 27605 (applicable only for $\geq$ 50MW$_{th}$).

The associated monitoring is described in BAT 2

Table 4.12 BAT-AELs for NO_x emissions from gas firing combustion with the exception of gas turbines

Parameter	**Type of combustion**	**BAT-AEL (monthly average) (*)**
		mg/Nm^3 at 3% O_2
NO_x expressed as NO_2 (2) (3)	Gas firing	30 – 150 for existing units (1)
		30 – 100 for new units

(1) For existing units using a high air pre-heat (i.e. > 200 ºC) or with a H2 content in the fuel gas higher than 50 %, the upper end of the BAT-AEL range is 200 mg/Nm3

(2) It must be reminded that for existing units there are ELVs in the annexes 6 and 7 of the by-law 27605, and for new units there are ELVs in the annexes 2 and 3 of the by-law 27605 (applicable only for $\geq$ 50MW$_{th}$).

(3) It must be reminded that for existing units there are ELVs of the by-law 27277 (applicable only for $\leq$ 50MW$_{th}$)

The associated monitoring is described in BAT 2

Note: A dissenting view between some members of the Technical Working Group (TWG) had to be assessed by the EIPPCB for this BAT Conclusion (See Section 4.7)

Table 4.13 BAT-AELs for NO_x emissions from multi-fuel combustion with the exception of gas turbines

Parameter	**Type of combustion**	**BAT-AEL (monthly average) (*)**

		mg/Nm^3 at 3% O_2
NO_x expressed as NO_2(3) (4)	Multi-fuel firing	30 – 300 (1) (2) for existing units
		30 – 150 for new units

1) For existing units < 100 MW with fuel oil nitrogen content higher than 0.5 % (w/w) and or with percentage liquid firing > 50 % or using air preheating, values up to 450 mg/Nm3 may occur

(2) The lower end of the range is achieved when using SCR

(3) It must be reminded that for existing units there are ELVs in the annexes 6 and 7 of the by-law 27605, and for new units there are ELVs in the annexes 2 and 3 of the by-law 27605 (applicable only $\geq$ $50MW_{th}$).

(3) It must be reminded that for existing units there are ELVs of the by-law 27277 (applicable only for $\leq$ $50MW_{th}$).

The associated monitoring is described in BAT 2

These BAT conclusions are based on information given in REF BREF Section 4.10.4.

What happens in the case of installations using only liquid fuel?

During the preparation of this guide appeared some questions about what could happen when only liquid fuel is used. In the REF BREF this case is not covered. The reason is that the REF BREF considers always multi-fuel because the substitution of liquid fuels by gas fuels is a BAT, and therefore it is implicitly assumed that installations will progressively abandon the only liquid fuel option. Independently of this approach of the REF BREF, the fact is that currently there are still several installations using only liquid fuel in Turkey. In order to include some considerations for only liquid fuel using installations, the following explanation has been prepared including references to European and Turkish legislation.

For the EU refining sector the Directive 2010/75/EU on industrial emissions (Annex V, Part 7) sets the emission limit values for multi-fuel firing combustion plants. According to this Annex V, multi-fuel firing combustion plants within a refinery, with the exception of gas turbines and gas engines, which use the distillation and conversion residues from the refining of crude-oil for own consumption, alone or with other fuels, have to comply with the following average emission limit values for SO_2:

a) For combustion plants which were granted a permit before 27 November 2002 or the operators of which had submitted a complete application for a permit before that date, provided that the plant was put into operation no later than 27 November 2003: 1000 mg/Nm^3;

b) For other combustion plants: 600 mg/Nm^3.

However, this Directive also states that, on the basis of the best available techniques, the European Commission shall review the need to establish EU-wide emission limit values and to amend these emission limit values. It would be expectable that this review would lead to the establishment of similar values to those in REF BREF.

In addition to this, the national legislation in Turkey establishes, through the 27277 By-Law on Control of Air Pollution caused by Industry, the emission limit values for combustion facilities using liquid fuels. As it has been explained in the beginning of this chapter, the refining industry in Turkey may have certain units that have not been designed according to the new European legislation and which still have an operation lifetime that can last for many years, and it could be the case of the combustion units that operate only with liquid fuels. For these units, a transition period can be regulated by the competent authorities taking into account the emission limit values set in Annex 5 paragraph 4.4 of the above mentioned 27277 By-Law.

BAT 27: Reduction of NO$_x$ emissions from the natural gas plant

In order to reduce nitrogen oxides emission to air from the natural gas plant, **BAT is to** apply BAT 26 (REF BREF, Section 5.13).

4.2.4 Techniques to reduce the CO emissions and BAT-AELs

Emissions of carbon monoxide come mainly from process furnaces/boilers, gas turbines, catalytic cracker regenerators, flare system, incinerators and cold vents.

Techniques applicable for the prevention and control of CO emissions are:

a) Combustion operation control: The increase in CO emissions due to the application of combustion modifications (primary techniques) for the reduction of NO$_x$ emissions can be limited by a careful control of the operational parameters.

b) Catalysts with carbon monoxide (CO) oxidation promoters: Use of a substance which selectively promotes the oxidation of CO into CO_2 (combustion).

c) Carbon monoxide (CO) boiler: 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 (REF BREF, Section 4.25.1).

BAT 28: Reduction of CO emissions from the regeneration of the catalyst (Catalytic Cracking process)

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 (REF BREF, Section 5.5):

Technique	Description	Applicability
1. Combustion operation control	See technique a)	Generally applicable
2. Catalysts with carbon monoxide (CO) oxidation promoters	See technique b)	Generally applicable only for full combustion mode
3. Carbon monoxide (CO) boiler	See technique c)	Generally applicable only for partial combustion mode

Table 4.14 BAT-AELs for CO emissions from partial mode catalytic cracking (regenerator stck)

Parameter	**Combustion mode**	**BAT-AEL (monthly average) mg/Nm^3**
Carbon monoxide, expressed as CO	Partial combustion mode	≤100 (*)
(*) May not be achievable when not operating the CO boiler at full load		

The associated monitoring is described in BAT 2

BAT 29: Reduction of CO emissions from the combustion units

In order to reduce carbon monoxide (CO) emissions to air, **BAT is to** use combustion operation control (REF BREF, Section 5.9)

Table 4.15 BAT-AELs for CO emissions from combustion units

Parameter	**BAT-AEL (monthly average)** **mg/Nm^3**
Carbon monoxide, expressed as CO$^{(1)}$	≤100
(1) It must be reminded that for existing units there are ELVs in the annexes 6 and 7 of the by-law 27605, and for new units there are ELVs in the annexes 2 and 3 of the by-law 27605 (applicable only for $\geq$ 50MW$_{th}$).	

The associated monitoring is described in BAT 2

This BAT conclusion is based on information given in REF BREF Section 4.10.3

4.2.5 Techniques to reduce the VOC and odour emissions and BAT-AELs

The main sources of VOCs from refineries are fugitive emissions from piping systems, waste water systems, fixed roof storage tanks (tank breathing), loading and unloading systems, other storage, handling and blowdown systems. Fugitive VOC emission sources such as seals from pumps, compressors, valves and flanges and leaks in pipelines and equipment may contribute significantly to the total VOC emissions. VOC losses can be calculated through various methods based on emission factors or directly measured. Extensive information on this issue is given in REF BREF Section 3.28.1.4, specifically related to VOC monitoring.

Techniques applicable for the prevention and control of VOC emissions include:

a) Vapour balancing: 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. This technique can be used where loading takes place from tanks, vessels or barges. Vapour can be stored prior to vapour recovery or destruction.

b) Vapour recovery: 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, for example:

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 can be condensed, further processed or incinerated or re-absorbed in an appropriate stream (e.g. of the product being recovered).

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 stream of the product being recovered in a downstream wash column. Residual gas from wash column is sent to further treatment.

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).

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.

Hybrid systems: combinations of available vapour recovery units (VRU) techniques

The achievable concentration is expressed for non-methanous VOC (NMVOC) as absorption and adsorption processes cannot notably reduce methane emissions.

c) 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. When a specific incinerator is not available for this purpose, an existing furnace may be used to provided the required temperature and residence times.

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.

d) 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 (described by EN 15446) and gas imaging methods are available for the identification of the leaks.

Sniffing method: The first step is the detection using hand-held VOC analysers measuring the concentration adjacent to the equipment (e.g. by using flame ionisation or photo-ionisation). The second step consists of bagging the component to carry out a direct measurement at the source of emission. This second step is sometimes replaced by mathematical correlation curves derived from statistical results obtained from a large number of previous measurements made on similar components.
Optical gas imaging methods: 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 to easily and rapidly locate significant VOC leaks. Active systems produce an image with a back-scattered infra red laser light reflected on the component and its surroundings. Passive systems are based on the natural infra red radiation of the equipment and its surroundings.

e) High integrity equipment: High integrity equipment include, for example:

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

f) VOC diffuse emissions monitoring: Full screening and quantification of site emissions can be undertaken with an appropriate combination of complementary methods, e.g. Solar occultation flux (SOF) or differential absorption lidar (DIAL) campaigns. These results can be used for trend evaluation in time, cross checking and updating/validation of the ongoing LDAR programme.

Solar occultation flux (SOF): The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband infra red or ultra violet/visible sunlight spectra along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes.

Differential absorption lidar (DIAL): DIAL is a laser-based technique using differential adsorption LIDAR (light detection and ranging) which is the optical analogue of sonic radio wave based

RADAR. 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.

BAT 30: Integrated refinery management - Reduction of diffuse VOC emissions

In order to prevent or reduce diffuse VOC emissions, **BAT is to** apply a combination of the techniques given below (REF BREF, Section 5.1.10):

Technique	Description	Applicability
1. Techniques related to plant design	Limiting the number of potential emission sources Maximising inherent process containment features Selecting high integrity equipment Facilitating monitoring and maintenance activities by ensuring access to potentially leaking components	Applicability of the techniques may be limited for existing units
2. Techniques related to plant installation and commissioning	Well-defined procedures for construction and assembly 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
3. Techniques related to plant operation	Risk-based leak detection and repair (LDAR) programme in order to identify leaking components, and to repair these leaks.	Generally applicable

BAT 31: Reduction of VOC emissions from storage and handling process

In order to reduce VOC emissions to air from the storage of volatile liquid hydrocarbon compounds, **BAT is to** use floating roofs storage tanks equipped with high efficiency seals or a fixed connected to a vapour recovery system (REF BREF, Section 5.17):

Description: High efficiency seals are specific device for limiting losses of vapour e.g. improved primary seals, additional multiple (secondary or tertiary) seals (according to quantity emitted).

Applicability: The applicability of high efficiency seals may be restricted for retrofitting tertiary seals in existing tanks.

BAT 32: In order to reduce VOC emissions to air from the storage of volatile liquid hydrocarbon compounds, **BAT is to** use a tank cleaning procedure.

Description	Applicability
1. Manual crude oil tank cleaning Oil tank cleaning is performed by workers entering the tank and removing sludge manually	Generally applicable
2. Use of a closed-loop system For internal inspections tanks have to be periodically emptied, cleaned and rendered gas-free. This cleaning includes dissolving the tank bottom. Closed-loop systems which can be combined with end-of-pipe mobile abatement techniques prevent or reduce VOC emissions	Applicability may be limited by e.g. the type of residues, tank roof construction or tank materials

This BAT conclusion is based on information given in Sections 4.21.4 and 4.21.11

BAT 33: Minimization of VOC emissions from loading and unloading operations

In order to prevent or reduce VOC emissions to air from loading and unloading operations of volatile liquid hydrocarbon compounds, **BAT is to** use one or a combination of the techniques given below to reach a recovery rate of at least 95 % (REF BREF, Section 5.17):

Technique	**Description**	**Applicability** (*)
Vapour recovery **a. Condensation**	See technique b)	Generally applicable to loading/unloading operations where annual throughput is >5 000 m^3/yr. Not applicable to

b. Absorption **c. Adsorption** **d. Membrane separation** **e. Hybrid systems**		loading/unloading operations for sea-going vessels with an annual throughput <1 million m^3/yr
(*) 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 Note: Directive 94/63/EC states that a vapour incineration unit may be substituted for a vapour recovery unit if vapour is unsafe or technically impossible because of the volume of return vapour		

Table 4.16 BAT-AELs for non methanous VOC and benzene emissions to air

Parameter	BAT-AEL (hourly values concentration) (1)
Non-methanous volatile organic compounds (NMVOC)	0.15 (**) – 10 g/Nm^3(2)(3)
Benzene	< 1 mg/Nm^3
(1) Hourly values in continuous operation expressed and measured according to Directive 94/63/EC (2) Lower value achievable with two-stage hybrid systems. Upper value achievable with single-stage adsorption or membrane system. (3) For Turkish installations it seems very difficult to reach values below 10g/Nm3, unless increased combustion and/or other measures which have other impacts on environment take place (4) Benzene monitoring may not be necessary where emissions of NMVOC are in the lower end of the range	

This BAT conclusion in based on information given in section 4.23.6.2

4.2.6 Techniques to reduce other pollutants (heavy metals, aromatic compounds, methane, etc.) emissions and BAT-AELs

Other air pollutants from refineries considered are methane (from storage and handling, cold vents and leaks), halon from fire-fighting equipment, H_2S, NH_3 and CS_2. Heavy metals emissions are generally associated to dust emissions and thus the techniques applicable for their reduction are given in Section 4.2.1.

BAT 34: Reduction of HF emissions from the hydrofluoric acid alkylation process

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 (REF BREF, Section 5.2.1).

BAT 35: Reduction of chlorinated compounds emissions from the isomerisation process

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 (REF BREF, Section 5.12)

BAT 36: Reduction of ammonia emissions from secondary treatment techniques

In order to prevent and reduce ammonia (NH_3) 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 NH_3 (REF BREF Section 5.1.5)

Table 4.17 BAT-AELs for ammonia emissions to achieve when using SCR or SNCR techniques

Parameter	**BAT-AEL (1) (monthly average)** **mg/Nm^3**
Ammonia expressed as NH_3	< 5 – 15 (2) mg/Nm^3
(1) The higher levels are associated with higher inlet NOx concentrations, higher NO_X reduction rates and the ageing of the catalyst. **(2)** The lower end of the range in associated with the use of the SCR technique	

4.2.7 Emissions of hazardous compounds (PAH, dioxins, Chloride, etc.)

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. Dioxins can also be emitted to air.

In aromatic extraction units, phenol, cresol and sulphur dioxide can be substituted by less hazardous substances such as furfural or n-methylpyrrolidone (NMP) (REF BREF, Section 4.3.2).

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) (REF BREF, Section 4.3.3).

BAT 37: Reduction of emissions of hazardous substances from base oil production processes

In order to prevent and reduce the emissions of hazardous substances to air (and water) from base oil production processes, **BAT is to** use one or a combination of the techniques given below

Technique	**Description**	**Applicability**
1. Closed process with a solvent recovery	Process where solvent, after being used during base oil manufacturing (e.g. in extraction, de-waxing units), is recovered through distillation and stripping steps	Generally applicable
2. Multi-effect extraction solvent based process	Solvent extraction process including several stages of evaporation (e.g. double or triple effect) for a lower loss of containment	Generally applicable to new units. The use of a triple effect process may be restricted to non-fouling feed stocks
3.Extraction units processes using less hazardous substances	Design (new plants) or implement changes (into existing) so that the plant operates a solvent extraction process with the use of less hazardous solvent, e.g. converting Furfural or Phenol extraction into n-methylpyrrolidone (NMP) process	Generally applicable to new units. Converting existing units to another solvent based process with different physico-chemical properties may require substantial modifications

4. Catalytic processes based on hydrogenation	Processes based on the conversion of undesired compounds via catalytic hydrogenation similar to hydrotreatment	Generally applicable to new units

Note: The solvent recovery unit consists in a distillation step where the solvents are recovered from the oil stream and a stripping step (with steam or an inert gas) in a fractionator. Using inert gas, in place of steam, for stripping the last traces of solvent from the dewaxed oil and waxes is favoured especially when chlorinated solvents are used and for the safety of the process. The solvents used may be a mixture (DiMe) of 1,2-Dichloroethane (DCE) and Dichloromethane (DCM). In wax-processing units, solvent recovery (e.g. for DCE) is carried out using two systems: one for the de-oiled wax and another one for the soft wax. Both consist of heat integrated flashdrums and a vacuum stripper. Streams from the dewaxed oil and waxes product are stripped for removal of traces of solvents.

BAT 38: Reduction of emissions of PCDD/F from the catalytic reforming unit

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 (REF BREF, Section 5.6):

Technique	**Description**	**Applicability**
1. Choice of catalyst promoter	Use of catalyst in order to minimise PCDD/F substances formation during regeneration (1)	Generally applicable
2. Treatment of the regeneration flue-gas		
a. Continuous regeneration gas recycling loop with absorption bed	Waste gas from the regeneration step is treated to remove chlorinated compounds (e.g. dioxins) are re-adsorbed	Generally applicable to new units. Retrofitting existing units may depend on the current regeneration unit design
b. Wet scrubbing	See REF BREF, Section 4.5.10.2	Not applicable to semi regenerative reformer

c. Electrostatic precipitator (ESP)	See REF BREF, Section 4.5.9.2	Not applicable to semi regenerative reformer
[1] 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		

BAT 39: Prevention of mercury emissions from the natural gas plant

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 (REF BREF 5.13)

4.3 BAT to reduce water consumption and waste water discharges

Flow and pollutant mass of waste water discharges

The quantity of waste waters generated and their characteristics depend on the process configuration. This can vary over time and also from one refinery site to another, depending on refinery complexities, variability of feed stocks, integration with petrochemical facilities, techniques, etc. The water and purges streams from refinery operations can become contaminated with dissolved gases, dissolved and suspended solids, hydrocarbons and 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) that needs stripping prior to further treatment or reuse as wash water.

Techniques applicable for the prevention and control of water discharges include:

a) Waste water pre-treatment techniques: In order to preserve treatment performance, the following techniques can be applied:

- Pre-treatment of sour water streams before reuse or treatment, i.e. sending generated sour water (e.g. from distillation, cracking, coking units) to an appropriate pre-treatment (e.g. stripper unit, REF BREF, Section 4.26.4)
- Pre-treatment of other waste water streams prior to treatment to preserve treatment performance

b) Waste water treatment techniques: The following techniques can be applied in order to reduce water consumption and the volume of contaminated water (REF BREF, Sections 4.26.6 and 4.26.7):

- Removal of insoluble substances by recovering oil
- Removal of insoluble substances by recovering suspended solid and dispersed oil
- Removal of soluble substances including biological treatment and clarification
- Additional treatments (e.g. nitrification denitrification process, ion exchange membrane processes or osmosis)

For more detailed information, see Section 4.26 in REF BREF.

General considerations

Unless stated otherwise, emission levels associated with the best available techniques (BATAELs) for waste water discharges given in these BAT conclusions refer to values of concentration (mass of emitted substances per volume of water) expressed in mg/l. As general condition, the averaging periods associated with the BAT-AELs are defined as follows:

Daily average	Average over a sampling period of 24 hours taken as a flow-proportional composite sample. Time-proportional sampling can be used provided that sufficient flow stability is demonstrated
Yearly / Monthly average	Average (weighted according to the daily flows) of the daily average values taken with the minimum frequency set for the relevant parameter within a year/ month

BAT 40: Reduction of water consumption and volume of contaminated water

In order to reduce water consumption and the volume of contaminated water, **BAT is to** use all of these techniques (REF BREF, Section 5.1.7):

Technique	**Description**	**Applicability**
1. Water stream	Reduction of process water produced	Generally applicable for

integration	at unit level prior to discharge by internal reuse of water stream from e.g. cooling, condensates, especially for use in crude desalting	new units. For existing units applicability may require a complete rebuilding of the unit or the installation
2. 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 pre-treatment such as a stripping unit	Generally applicable for new units. For existing units applicability may require a complete rebuilding of the unit or the installation
3. 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 for new units. For existing units applicability may require a complete rebuilding of the unit or the installation
4. 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,	Generally applicable

This BAT conclusion is based on the information given in REF BREF Sections 4.15.7.1, 4.15.7.2 and 4.26

BAT 41: Reduction of the emission load of pollutants

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 all of the techniques given below (REF BREF, Section 5.1.7):

Technique	Description	Applicability
1. 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	Generally applicable
2. 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	Generally applicable
3 Removal of soluble substances including biological treatment and clarification	Biological treatment techniques may include: Fixed bed systems (e.g. biofiltration or trickling filter) Suspended bed systems (e.g. activated sludge process)	Generally applicable

This BAT conclusion is based on the information given in REF BREF Section 4.26

Table 4.18 BAT-AELs for direct waste water discharges from the refining of mineral oil and monitoring frequencies associated with BAT (5)

Parameter	**Unit**	**BAT-AEL (yearly average)**	**Monitoring (1) frequency**
Hydrocarbon Oil index (HOI)	mg/l	0.1 – 2.5	Daily with EN 9377-2 analytical method (4)
Total suspended solids (TSS)	mg/l	5– 25	Daily

Chemical oxygen demand (COD)(2)	mg/l	30 – 125	Daily
BOD$_5$	mg/l	No BAT-AEL	Weekly
Total nitrogen (3) **(expressed as N)**	mg/l	1 – 25(6)	Daily
Lead, expressed as Pb	mg/l	0.005 – 0.030	Quarterly
Cadmium, expressed as Cd	mg/l	0.002 – 0.008	Quarterly
Nickel, expressed as Ni	mg/l	0.005 – 0.100	Quarterly
Mercury expressed as Hg	mg/l	0.000 1 – 0.001	Quarterly
Vanadium	mg/l	No BAT-AEL	Quarterly
Penol Index	mg/l	No BAT-AEL	Monthly with EN 14402 analytical method
Benzene, toluene Ethyl benzene, Xylene (BTEX)	mg/l	Benzene: 0.001 – 0.050 No AEL for T,E ,X reporting only	Flow proportional sample(1)/monthly

(1) Refers to a flow-proportional composite flow proportional sample taken over a period of 24 hours. Time-proportional sampling can be used provided sufficient flow stability is demonstrated

(2) Where on-site correlation is available, COD may be replaced by TOC. The correlation between COD and TOC should be elaborated case by case.

(3) Where Total-Nitrogen = TKN + Nitrates + Nitrites

(4) Moving from the current method to EN 9377-2 may require an adaptation period

(5) Not all parameters and sampling frequencies are applicable to effluent from gas refining sites

(6) When nitrification/denitrification is used, levels below 15 mg/l can be achieved

Note: A dissenting view between some members of the Technical Working Group (TWG) had to be assessed by the EIPPCB for this BAT Conclusion (See Section 4.7)

BAT 42: When further removal of organic substances or nitrogen is needed, **BAT is to** use an additional treatment step as described in Section 5.22.2 of REF BREF.

BAT 43: Reduction of water discharges from the hydrofluoric acid alkylation process

In order to reduce discharges to water from the hydrofluoric acid alkylation process (REF BREF, Section 4.2.1), **BAT is to** use a combination of the techniques given below (REF BREF, Section 5.2):

Technique	Description	Applicability
1. Precipitation/Neutralisation step	Precipitation (with, e.g. calcium or aluminium-based additives) or system neutralisation (where the effluent is indirectly neutralised with KOH)	Generally applicable. Safety requirements due to the hazardous nature of HF are to be considered
2. Separation step	The insoluble compounds produced at the first step (e.g. CaF_2 or AlF_3) are separated in, for example, a settlement basin	Generally applicable.

BAT 44: Reduction of water discharges from the sulphuric acid alkylation process

In order to reduce the discharges 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 (REF BREF, Section 5.2).

BAT 45: Reduction of water consumption and discharges from the desalting process

In order to reduce water consumption and discharges to water from the desalting process, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.8):

Technique	Description	Applicability
1. Recycling water and optimisation of desalting process	An ensemble of good desalting practices aiming at increasing the efficiency of the desalter and reducing wash water usage e.g. using low shear	Generally applicable

	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.	
2. Multistage desalter	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.	Applicable for new units
3. Additional separation step	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	Generally applicable

BAT 46: Control of the waste water streams from etherification process

In order to prevent upset of biotreatment, **BAT is to** use a storage tank and an appropriate unit production plan management to control the toxic components dissolved content (e.g. methanol, formic acid, ethers) of the waste water stream prior to final treatment (REF BREF, Section 5.10).

BAT 47: Minimization of waste water from distillation process

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 (REF BREF, Section 5.15)

Applicability: May not be applicable in some retrofit cases. For new units, vacuum pumps either or not in combination with steam ejectors may be needed to achieve high vacuum (10 mm Hg), and to have a spare in case the vacuum pump fails.

BAT 48: Minimization of water pollution from the distillation process

In order to prevent or reduce water pollution from the distillation process, **BAT is to** route sour water to stripping unit (REF BREF, Section 5.15).

BAT 49: Reduction of water discharges from visbreaking and other thermal processes

In order to reduce discharges 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 42 (REF BREF, Section 5.18)

BAT 50: Monitoring of water discharges

BAT is to monitor discharges to water by using the monitoring techniques with at least the minimum frequency given in the Table 4.18, in accordance with EN standards. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality (REF BREF, Section 5.1.6).

4.4 BAT for waste management

Waste management plans may be applied in order to prevent the generation of waste and reduce its final quantity, including, for example, the following techniques:

- Implementation of a sludge master plan with the aim to reduce the sludge generated.
- Providing enclosed sampling loops
- Cleaning and assembly only in specially constructed and dedicated areas
- Providing dedicated drainage systems
- 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 entering the sewer system become coated with oil and are deposited as oily sludges in the API oil/water separator. 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.
- Segregation of the relatively clean rainwater runoff from the process streams can reduce the quantity of oily sludges generated.

Techniques to consider in the determination of BAT for waste treatment include:

Sludge treatment by dewatering, drying and/or incineration with the purpose of reducing the volume and the residual hydrocarbon content in order to save 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. The cross media effects of sludge incineration are addressed in the Waste Incineration BREF.

Decanter centrifuges are the most widely used for dewatering biosludges. Steam dryers are almost exclusively applied for biosludge and often as a pretreatment step for incineration. 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 applied. Drying is hardly employed by refineries due to safety risks. Deoiling/dewatering of sludges gives a 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, depending on the availability of this unit and specifications of final product. 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). 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).

The techniques used for the recovery of metals from secondary materials such as catalysts used in the oil and gas refining industry, are described in the Non-Ferrous Metals BREF.

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. The principle of spent catalyst management is a scheduled, strictly regulated and safe handling of the materials involved, usually executed by specialised contractors (see Section 4.27.3 of REF BREF).

Three 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 minimised 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.

BAT 51: Waste management plans

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 priority order, ensures that waste is prepared for reuse, recycling, recovery or disposal (REF BREF Section 5.1.8)

BAT 52: Reduction and treatment of waste sludge

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 (REF BREF, Section 5.1.8):

Technique	**Description**	**Applicability**
1. Sludge pre-treatment	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 and to recover oil from slop equipment	Generally applicable
2. Re-use of sludge in process units	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	Applicability is restricted to sludges that can fulfil the requirements to be processed in units with appropriate treatment

This BAT conclusion is based on information given in REF BREF Section 4.27.2

BAT 53: Reduction and treatment catalyst waste

In order to reduce the generation of spent solid catalyst waste, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.1.8):

Technique	**Description**
1. Spent solid catalyst management	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
2. Removal of catalyst from slurry decant oil	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.

BAT 54: Reduction of wastes from the product treatment process

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 (REF BREF, Section 5.16)

4.5 Soil and groundwater risks

The main sources of contamination of soil and groundwater by oil 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.

In order to prevent pollution of the soil, **it is not BAT** to use biodegradation of oily sludge by spreading on land (land farming).

BAT 55: Minimization of emissions to soil and groundwater from the storage of liquid hydrocarbon compounds

In order to prevent or reduce emission to soil and groundwater from the storage of liquid hydrocarbon compounds, **BAT is to** use one or a combination of the techniques given below (REF BREF, Section 5.17):

Technique	Description	Applicability
1. Maintenance programme including corrosion monitoring, prevention and control	A management system including leak detection and operational controls to prevent overfilling. Inventory control and risk-based inspection procedures on tanks at intervals to prove their integrity, and maintenance to improve tank containment. It also includes a system response to spill consequences to act before spills can reach the groundwater.	Generally applicable

	To be especially reinforced during maintenance periods.	
2. Double bottom tanks	A second impervious bottom that provides a measure of protection against releases from the first material	Generally applicable for new tanks and after overhaul of existing tanks (*)
3. Impervious membrane liners	A continuous leak barrier under the entire bottom surface of the tank	Generally applicable for new tanks and after overhaul of existing tanks
4. Sufficient tank farm bund containment	A 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	Generally applicable
5. Maintenance programme including corrosion monitoring, prevention and control	A management system including leak detection, inventory control and inspection procedures on tanks at intervals to prove their integrity.	Generally applicable
(*) Techniques 1 and 2 may not be fully applicable where tanks are dedicated to products that require heat for liquid handling, (e.g. bitumen) and where no leak is likely because of solidification.		

This BAT conclusion is based on information given in REF BREF Sections 4.21.8 and 4.21.9

4.6 Environmental Management Systems: BAT for the environmental management

An environmental management system (EMS) is a technique that allows the operators of installations to address environmental issues in a systematic and demonstrable way. EMS are most effective and efficient where they form an inherent part of the overall management and operation of an installation. 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.

BAT 56: Environmental management systems

BAT is to implement and adhere to an environmental management system (EMS) that incorporates all of the following features (REF BREF, Section 5.1.1):

1. Commitment of the management, including senior management;
2. Definition of an environmental policy that includes the continuous improvement for 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 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.
5. 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;
6. Review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;

7. Following the development of cleaner technologies;
8. 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;
9. Application of sectoral benchmarking on a regular basis.

4.7 Assessment of the dissenting views on BAT Conclusions

As explained at the beginning of this chapter, during the final meeting of the Technical Working Group (TWG) for the revision of the REF BREF (which is the basis for drafting this guide), some BAT Conclusions were not approved unanimously by all the members of the TWG. The dissenting views presented during the meeting have been assessed by the European IPPC Bureau (EU institution coordinating the preparation of BREF documents) and, those considered to be valid, will be reported in the section of *'Concluding remarks and recommendations for future work'* of the final approved and published version of the REF BREF (expected to come within 2013 or latest 2014).

The dissenting views imply no obligation, they just express some aspects which in another future review of the BREF should be taken into account. In this Section, a summary of these dissenting views and their rationale is given:

<u>1. Waste water discharges: expression of BAT-AELs (units and averaging periods)</u>

Three members of the TWG (Austria, Germany and the European Environment Bureau-EEB) requested to set short-term average BAT-AELs (i.e. daily averages) for water discharges.

Another member (Sweden) raised a dissenting view concerning the use of concentrations exclusively and proposed the following values (yearly average):

- COD: 10-50 g/t crude
- Total Nitrogen: 2-15 g/t crude

According to the EIPPCB assessment, the information on which Table 4.18 (in this guide) is based has been extracted from plant specific questionnaires where emissions to water are referred as *annual emissions from the whole refinery*. Moreover, the fluctuation of daily emission levels varies widely between different sites (for COD, TSS and THC) and the submitted data were not sufficient for deriving short-term BAT-AELs. Nevertheless, an assessment of the daily variability for COD, TSS and TPH can be found in Section 4.26 of the REF BREF, which can be very useful for the competent authorities at the time of establishing short term emission limit values.

2. Emissions to air: Expression of BAT-AELs (averaging periods)

Four members (Austria, Germany, the Netherlands and EEB) requested to set short-term average BAT-AELs (i.e. daily averages) for emissions to air. However, the information on SO_2, dust and NO_x emissions in which BAT Conclusions are based has been extracted from plant specific questionnaires where emissions to air are referred to *annual emissions from the whole refinery* (only a very limited number of sites have provided daily values for SO_2 and NO_x).

3. Emissions to air: reference to economic viability in relation to the application of BAT

CONCAWE requested to re-instate the applicability restrictions for existing units due to economic considerations that were deleted during the final TWG meeting for BAT 10, 15, 12 and 17.

4. BAT-AEL for dust emissions from FCC in existing units

Three members of the TWG (Greece, Spain and CONCAWE) did not support the BAT-AEL proposed and requested to modify it by adding the following footnotes in Table 4.1 (in this guide):

([3]) When only a multi-stage cyclone is used, the upper end of the BAT AEL range is 100 mg /Nm^3

([4]) When a 3-fields ESP is applied and when SO_2 reducing agents are used the upper end of the BAT-AEL range is 70 mg/Nm^3

The EIPPCB assessment stated that the use of multi-stage cyclones alone cannot be considered BAT for the abatement of dust emissions from FCC units and that there is not sufficient scientific and technical data to define a specific BAT-AEL upper end value of 70 mg/ Nm^3. In the section for *future work* it would be explained that it may be valuable to collect specific data in order to assess the potential detrimental effect of the use of additives for sulphur reduction on dust emissions and the related abatement systems.

5. BAT-AEL for SO_x emissions from FCC in existing units

Four members of the TWG (the Czech Republic, Greece, Spain and CONCAWE) requested to change the upper end of the BAT-AEL range for existing FCC units (based on the technique of SO_x reducing additives) as follows:

- For full combustion mode: 800 - 1 000 mg/Nm^3
- For partial combustion mode: 1200 - 1700 mg/Nm^3

The EIPPCB assessment concluded to report this dissenting view in the section “*Concluding remarks and recommendations for future work”* as follows:

- *100 – 1 000 mg/Nm^3 for existing units in full combustion mode,*
- *100 – 1 700 mg/Nm^3 for existing units in partial combustion mode*

6. BAT-AEL for NO_x emissions from FCC in existing units

Five members of the TWG (CONCAWE, the Czech republic, Greece, Finland and Portugal) requested to change the upper end of the range for existing units in full combustion mode (300 - 400 mg/Nm^3) including an additional footnote: *'in case NO_X additive reduction efficiency is limited to less than 50 % NO_X, levels up to 400 mg/Nm^3 may occur'.*

7. BAT associated environmental performance level SRU in existing units

Two dissenting views were formulated in BAT 17 Conclusion:

- Two members (the Netherlands and EEB) requested to set a single BAT_AEPL range of 99.5 – 99.9% for the sulphur recovery efficiency of new and existing sulphur recovery units.
- Other two members (Belgium and Sweden) requested to define a 'sulphur recovery efficiency for existing units: ≥ *99 %*'.

8. BAT-AEL for NO_x emissions from gas fired combustion existing units

Four members (CONCAWE, the Czech Republic, Greece and Italy) requested to set a NO_x BAT-AEL range of 30 – 300 mg/Nm^3 for gas fired existing combustion units of less than 50 MW.

9. BAT-AEL for coking units

The European Environment Bureau requested to have BAT-AEL for emissions of NO_x from coking units but the EIPPCB decided not to report it for not having received any rationale.

10. Reference to the “Bubble approach”

Eleven members of the TWG (CONCAWE, the Czech Republic, Greece, Spain, Finland, France, Italy, Portugal, Sweden, Slovakia as well as Norway as observer) supported the proposal of including the concept of “Bubble approach” in the Decision on the BAT Conclusions. Different proposals were given within the TWG. Nevertheless, according to the EIPPCB, the links between the ‘Bubble approach’ and the implementation of the IED need further legal consideration. The Commission Services will consider the most appropriate way to take into account the outcome of the TWG meeting and to continue the work on this issue over the next months.

Recommendations for future work: the following issues would need to be re-assessed by the TWG and further information should be gathered during the next review of the REF BREF:

Emissions to water:

- Collect short term emissions data, expressed both in loads and in concentrations linked to the use of the techniques
- Consider the data from monitoring of the phenol index.

Emissions to air:

- Emissions to air of dioxins and furans (PCDD/F) from catalytic reformer units should be further assessed
- Emissions of metals from FCC units and combustion units should be further assessed (including from gas-firing combustion units)
- The impact of the use of low N feedstock on NO_x emissions from FCC units should be further studied
- Specific data should be collected in order to assess the potential detrimental effect of the use of additives for sulphur reduction on dust emissions and the related abatement systems Reconsider the issue of new combustion units (both gas and multi-fuel firing) as, due to lack of data, no BAT conclusions and AELs for SO_2 and NO_x have been set for new units
- Consider collecting robust data on NO_x emissions from coking processes
- Consider the ongoing work in the EU regarding an EN standardisation for VOC diffuse emissions monitoring methods.

5 MEASUREMENT AND MONITORING OF EMISSIONS

General considerations

One must keep in mind the following considerations in order to express the different BAT Associated Emissions Levels (BAT-AELs) in the way they have been expressed in the Chapter 4.

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 this Section refer to monthly average values under the following standard conditions: dry gas, temperature 273.15 K, pressure 101.3 kPa.

For periodic measurements, BAT-AELs refer to the average value of three spot samples of at least 30 minutes each. For continuous measurements BAT-AELs refer to monthly average values, unless stated otherwise.

For combustion and catalytic processes, reference conditions for oxygen must be given together with the associated data. Usually, these values are 3% O_2 for combustion process (using liquid or gaseous fuels), catalytic cracking and SRU. For gas turbines and engines the reference percentage of oxygen is 15% O_2.

The formula for calculating the emissions concentration at a reference oxygen level is shown below:

$$E_R = (21 – O_R / 21 - O_M) \times E_M$$

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, BAT-AELs for waste water emissions given in these BAT conclusions refer to values of concentration (mass of emitted substances per volume of water) expressed in mg/l. The averaging periods associated with the BAT-AELs are defined as follows:

Daily average: Average over a sampling period of 24 hours taken as a flow-proportional composite sample. Time-proportional sampling can be used provided that sufficient flow stability is demonstrated

Yearly / Monthly average: Average (weighted according to the daily flows) of the daily average values taken with the minimum frequency set for the relevant parameter within a year/ month

5.1 Air

5.1.1 Emissions

The monitoring methodologies most commonly used by large installations, such as refineries, to estimate emissions to air are direct measurement methods: continuous emission monitoring systems (CEMs), predictive or parametric emission monitoring systems (PEMs), source testing; and indirect methods: mass balance calculations, emission models and factors, and engineering estimates.

CEMs are consolidated technologies. CEMs instrumentation monitors emissions directly and continuously, determines the flow rate, analyzes the gas, measures the pollutant concentration, and records the data. CEMs can be the most accurate method of quantifying emissions under certain circumstances but are the most expensive alternative.

The regulations usually require CEMs to monitor sulphur dioxide and nitrogen oxide emissions from sulphur plant incinerators, fluidized bed catalytic cracking units (FCC), and boilers. Sulphur dioxide and nitrogen oxide emissions are considered to be the most significant pollutants, and the three sources are generally the largest at refineries under normal operating conditions.

CEMs require certification and verification of quality assurance/control activities, as well as routine maintenance, according to the recent Turkish "Communiqué 28042 on continuous emission monitoring systems" based on the TS EN 14181 standard.

Continuous monitoring can be done using either "extractive CEMs," in which case the sample gas is extracted from the emission stream and transported to a gas analyser for the measurement and recording of the pollutant concentration; or "in-situ CEMs," which measure and analyze the emissions directly in a stack. The main benefits of extractive CEMs is that the instruments are not subject to heat, vibration, and corrosive conditions; maintenance is easier at ground level; and analyzers for extractive CEMs are generally less expensive than those for in-situ systems. The disadvantages are that sample lines can leak, freeze, or clog, and pollutants can be lost to adsorption, scrubbing effects, or condensation. The main benefits of in-situ CEMs are minimization of sample loss and elimination of the expensive sampling and conditioning system. However, maintenance and replacement inside the stack are more difficult, and calibration gas must be taken to the analyzer location.

A predictive or parametric emission monitoring system (PEM) can provide a less expensive alternative to CEMs. A PEM calculates emissions based on their known correlation to operating parameters (e.g., fuel use), instead of by direct sampling. However, PEMs are barely used because of the complexity of the chemical reactions involved in some process units (FCC).

Source testing, also known as stack testing or stack sampling, is the regulatory standard. Done by trained and experienced staff during typical operating conditions, using accredited methods, and at appropriate intervals, source testing can provide accurate annual emission estimates. It is often required to determine compliance with air discharge permits and for certification of CEMs, and emission factors are often a collection of source tests at various operating rates.

A mass balance calculation applies the law of conservation of mass stating that the quantities of materials going in and coming out of a process unit remain unchanged provided there is no accumulation in the unit. The cost depends on the availability of accurate data and staff time.

The general equation for the mass (M) balance calculation is

Min=Mout+ Maccummulated + Mdepleted

A refinery example is the combustion of fuel oil containing sulphur. If one assumes all the sulphur converts to SO_2 then the following equation could be used to estimate SO_2 emissions.

SO_2 emissions (kg) = amount of fuel oil burned (m^3/d) x sulphur content (mg/m^3) x (days units operates) x (molecular weight of SO_2/S) x 1(kg) / 106 (mg)

Emission models and factors are widely used to measure air emissions from refineries. If default data are not applicable to local conditions or type of facility, emission models do require detailed input of data, such as meteorological data or equipment specifications.

Examples for the petroleum refining sector include the European CORINE-AIR factors and U.S. Environmental Protection Agency (EPA) TANKS and WATER9 models, both of which can be used to calculate VOCs and other air pollutants. An emission factor is a simplified emission model: it relates emissions from a source to some activity associated with the source. A large number of published emission factors are available for many processes, and they are generally the cheapest method and the easiest to apply. U.S.EPA provides ratings of reliability with its AP-42 emission factors.

5.1.1.1 Ways to calculate SO_2 and NO_x emissions

Besides these methods, for its special interest and application in refineries, the “bubble approach” is explained below. This concept has in any case been already used in the Article 14.3 of the by-law 27605 “regulation regarding large combustion plants” because it could be used as an alternative for the calculation of emission limit values when distillation and conversion of waste is used alone or with other fuels in multiple ignition units:

‘Bubble approach’ and how it could be applied in a refinery

A specific approach based on a 'bubble concept' can nevertheless be used by the competent authority to regulate one refining site. It will aim at defining a single value as a target for the refinery as a whole.

This approach consists of considering all concerned emissions together, as emitted through a single 'virtual stack'

This approach takes into account the specificity of the refining sector, in particular the following factors:

- the recognised complexity of refining sites, with multiplicity of combustion and process units, often interlinked through their feedstock and energy supply
- the frequent (e.g. weekly or even daily) process adjustments required as a function of the quality of the crude oil received
- the technical necessity for many sites to keep burning a part of their internal residues as energy-producing fuels, and to frequently adjust the site fuel mix according to process requirements
- the need for enabling, quantifying and monitoring a total emission reduction at site-level for sites where some key specific installation controls are not possible and have to be compensated elsewhere

This approach assumes, as prior condition, that the global reduction of the environmental impact should be at least as efficient as if BAT-AELs were achieved for every individual processes.

Bubble perimeter

The exact bubble perimeter to be considered for a given site will depend on the site processes. That 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)

Bubble substances or parameters covered

SO_2 and NO_x have been recognised as the two parameters which deserve priority in the definition of 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 this particular context, the methodology proposed is 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 an individual BAT AEL

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

- a first term related to the energy generation system, including at least all furnaces, standalone boilers, cogeneration plants 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 plants where energy is exported and excludes emissions from external (out of permit) power plants.

- 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 SO_2) and PERMANENT emissions of flaring (pilot flames). It excludes emissions from SWS (sour water stripping) and non-condensable untreated gases.

Site Bubble = Energy system term + Σ process units terms = $FL_{comb} \times [Comb] + FL_{FCC} \times [FCC] + FL_{SRU} \times [SRU] + FL_{other} \times [other]$

For the purpose of expressing a 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 four following steps:

A. Exhaustive identification and geographical mapping of all included sources.
B. Determination of the off-gas volumetric contributions expected from all included sources.
C. Determination of the mass contributions expected from all included sources.
D. Determination of the bubble-associated monitoring regime.

A.- Exhaustive identification and geographical mapping of all included sources

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) involve:

- 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 monitoring required for the corresponding source

The method is based in mapping having in mind:

- to include all combustion processes and identify those using ‘non standard fuels’
- to include all refining processes as far as they are in the bubble area
- to exclude processes that could be on site but are not properly refining (e.g. petrochemical units)

And then, show on a map and in table form all the available operational data (flue-gas volume, load, average or spot concentration measurements, etc.)

B.- Determination of the off-gas volumetric contributions expected from all included sources

This second step may be performed following the next recommendations, which are included in the Appendix B of the Annex VI of the new BREF for Refineries.

FLUE-GAS FLOW RATE - 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.

EXPRESSION OF MEASUREMENTS

In all circumstances the quantity of flue-gases 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 Nm^3.

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 (dry flue-gas/wet flue-gas) relating to flue-gas composition:

Dry flue-gas flow = wet flue-gas flow x (1- % water in the flue-gas) Flow at y % O_2 *= flow at x %* O_2 ** (21-x)/(21-y)*

USING THE RESULTS

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.

FLUE-GASES FROM FURNACES AND BOILERS (COMBUSTION)

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 Nm^3 of dry flue-gas corrected to 3 % O_2 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 (Emissions Trade Scheme) provisions. Statutory obligations for drawing up CO_2 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.

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 C % + 0.211 H % + 0.0333S % + (6.8 x k + 0.8) N % - 0.0263O %] x (21/18)/NCVFO (MJ/kg)

In Nm^3/kg of fuel oil equivalent at 3 % O_2 dry gases

With k the proportion of nitrogen which is wholly oxidised.

Based on the above, it is proposed to take the typical value of 12.3 Nm^3/kg of fuel oil equivalent at 3 % O_2 (dry gases) as a standard flue-gas factor for liquid fuels.

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 flue-gases = (a x (4.76n + 0.94p)+ b x 1.88 + c) x 22.4/(a x (12 n + p) + b x 2 + c x 28)

as Nm^3/kg

This flue-gas volume is expressed per kg of fuel gas at 0 % O_2 (neutral combustion) on dry gases.

In order to have the factor expressed in Nm^3/kg foe, the result has to be divided by the fuel Net Calorific Value.

Based on the above, it is proposed to take the typical value of 11.3 Nm^3/kg of fuel oil equivalent at 3 % O_2 (dry gases) as a standard flue-gas factor for gaseous fuels.

FLUE-GASES FROM SOUR WATER STRIPPER (SWS) GASES

Flue-gases and/or incondensables 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 practises 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.

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 H_2S + b HC + c inerts.

Where:

a = %v H_2S

b = %v hydrocarbons

c = %v inerts

and a + b + c = 1

For simplicity the HC are considered to be C_2H_6 (MM= 30) and the inert components are essentially CO_2. (MM = 44). These approximations generally have little effect on the result (with a low HC content).

MAKE-UP FUEL GAS

Fuel Gas (FG) is injected in the incinerator in order to entirely burn residual H_2S. The flow of FG is represented by the ratio: j = % m of FG to AG

ANALYSERS

Gas analysers are mainly:

- H_2S and SO_2, in the tail gas (TG) downstream of the main reaction zone,
- SO_2 and O_2 in the flue-gas at the exit of the incinerator.

In the following, unless specified otherwise, concentrations are given on dry gases.

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 % O_2 is:

$f = Q\ TG\ mol = (1.88a + 15.2b + c)/(1 – 4.76 * \%\ SO_2\ TG + 0.88 * \%\ H_2S\ TG)$

Flue-gas volume exiting the incinerator:

$Qincin\ vol = (1 + 5.64 \times \%\ H_2S\ TG) \times (1.88a + 15.2b + c)/(1 – 4.76 * \%\ SO_2tg + 0.88 * \%H_2Stg) + j\ \% \times QGA \times 1\ 000 \times PF$ (Nm^3/h of dry flue-gas at 0 % O_2)

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 H_2S) 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.

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).

DETERMINATION OF THE FLUE-GAS VOLUME AS A FUNCTION OF SULPHUR RECOVERY EFFICIENCY

By definition efficiency is:

η = 1- %H_2S unconverted

for 1 mole of AG it gives %S incin mol expressed as a function of .:

%S incin mol = (100 % -η) x a/Q incin mol (i)

%S incin = (100 % - η) x a/(f0 + 4.76 x (100 % -η) x a)

Q incin vol = (f0 + 4.76 x (100 % - η) x a) x 22400/MMGA

in Nm^3 of dry flue-gas at 0 % O_2/t of AG

With f0 = 1.88a + 15.2b + c

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 1500 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_2S 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.

DETERMINATION OF THE SRU SO_2 EMISSION LEVEL AS A FUNCTION OF SULPHUR RECOVERY EFFICIENCY

Using the same calculations and knowing %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:

$[SO_2]$ = %Sincin x 64/22.4 x 106 x 18/21 mg/Nm^3 at 3 % O_2 dry gases

FLUE-GAS FLOW FROM THE FCC

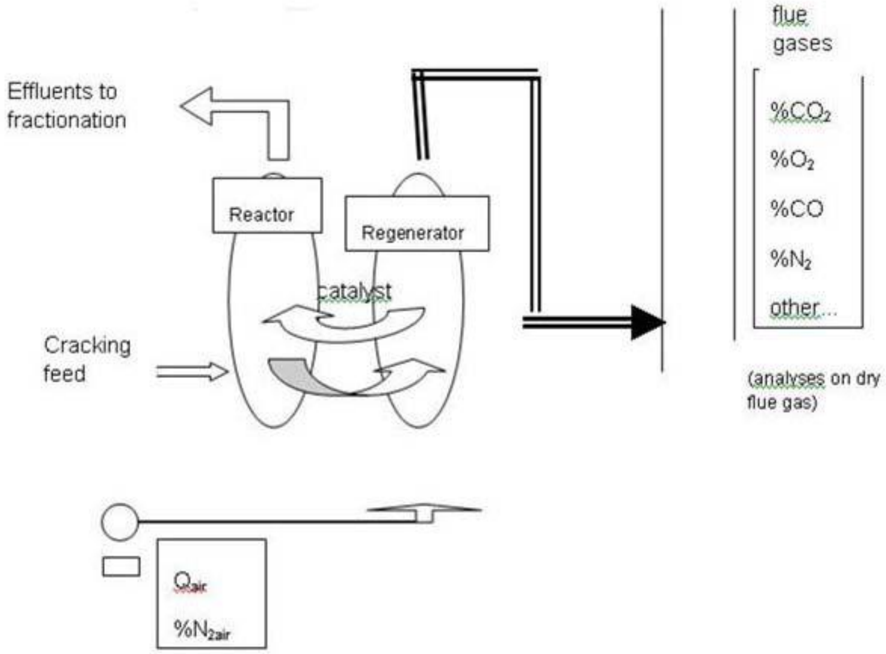
The methodology presented under is the most precise and is used within the framework of the ETS reporting. However it requires a significant amount of data, including measurements which are site and unit-specific.

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.

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 reestablishment of the normal activity of the catalyst.

FCC simplified diagram



$$Q_{vol\ flue-gases} = \frac{Q_{massof\ enteringair} \times 0.79 \times \dfrac{1}{MM_{dryair} + MM_{H_2O} \times \dfrac{\%water}{1-\%water}} - Q_{N_2 massto\ fractiont} \times \dfrac{1}{MN_{N_2}}}{\%N_{2\ fluegases}} x22.4x1000\ as\ Nm^3/h$$

Where:

Qmass entering air as t/h moist air

MMdry air = 28.97 kg/kMol

MMH_2O x %water/(1- %water) = 0.25 kg/kMol for air at 20 °C and 60 % relative humidity

QN2 mass to fraction as t/h

MMN_2 = 28 kg/kMol

Let:

$$Q_{vol\ flue-gases} \approx \frac{Q_{mass of\ entering air} \times 605 - Q_{N_2 mass to\ fraction} \times 800}{\%N_{2\ flue gases}} as\, Nm^3/h \quad dry\ fluegas with\ the measured\, O_2\ content$$

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.

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.

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.

$CO + ½\ O_2 = CO_2$

As the volume flowrate of the CO_2 is equal to that of the CO. The additional quantity of fluegases generated by CO combustion is:

Qflue-gas CO = quantity of nitrogen in air used for combustion of the CO.

The total volume of flue-gases generated by the FCC, expressed for 0 % O_2 becomes:

$$\boxed{Q_{total\ flue-gas} = Q_{vol\ flue-gas} \times \left[\frac{21\% - \%O_2}{21\%} + \%CO \times 1.88\right] \text{in Nm}^3\text{/h dry flue-gas for 0 \% O}_2}$$

$$Q_{total\ fluegas} = Q_{vol\ fluegas} \times \left[\frac{21\% - \%O_2}{21\%} + \%CO \times 1.88\right] in\, Nm^3/h\, dry\ fluegas\ for\, 0\%\, O_2$$

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 CO_2 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 Nm^3/kg of coke (foe) at 3 % O_2 (dry gases) as a standard flue-gas factor for FCC UNIT.

C.- Determination of the mass contributions expected from all included sources

This determination will be done with the NO_x and SO_2 average concentration of each source of emission. In the paragraph 5.1.1.2 of this chapter the best way to obtain these concentrations is shown.

The bubble limit will be established as a function of the BAT-AEL of every unit.

The real bubble emission will be a function of the real emissions.

D.- Determination of the bubble-associated monitoring

Make use of the *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 relevance level, as for example, following a growing level of emissions:

- use of emission factor and activity parameter monitoring (low emissions);
- idem + periodic stack measurements;
- idem + continuous stack measurements (high emissions).

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.

5.1.1.2 Selection of parameters and pollutants and reporting

According to section 4.2 of this document, BAT consists in monitoring air emissions and key process parameters using the units mentioned in the table of that section and using the indicated monitoring techniques with at least the minimum frequency given in the same table which is reproduced below:

Description	**Process unit**	**Minimum frequency**	**Monitoring technique**
1. Monitoring of emissions to air			
1.1 Monitoring of SO_x, NO_x, and dust	Catalytic cracking	Continuous (2, 4)	Direct measurement
	Combustion units ≥100 MW(6) and calcining units	Continuous (2, 4)	Direct measurement (5)
	Other combustion units of 50 up to 100 MW (6)	Continuous	Direct measurement of indirect monitoring (2)
	Other combustion units	Once a year and after significant fuel changes (1)	Direct measurement of indirect monitoring (2)
	Sulphur recovery units (SRU)	Continuous for SO_2 only (4)	Direct measurement of indirect monitoring (3)
1.2 Monitoring of NH_3 emissions	All units equipped with SCR or SNCR	Continuous	Direct measurement
1.3 Monitoring of CO	Catalytic cracking and combustion units ≥ 100 MW	Continuous	Direct measurement
	Other combustion units	Once every 6 months (1)	Direct measurement
1.4 Monitoring of emissions of metals (Ni, Sb, V),	Catalytic cracking	Once every 6 months and after significant changes to the unit (1)	Direct measurement or analysis based on metals content in the catalyst fines and in the fuel
	Combustion units (8)		
1.5 Monitoring of PCDD/F	Catalytic reformer	Once a year or once a regeneration	Direct measurement

		whichever the longer	
2 Monitoring of parameters linked to pollutant emissions, e.g. O_2 content in flue-gas, N and S content in fuel or feed [9)]	Catalytic cracking and combustion units > 50 MW_{th}	Continuous for O_2 content. For N and S content, periodic at a frequency based on significant fuel/feed changes	Specific to each relevant paramenter

(1) Continuous SO_x emissions from SRU may replaced by a material balance provided appropriate measurements of SRU efficiency are based on regular plant performance tests

(1) Monitoring frequencies may be adapted if, after a period of one year, the data series clearly demonstrate a sufficient stability

(2) Continuous measurement of SO_2 emissions may be replaced by calculations based on measurements of the sulphur content of the fuel or the feed where it can be demonstrated that this leads to an equivalent level of accuracy

(3) SO_2 emissions measurements from SRU may be replaced by a continuous material balance or other relevant process parameter monitoring provided appropriate measurements of SRU efficiency are based on periodic (e.g. once every 2 years) plant performance tests

(4) Only SO_2 is continuously measured, SO_3 is only periodically measured (e.g. during calibration of the SO_2 monitoring system).

5) Or indirect monitoring of SO_x

(6) Refers to the capacity connected to the stack where emissions occur

(7) Sb is to be monitored only in catalytic cracking units when Sb injection is used in the process (e.g. for metals passivation)

(8) With the exception of combustion units firing only refinery fuel gas

(9) N and S monitoring in fuel or feed is not applicable when continuous measurements of NOx and SOx are carried out at the stack

On the other hand, throughout the Chapter 4 the different parameters to be controlled in order to achieve BAT-AELs have been fixed:

5.1.1.2.1 Pollutants which have to be controlled with ELVs

Sulphur dioxide

Sources of sulphur dioxide emissions include processes for heat generation, sulphur recovery, catalyst regeneration and flares.

Possible methods for monitoring sulphur dioxide emissions from refinery sources include mass balance calculations, emission factors, stack surveys, and CEMs. In additionto the bubble emission, of course.

Chapter 4 shows that the permits could impose as BATs monitoring sulphur dioxide emissions specify CEMs for catalytic cracking, combustion units and sulphur plants, and it determined that stack surveys should be performed on three heaters or boilers and four FCCUs.

The recommendations in this regard are:

- use of emission factors (with verification) or CEMs for FCCUs
- mass balance calculations or CEMs for sulphur plants
- mass balance calculations for boilers and heaters (solid and liquid fuels)
- and emission factors for flares.

Nitrogen oxides

Sources of nitrogen oxide emissions are combustion in heaters and boilers, flaring, incineration of waste gases from sulphur plants, and catalyst regeneration.

Possible methods for monitoring nitrogen oxide emissions from refinery sources include emission factors, stack surveys, CEMs, and PEMs. In the case of flares, only emission factors can be used. In additionto the bubble emission, of course.

Usually stack surveys are required for four boilers or heaters, some FCCUs, and some sulphur plants; and CEMs in some sulphur plants.

The recommendations in this regard are::

- use of emission factors (with verification) or CEMs for FCCUs
- emission factors (with verification) for sulphur plants

- annual stack surveys (with continuous verification) for boilers and heaters with high capacity
- UNE emission factors for the smaller ones
- and emission factors for flares.

Carbon monoxide

Carbon monoxide emissions come from incomplete combustion in heaters and boilers, flares, incineration of waste gases from sulphur plants and catalyst regeneration.

Possible methods for monitoring carbon monoxide emissions from refinery sources include emission factors, stack surveys, and CEMs for catalyst regeneration, and boilers and heaters; and emission factors for flares.

Based on available permit data, stack surveys are normally used to measure carbon monoxide emissions and perform stack surveys on heaters and the sulphur plant.

The recommendations in this regard are:

- use of emission factors or CEMs for FCCUs
- emission factors for boilers and heaters
- and emission factors for flares.

Particulate matter (dust)

Particulate matter (PM) can be primary or secondary; filterable or condensable; and total (TPM), total suspended (TSP), inhalable (PM10), or breathable (PM2.5). Significant sources of PM emissions are external combustion (from boilers, heaters, and flares) and catalyst regeneration (in CCUs).

Possible methods for monitoring PM emissions from refinery sources include emission factors and stack surveys. Based on available permit data, for this pollutant stack surveys are used in some boilers and heaters and sulphur plants.

The recommendations in this regard are:

- use of CEMs or emission factors (with verification) or mass balance calculations (measured catalyst losses) for FCCUs
- emission factors (with verification) for boilers and heaters that use solid and liquid fuels; emission factors alone for boilers and heaters that use gaseous fuels
- and emission factors for flares.

Volatile organic compounds (VOCs)

Sources of emissions of VOCs are incomplete combustion in heaters and boilers, catalytic cracking unit regenerators, catalytic reforming unit regenerators, steam methane reformers or hydrogen units, and flares; as well as fugitive emissions (i.e., leaks from equipment [valves]); storage tanks; loading operations; waste or soil landfarm operations; wastewater sources; and non-routine releases, such as spills.

Possible methods for monitoring VOCs emitted are best limited to emission models and factors, because the sources of VOC emissions are numerous and not appropriate for direct monitoring. In addition, it is difficult to achieve accuracy using mass balance calculations, although these may be used to estimate total VOC emissions from fugitive or wastewater sources, whenever emission models or factors are not applicable.

Based on available permit data, VOC emissions are the only class of substances for which permits have an emission inventory requirement. Also stack surveys are required for some combustion sources, primarily FCCUs.

Because of the relevance of these pollutants more detailed explanations about them are shown in the subsection 5.1.1.2.3 of this Chapter (Odour control and VOC emissions)

5.1.1.2.2 Others pollutants to be reported to the European Pollutant Release and Transfer Register (E-PRTR)

According to Article 5 of the E-PRTR Regulation, operators of refineries are obliged to report specific information if the applicable capacity threshold(s), Annex I to the EPRTR Regulation, and release threshold(s), Columns 1a, b, and c of the table set out in Annex II to the E-PRTR Regulation, and/or the applicable capacity threshold(s) and off-site transfer threshold(s) are surpassed.

The column 1a, of the table in Annex II to the E-PRTR Regulation contains a total of 60 pollutants which are specified as relevant air pollutants. Releases from a facility of air pollutants in excess of the threshold values in column 1a must be reported. This is the case for each of those 60 air pollutants.

As a help, the Appendix 4 of the European Commission Document “Guidance for the implementation of the European PRTR”, contains an indicative sector specific sub-list of air pollutants. This list shows for all Annex I activities those air pollutants that are likely to be emitted and helps in the identification of relevant pollutants at a given facility. According to this list, the pollutants to be reported by the refineries would be:

- Methane (CH_4)
- Carbon monoxide (CO)
- Carbon dioxide (CO_2)
- Hydro-fluorocarbons (HFCs)
- Nitrous oxide (N_2O)
- Ammonia (NH_3)
- Non-methane volatile organic compounds (NMVOC)
- Nitrogen oxides (NO_x/NO_2)
- Sulphur oxides (SO_x/SO_2)
- Hydrochlorofluorocarbons (HCFCs)
- Arsenic and compounds (as As)
- Cadmium and compounds (as Cd)
- Chromium and compounds (as Cr)
- Copper and compounds (as Cu)
- Mercury and compounds (as Hg)
- Nickel and compounds (as Ni)
- Lead and compounds (as Pb)

- Zinc and compounds (as Zn)
- Benzene
- Polycyclic aromatic hydrocarbons (PAHs)
- Chlorine and inorganic compounds (as HCl)
- Particulate matter (PM10)

However, there are some additional pollutants that may be necessary to report, such as dioxins. Because of that, the sub-list is not a “closed list”.

Reported PRTR emission data must include a code to identify the type of estimation methodology used. The classification codes are simple letters:

- Class M: emission data are based on measurements using standardised or accepted methods; often additional calculations are needed to convert the results of measurements into annual emission data.
- Class C: emission data are based on calculations using nationally or internationally accepted estimation methods and emission factors, which are representative of the industrial sectors.
- Class E: emission data are based on non-standardised estimations derived from best assumptions or expert guesses.

The most accurate data will be those derived from measurements e.g. from continuous emission monitoring or using the results of short term measurement exercises to improve calculated estimates.

The estimation methodologies provided within this report would allow reported calculated emissions to be indexed as Class C.

There are a number of sources of emission estimation methodologies which satisfy Class C nomination:

- Oil industry associations API, UK Energy Institute (formerly IP), etc.
- Oil companies who have published methods in the professional press

- National and international environmental authorities e.g. US EPA,
- European Environment Agency, etc.
- International organisations e.g. IPCC, etc.

Within this context, because of its usefulness, the European CONCAWE methodology is recommended as a reference. It is a complete study which allows evaluating the PRTR pollutants.

This report is available, as an Adobe pdf file, on the CONCAWE website (www.concawe.org in Publications --> Reports Subsection (search for “PRTR”))

5.1.1.2.3 Odour control and VOC emissions.

Odour Control

The study of odours is a growing field but is a complex and difficult one. The human olfactory system can detect many thousands of scents based on only minute airborne concentrations of a chemical. The study of odours is also further complicated due to the complex chemistry taking place at the moment of a smell sensation. Odours must be linked back to a chemical compound causing the fragrance or smell in order to qualitatively and quantitatively identify and control the source compound, if it is deemed economically and technically feasible to do so.

Another key issue related to odour regulations is the several technical challenges related to odour identification, monitoring, and enforcement. To make things worse, a phenomenon known as olfactory fatigue needs to be taken into account. Olfactory fatigue is a temporary adaptation of the normal ability to distinguish a particular odour after a prolonged exposure to that airborne compound. Human bodies become desensitized to stimuli in order to prevent the overloading of the nervous system, thus allowing it to respond to new stimuli.

The most significant technical challenge associated with regulating odours is that an identified odour must be traced back to an individual chemical compound that can be monitored. Without direct correlations to a monitored chemical compound, compliance and enforcement become subjective and problematic. Some smells and odours are a combination of chemicals and compounds thus requiring multiple compounds to be monitored. Further complications present themselves as chemical reactions take place in ambient air from multiple sources to create nuisance odours.

Crude oil processing can potentially release multiple compounds that may produce strong and offensive odours. Refinery operational smells are generally associated with compounds containing sulphur where even insignificant losses are capable of causing a noticeable odour. There are several sources of potential odour that are emitted as a fugitive emission or via a point source from refineries.

Fugitive emissions are harder to monitor and control. Nowadays it begins to be imposed, in the different Permits, the implementation of a Leak Detection and Repair (LDAR) program to control fugitive emissions. Fugitive emissions occur in valves, pumps, compressors, pressure relief valves, flanges, connectors and other piping components.

The Permit may impose the implementation of an Odour Management Plan, which could include:

- LDAR Programme
- Periodical monitoring programme based in EN 13725 Standard. “Determination of odour concentration by dynamic olfactometry” which defines the European standard defining olfactometry measurement methods.

LDAR Programme

A typical refinery or chemical plant can emit 600-700 tons per year of VOCs from leaking equipment, such as valves, connectors, pumps, sampling connections, compressors, pressure-relief devices, and open-end lines.

- Leaks from pumps typically occur at the seal.
- Leaks from valves usually occur at the stem or gland area of the valve body and are commonly caused by a failure of the valve packing or O-ring.
- Leaks from connectors are commonly caused from gasket failure and improperly torqued bolts on flanges.

- Leaks from sampling connections usually occur at the outlet of the sampling valve when the sampling line is purged to obtain the sample.
- Leaks from compressors most often occur from the seals.
- Leaks from pressure relief valves can occur if the valve is not seated properly, operating too close to the set point, or if the seal is worn out or damaged.
- Leaks from rupture disks can occur around the disk gasket if not properly installed.
- Leaks from open-end lines occur at the point of the line open to the atmosphere and are usually controlled by using caps, plugs, and flanges. Leaks can also be caused by the incorrect implementation of the block and bleed procedure.

Valves and connectors account for more than 90% of emissions from leaking equipment with valves being the most significant source. Newer information suggests that open-ended lines and sampling connections may account for as much as 5-10% of total VOC emissions from equipment leaks.

LDAR programs consist of five basic elements:

a) Identifying Components
b) Leak Definition
c) Monitoring Components
d) Repairing Components
e) Record keeping

Identifying Components

- Assign a unique identification (ID) number to each regulated component.
- Record each regulated component and its unique ID number in a log.
- Physically locate each regulated component in the facility, verify its location on the piping and instrumentation diagrams (P&IDs) or process flow diagrams, and update the log if necessary
- Identify each regulated component on a site plot plan or on a continuously updated equipment log.
- Promptly note in the equipment log when new and replacement pieces of equipment are added and equipment is taken out of service.

Leak Definition

- A leak is detected whenever the measured concentration exceeds the threshold standard (i.e., leak definition)
- Leak definitions vary by component type, service (e.g.light liquid, heavy liquid, gas/vapor), and monitoring interval.
- A leak definition of 10.000 ppm is usual Also a 500-ppm or 1.000-ppm leak definition may be used.
- A leak can also be defined based on visual inspections and observations (such as fluids dripping, spraying, misting or clouding from or around components), sound (such as hissing), and smell.

Note: The LDAR requirements could specify weekly visual inspections of pumps, agitators, and compressors for indications of liquids leaking from the seals.

Monitoring Components:

- The usual method is a procedure used to detect VOC leaks from process equipment using a portable detecting instrument.
- Monitoring intervals vary but are typically weekly, monthly, quarterly, and yearly. For connectors, the monitoring interval can be every 2, 4, or 8 years. The monitoring interval depends on the component type and periodic leak rate for the component type.

Repairing Components:

- Repair leaking components as soon as practicable, but not later than an especified number of calendar days (usually 5 days for a first attempt at repair and 15 days for final attempt at repair) after the leak is detected.
- If the repair of any component is technically not feasible without a process unit shutdown, the component may be placed on the Delay of Repair list, the ID number is recorded, and an explanation of why the component cannot be repaired immediately is provided. An estimated date for repairing the component must be included in the facility records.
- The component is considered to be repaired only after it has been monitored and shown not to be leaking above the applicable leak definition.

Record keeping:

For each regulated process:

- Maintain a list of all ID numbers for all equipment subject to an equipment leak regulation.
- For valves designated as "unsafe to monitor," maintain a list of ID numbers and an explanation/review of conditions for its classification as "unsafe".
- Keep detailed schematics, equipment design specifications (including dates and descriptions of any changes), and piping and instrumentation diagrams.
- Keep the results of performance testing and leak detection monitoring, including leak monitoring results the leak frequency, and non-periodic event monitoring.

For leaking equipment:

- Attach ID tags to the equipment.
- Maintain records of the equipment ID number, the instrument and operator ID numbers, and the date the leak was detected.
- Maintain a list of the dates of each repair attempt and an explanation of the attempted repair method.
- Note the dates of successful repairs.
- Include the results of monitoring tests to determine if the repair was successful.

The scope of a LDAR programme is, typically, from 20.000 to 40.000 monitoring points. (i.e. Puertollano-Spain refinery has implemented its LDAR over 25.000 points) (the cost is approximately 100.000 € per year)

The standards used in this methodology are the EN 15446[4] and EPA21[5]

Periodical monitoring programme based in EN 13725 Standard ("Determination of odour concentration by dynamic olfactometry")

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[4] **EN 15446:2008 'Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks'**

[5] **EPA METHOD 21 "Determination of volatile organic compound leaks"**

The most important definitions and aspects of that European Standard are:

European odour unit per m^3 *(*$ou_E.m^{-3}$*)*

Amount of odorant(s) that, when evaporated into 1 cubic metre of neutral gas at standard conditions, elicits a physiological response from a panel (detection threshold) equivalent to that elicited by one European Reference Odour Mass evaporated in one cubic metre of neutral gas at standard conditions.

European Reference Odour Mass (EROM)

Accepted reference value for the European Odour unit, equal to a defined mass of a certified reference material. One EROM is equivalent to 123 mg n-butanol (CAS-nr. 71-36-3). Evaporated in 1 cubic meter of neutral gas this produces a concentration of 0,040 µmole/mol.

Odour concentration

The concentration of an odorant mixture is conventionally defined as the dilution factor to be applied to an effluent so that it is no longer perceived as an odour by 50% of people in a sample population.
Odour concentration is expressed in odour units per cubic meter.

Odour intensity

Odour intensity is the intensity of olfactory sensation. It is related to the concentration of odorant mixture. The following equation, called «Stevens' Law» or «Odour power law» defines the relationship between odour intensity and the concentration of the odorous mixture :

- $I = k.(C-Co)^n$ or $\log I = \log k + n \log(C-Co)$
- I : perceived intensity
- C : concentration of odorant mixture in the inhaled air (ppm)
- Co : concentration at the perception threshold of the odorant mixture (ppm)
- n : coefficient of odour increase, usually between 0.2 and 0.8
- k : constant for each mixture

The scope of the periodical VOCs monitoring programme can be as follows:

- Select a representative number of points in the perimeter of the refinery (between 5 and 10).
- The sampling points will be removed, at least, one meter of buildings or other major obstacles to prevent the effects of local perturbations.
- The methodology must be based in the use of diffusive samplers. (see the section 5.1.1.5 of this Chapter: “*Active and Passive Sampling Techniques (i.e. bags, canisters, tubes, badges”)*
- Carry out measurements of concentrations of VOCs in this perimeter, through sampling of 24 hours, to be held weekly
- For the measurement of VOCs the analysis and sampling methodology to be used is established in the norm EN-13528-2[6] and en-13528-3[7] standards, and for BTEX in addition to the above two, to the EN-14662-5[8] standard.
- The final frequency of routine checks shall be determined in the light of the results obtained.

The scope of the odour studies:

There are databases of thresholds for the odours of various VOCs, but these databases contain information generally unverified with respect to vapour-phase concentration. They often rely upon results collected years ago and also lack information about the relationship between concentration and probability of detection both within and across individuals. So a database may contain values of concentrations that 50% of people can detect but contain no information about how much attenuation would be necessary for detection to fall to 10%, 5% and so forth. Of even of greater concern, the databases have notorious levels of error, as high as orders of magnitude.

On the other hand, the standard methodology, based on EN 13725, requires applying a dispersion model which has always several uncertainties.

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[6] **EN-13528-2 Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Specific requirements and test methods**

[7] **EN-13528-3 Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Guide to selection, use and maintenance**

[8] **EN 14662-5 Ambient air quality - Standard method for measurement of benzene concentrations - Part 5: Diffusive sampling followed by solvent desorption and gas chromatography**

An alternative could be the use of a “field olfactometer”. Its components are shown below:

It is a nasal organoleptic instrument, that directly measures and quantifies odour strength in the ambient air using the operating principle of mixing odourous ambient air with odour-free filtered air in discrete volume ratios. This discrete volume ratios are called “Dilution-to-Threshold” ratios (D/T ratios).

D/T = Volume of Carbon-Filtered Air/ Volume of Odorous Air

The instrument measures the “total volume” of mixed airflow that is traveling down on the way to the nasal mask and determines the orifice size and, therefore, the volume of odorous air that enters through the selected orifice. A large orifice allows more odorous air through to mix with odour-free filtered air. A small orifice allows less odorous air through to mix with odour-free filtered air. The volume ratio of the filtered odour-free air and odorous air is called the Dilution-to-Threshold (D/T) ratio.

The main disadvantage of this simple and efficient method is that it is not standardized. However, it is a strong qualitative method and, very importantly, much cheaper than dynamic olfactometry.

There exists an approximate relationship between European odour unit per m^3 ($ou_E.m^{-3}$) and D/T ratios, that can be used in order to correlate field measurements with odour units.

The Permit could impose the combination of the periodical VOCs monitoring programme with periodical dynamic or field olfactometry studies.

5.1.1.3 Operation conditions and measurement techniques

In the evaluation of compliance with emission limits (pollutant concentrations) the following aspects shall be taken into account:

- Periods of start-up, blowing and shut-down shall not be taken in account.
- The days in which more than three hourly values were invalid, due to malfunction or maintenance of the continuous measurement system, shall not be taken in account.

These considerations do not applicable only if mass limits are imposed to the refinery. In that case, to evaluate the total amount of pollutant emitted, these periods should be taken in account.

BLOWING OPERATIONS

It must be implemented a programme of blowing operations, that specify the units, frequency and average duration of these operations.

The following aspects must be taken into consideration for the implementation of the programme:

- Update the number of blowings, to the conditions of the ovens.
- Blow preferably overnight, to reduce the visual impact.
- For stacks with opacimeter:
    - in stacks associated to more than one oven, sequencing the blowing.
    - programming start and end time of blowing, at the same stack, in the same civil hour in order to avoid the delay in more than one hour average by the blowing.

In addition, indicate in the book of registries not only the blowings, but others events such as repairs of blowers, to help in the validation of the emission data.

The blowing programme can be reported using the next format:

STACK (number permit)	STACK DESCRIPTION	ESTIMATED DURATION	HOURS	EQUIPMENT	ANALYZER
(i.e.) 1	Vacuum -1	45 min.	02:05-02:50	Ovens 12 y 13	Opacimeter
…					
…					
…					

5.1.1.4 Calculations related to start-up and shutdown periods

In July 2011 the draft final report named "Support for developing the definition of start-up and shut down periods for Large Combustion Plants (LCPs) under the Industrial Emissions Directive (IED)" was published. The report is based on the work carried out for the study "Analysis and summary of the Member States' emission inventories 2007-2009 and related information under the LCP Directive (2001/80/EC) and support for developing of start-up and shut-down periods for large combustion plants under the IED".

Recently, the Commission has adopted the DECISION of 7 May 2012 concerning the determination of start-up and shut-down periods for the purposes of Directive 2010/75/EU; which has been published in the Official Journal of the European Union of 9 May 2012 (available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:123:0044:0047:EN:PDF)

Decision (Double click)

It is important to remark that this Decision lays down rules concerning the determination of the start-up and shut-down periods referred to in point (27) of Article 3 and in point 1 of Part 4 of Annex V to Directive 2010/75/EU and, therefore, they will apply to LCPs when those sections of Directive 2010/75/EU are transposed into national legislation: For refineries, they are applicable partially, for some units and conditions.

The most important aspects of this Decision are:

- For heat-generating combustion plants, the start-up period shall be considered to end when the plant reaches the minimum start-up load for stable generation and when heat can be safely and reliably delivered to a distributing network, to a heat accumulator or used directly on a local industrial site.

- The shut-down period shall be considered to begin after reaching the minimum shut-down load for stable generation and when heat can no longer be safely and reliably delivered to a network or used directly on a local industrial site.

- The load thresholds to be used for determining the end of the start-up period and the beginning of the shut-down period for heat generating combustion plants and to be included in the plant's permit shall be a fixed percentage of the rated thermal output of the combustion plant.

- Periods in which heat-generating plants are heating up an accumulator or reservoir without exporting heat shall be considered as operating hours and not as start-up or shut-down periods.

5.1.1.5 Monitoring of emissions.

The recently adopted Standard TS-EN 14181 describes the quality assurance procedures needed to ensure that Automated Measurement Systems (CEMs), installed to measure air emissions at stack are able to meet the requirements.

This rule establishes three levels of quality assurance:

- QAL1 to demonstrate the suitability of equipment for the measurement target as set out in EN-ISO 14956.
- QAL2, which also verifies the correct location and implementation of CEMs, performs a functional test and a comparison with standard reference methods for calibration function.
- QAL3 is a procedure used to check drift and precision in order to demonstrate that the CEMs is under control.

It also annually provides that a trial should be performed, the Annual Validity Test (AVT), to assess the proper functioning and validity of the calibration function and variability test obtained during the QAL2.

Laboratories conducting the QAL2 and AVT should have a quality assurance system certified under the EN ISO / IEC 17025:2005

5.1.2 Air quality

5.1.2.1 Air quality control

The ambient air quality monitoring network involves measurement of a number of air pollutants at a number of locations in the refinery's area of influence, as to meet objectives of the monitoring. Any air quality monitoring network thus involves selection of pollutants, selection of positions, frequency, duration of sampling, sampling techniques, infrastructures , man power and operation and maintenance costs. The network design also depends upon the type of pollutants emitted: Particulate Matter (PM10 and PM2,5), Sulphur dioxide(SO_2), Oxides of Nitrogen (NO_x), Carbon Monoxide (CO), Ozone (O_3) etc.

Meteorology plays a significant role in the study of air pollution and it is necessary to measure meteorological parameters. The essential meteorological parameters that should be measured are wind speed and direction, ambient air temperature, relative humidity, rainfall, atmospheric pressure and mixing height.

The design of the air quality monitoring network basically involves, therefore, determining the number of stations and their location, and monitoring methods, with a view to the objectives, costs and available resources. The typical approach to design an appropriate network design involves placing monitoring stations or sampling points at carefully selected representative locations, chosen on the basis of required data and known emission/dispersion patterns of the pollutants under study. This scientific approach will produce a cost effective air quality monitoring program. Sites must be carefully selected if measured data are to be useful. Moreover, modeling and other objective assessment techniques may need to be used to "fill in the gaps" in any such monitoring strategy.

The main objectives for the development of an air quality measurement and surveillance program might be related to:

- Population exposure and health impact assessment
- Determining compliance with national and international standards.

- Setting priorities for management action over the emissions in the refinery.
- Validating management tools such as dispersion models.
- Quantifying trends to identify future problems as in refinery emissions or air quality.

Types of Monitoring Technology (multiparameter)

There are two main types of monitoring technology: remote sensing (detection over a path) and air sampling collection devices (detection at a point). Remote sensing can be broken down into two categories: plume imaging and optical. There are a number of optical methods available in the market: Open path Fourier Transform Infrared (OP-FTIR), Light Detection and Ranging (LIDAR), Tunable Diode Lasers (TDLs), and Ultraviolet Differential Optical Absorption Spectrometry (UV-DOAS). Optical technologies measure the concentrations of chemicals or particulates across an open path of air. It is done by emitting a concentrated beam of electromagnetic energy into the air and measuring its interactions with the air’s components. A gas can be identified because the light it absorbs has a characteristic pattern at a specific wavelength. These patterns and wavelengths are like “fingerprints” for the gas and allow it to be identified. The strength of the fingerprint is proportional to the concentration of the gas. The most practical use of these instruments is to provide an average value for the compounds they are sensitive to over a set distance. However, they are expensive and their calibrations are, in general, non standardized.

Air sampling collection devices, such as cartridges, badges, canisters collect atmospheric conditions at a single point and usually have the device sent to a laboratory for analysis.

Active and Passive Sampling Techniques (i.e. bags, canisters, tubes, badges)

A passive sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process, such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler. This type of passive sampler should not be confused with the annular or aerosol denuders, which not only rely on diffusion to collect the gas or vapours, but also upon the air in question being simultaneously pumped through the annular inlet into the sampler (active sampler). The theoretical basis for passive sampling is in derivations of Fick’s first law of diffusion, which result in expressions relating the mass uptake by the sampler to the concentration gradient, the time of exposure, and the sampler area exposed to the pollutant atmosphere.

Active sampling which entails a pump pulling air into the sampler are done via various media. Canisters, bags, and cartridges are all types of data collection devices for active sampling. For passive sampling, badges and cartridges are the most common collection devices.

Sample bags are a convenient and accurate way of collecting gas samples in air. The most common bag sampling device is the Tedlar bag. Tedlar resists gas permeation, both into and out of the bag, which assures sample integrity. Tedlar is rated for continuous use from -70° to 100°C and is inert to a varied range of chemicals. Once the bag is filled with an air sample, it must be shipped to a laboratory for analysis.

Canisters are another method of collecting gas samples. Canisters are specifically designed and treated to regulate the collection, storage, and analysis of VOCs. Canisters are spherical or cylindrical in shape and made of stainless steel. Like sample bags, canisters must be sent to a laboratory for analysis once filled. After the sample is analyzed, canisters can be cleaned, certified that they are clean, and pre-evacuated by a qualified laboratory so they can be sent back into the field for additional sampling. Multiple compounds (50+) can be analyzed from a single canister sample.

Another media in the active sampling arena is sorbent tubes/cartridges. A sample is collected by opening the tube/cartridge, connecting it to an air pump, and pulling air through the tube. The airborne chemicals are trapped onto the surface of the sorbent and then the tube/cartridge is sealed and sent to the laboratory for analysis.

Passive or diffusive samplers are a simple, reliable, and economical method for air sampling. They are usually small and lightweight and come in the form of clip-on badges, tubes, and patches. Due to their design, passive samplers are subject to factors such as face velocity and reverse diffusion not associated with the active sampling. These samplers also have a sorbent material inside and once used, must be sent to a laboratory for analysis.

Sampling bags

Canister sampling equipment

Tube sampling equipment Badge-type samplers

Air Monitoring Stations

AIR QUALITY MONITORING NETWORK DESIGN

A consideration in the basic approach to the network design is the scale of the air pollution problem:

− To control the refinery impact, it must consider that the air pollution is of predominantly local origin.

The network is then concentrated on the main pollutants (e.g. NO_2, SO_2, PM10, CO, benzene).

MONITORING OBJECTIVES

The air quality monitoring programme design will depend upon the monitoring specific objectives specified for the air quality management in the selected area of interest: the influence area of the refinery.

The initial purpose must be the design of the Air Quality Network in order to outline an air quality assessment that provides ground level air quality monitoring data in the neighbourhoods surrounding the Refinery. In this initial study the neighbourhoods of particular interest must be identified.

The output of the initial study will influence the design of the network and optimise the resources used for monitoring. It will also ensure that the network is specially designed to optimise the information on the problems at hand.

There might be different objectives for the development of the environmental monitoring and surveillance system. Normally, the system will have to provide on-line data and information transfer with a direct /automatic/ on-line quality control of the collected data. Several monitors, sensors and data collection systems may be applied to make on-line data transfer and control possible. Besides, the data must be transferred to the relevant Competent Authorities' system.

The main objectives stated for the development of an air quality measurement and surveillance programme might be to:

- facilitate the background concentrations measurements,
- monitor current levels as a baseline for assessment,
- check the air quality relative to standards or limit values,
- observe trends (related to emissions),
- develop abatement strategies in the refinery emissions,
- develop warning systems for the prevention of undesired air pollution episodes,
- facilitate the source apportionment and identification,
- develop/validate management tools (such as dispersion models),

The relationships between the data collected and the information to be derived from them must be taken into account when a monitoring programme is planned, executed and reported. This emphasizes the need for users and potential users of the data to be involved in planning surveys, not only to ensure that the surveys are appropriate to their needs but also to justify committing the resources.

SCREENING STUDIES AND OPERATIONAL SEQUENCE

Before a final programme design is presented it is also important to undertake a preliminary field investigation, often referred to as a screening study.

This may consist of some simple inexpensive measurements (e.g. using passive samplers, whose characteristics have been explained above) and/or simple dispersion models. The data will give some information on the expected air pollution levels, high impacted areas by the refinery emissions and the general background air pollution in the area.

The number of monitoring stations and the indicators to be measured at each station in the final permanent network may then be decided upon as based on the results of the screening study as well as on the knowledge of the sources and prevailing winds.

Once the objective of air sampling is well-defined and some preliminary results of the screening study are available, a certain operational sequence has to be followed. The best possible definition of the air pollution problem, together with the analysis of the personnel, budget and equipment available, represent the basis for the decision on the following questions:

- How many sampling stations are needed?
- Where should the stations be located?
- What kind of equipment should be used?
- How many samples are needed and during what period?
- What should the sampling (averaging) time and frequency be?
- What additional background information is needed?
    - meteorology;
    - topography;
    - population density;
    - emission sources and emission rates;
    - effects and impacts.
- What is the best way to obtain the data (configuration of sensors and stations)?
- How will the data be accessible, communicated, processed and used?

Site selection

The quality monitoring programme will normally provide the information to support and facilitate the assessments of the air quality in the influence area of the refinery.

This normally means that for designing a monitoring programme in a refinery area, several monitoring stations are needed for characterising the air quality in the total area.

When considering the location of individual samplers, it is essential that the data collected are representative for the location and type of area without the undue influence from the immediate surroundings.

In this context, it will be necessary, additionally, to take in account the following two Annexes of the DIRECTIVE 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe:

Annex V: Criteria for determining minimum numbers of sampling points for fixed measurement of concentrations of sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter (PM10, PM2,5), lead, benzene and carbon monoxide in ambient air

Annex VIII: Criteria for classifying and locating sampling points for assessments of ozone concentrations

On the other hand, the Criteria of BY-LAW 26.898 on ambient air quality assessment and management must be observed.

When measuring air quality or analysing the results from measurements it is important to keep in mind that the data you are looking at are a sum of impacts or contributions originating from different sources on different scales.

In any measurement point in the refinery area the total ambient concentration is a sum of:

- impact from refinery
- emissions from other industries
- natural background concentration
- local impact from traffic and other area sources like open air burning (waste and cooking)

To obtain the information about the importance of these different contributions it is therefore necessary to locate monitoring stations so that they are representative, mainly, of the impact from refinery.

The most commonly selected air quality indicators for air pollution in refinery areas are:

- nitrogen dioxide (NO_2),
- sulphur dioxide (SO_2),
- carbon monoxide (CO),
- particles with aerodynamic diameter less than 10 µm (and 2,5 µm), PM10 (and PM2,5)
- ozone (O_3).
- BTEX.

Other elements in the design

It is very interesting to install, additionally, SH_2 analyzers in order to guarantee the safety of the population. The possibility of accidental shutdowns of flares could cause episodes of high concentration of this hazardous pollutant.

In the design of the air quality monitoring programme we will also have to include the measurements of meteorology. Weather stations should be located in order to assess the general wind flow over the area of influence of the refinery.

Data retrieval and storage

For every site there is a need for a data acquisition system (DAS) to receive the measurement values collected by one or several gas or dust analysers, meteorological sensors or other parameters.

These parameters must be stored, every minute, every 5 min, 15 min, 30 min or every hour locally and then transmitted to a central computer. The local storage time must be several days or up to some months in case of problems with the transmission lines or the central computer. (Data may also be transferred to the central database through a wireless service)

The data retrieval from monitoring stations, which are equipped with data transmission systems, may be performed using a variety of different ways. These may be:

- The Computer centre data base system asks for data automatically once a day.
- The Computer centre operator initiates downloading (manually) which requires that the transmission is functioning.
- Data are automatically retrieved from the station every hour or every five minutes into the central database.
- Data must be sent to the corresponding Government Computer Centre with the periodicity fixed by the authorities: once a day
    - Once a day (normally at 6:00)
    - Continuously during pollution episodes.

5.1.2.2 Compliance assurance of current and future air quality standards

Before the air quality data can be used to assess the situation in the area, it is important to assure that the data collected are real concentration values.

For each pollutant which is measured as the input to the air quality assessment and evaluation, the following main questions may be asked:

- Have the suitable quality assurance procedures been set up for all stages and activities?
- Is technical advice available?
- Is monitoring being carried out at suitable locations?
- Have suitable arrangements for data handling and storage been made and implemented?

The documentation to support the credibility of data collection and the initial data quality assurance are the responsibility of the data provider. This includes the process of data collection, application of calibration factors, initial Quality Assurance procedures (QA/QC), data analysis, data “flagging”, rollups (averaging) and reporting.

A combination of data record notes, data quality flags and process documentation are all part of this first phase of processing. During the data collection phase, one role of the data provider is to assist in maintaining the process credibility and validity of the data. Good data quality is essential for adequate reporting of the air quality.

The air quality standards to be respected will be the ones included in the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe and the ones in the By-Law 26.898 on ambient air quality. The requirements stated in future regulations must be, of course, respected as well by the refinery when they come into force.

In the case of pollution episodes, registered by the Air Quality Monitoring Network, in the course of which the alert or information thresholds are exceeded (or even expected to be exceeded -by the dispersion model-), the refinery operator will adopt corrective measures, even though the emission limits specified in the permit are respected.

This is a new approach to the control of pollution that consists in implementing protocols during contamination episodes that allow decreasing the total emissions, even when the refinery is emitting under its limits.

The following measures could be, in those cases, adopted:

- Restriction of maintenance and production operations that involve diffuse emission of some kind of hydrocarbons into the atmosphere.
- Postponement of the scheduled start-up operations.
- Use of lightweight alternative fuels and/or lower in sulphur concentrations.
- Reducing the feeding to certain units.
- If some of the sulphur plants shut-down, to avoid acid gas flares downloads:
    - Distribution of the total load among the available sulphur plants until the closure of the automatic valve.
    - Modulating the feeding of that acid gas to the following production units: FCC, Coker, HDS or distillation units

5.2 Waste water discharges (emissions)

The composition of refinery effluent discharges will vary depending on a number of factors including crude oil feedstock and the extent of the hydrocarbon processing. However a similar range of process operations are involved and this leads to the production of effluents that contain similar contaminants albeit at differing concentrations.

In order to manage refinery effluents effectively, it is important to identify the sources of waste water that contribute to the final effluent. Refineries use significant volumes of water for heating (steam) and as a coolant. The water (with the exception of “closed loop” refineries) is ultimately discharged in refinery effluents. Refinery effluents can also include ballast water (which comes from product tankers arriving at the refinery), water derived from the crude oil itself and from rainwater run-off.

The water that contributes to a refinery effluent can become contaminated with hydrocarbons to varying degrees. For example, cooling water should not, under normal circumstances, be contaminated with hydrocarbons but it can be if there is a failure in heat exchanger tubes. At the other end of the scale process water (originating from a number of sources including the drainage of water from crude oil and product tanks, from steam used in the distillation and conversion units, wet chemical treatment or from water washing of crude and oil products) which has been in intimate contact with hydrocarbons, can contain significant levels of dissolved and free hydrocarbons.

The main sources of hydrocarbon-contaminated water at a refinery are likely to include some or all of the following:

- Desalter units.
- Distillation units.
- Hydro-treatment units.
- Sour water strippers.
- Visbreakers (thermal cracker).
- Catalytic cracking units.
- Hydrocracking units.

- Lube oils.
- Spent caustic.

Refinery wastewaters will contain various hydrocarbon constituents (aliphatic and aromatic), phenols, sulphides and mercaptans, ammonia and amines, heavy metals and various salts that originate from these process-related sources.

In addition to cooling and process water, natural rain water can also be contaminated when it falls on hydrocarbon contaminated surfaces. Owing to the potential for spills and leaks during maintenance and operations, rain water run-off from process areas is likely to be the most heavily contaminated. Treatment of this water can be difficult owing to the volumes and spikes that can occur.

Ballast water from crude oil transport by tanker will be contaminated with hydrocarbons and will require some form of treatment before it is finally discharged to the environment.

Different waste water treatment systems can be used singly or in combination to remove oil and other contaminants from refinery waste water prior to discharge.

The systems operated by refineries can be divided into the following categories:

- Gravity separation, e.g. API separators, plate interceptors, tank separation
- Advanced treatment, e.g. flocculation, gas flotation, sedimentation, filtration,
- Biological treatment, e.g. biofilters, activated sludge, aerated ponds, etc.
- Biological treatment followed by additional polishing treatment (GABP)
- Physical treatment followed by biological treatment in shared offsite facilities.
- Effluents sent to external waste-water treatment plant

5.2.1 Selection of parameters and pollutants and reporting

In this subsection the monitoring effluent is considered under the light of data from a European study, carried out in 2005, which allows a comparison with the probable current situation in Turkish refineries.

5.2.1.1 Pollutants which have to be controlled with ELVs[9]

It is important to emphasize that the sampling (location, methods, volumes and frequency) and analysis (pre-treatment, sample preparation, quantification method and limits of detection) protocols that are used to obtain data on effluent quality are, in most cases, different. This certainly can contribute to the wide variation in the data from effluent analysis.

OIL DISCHARGED WITH AQUEOUS EFFLUENTS. TOTAL HYDROCARBON CONTENT (THC)

The most frequently used measure of refinery effluent quality is hydrocarbon content (oil in water). There is a wide variety of analytical methods that are being used to quantify this parameter.

Methods for the determination of the oil content of aqueous effluents based on infrared (IR) spectrophotometry are largely used by most refineries. However, although the majority currently still use IR techniques, there are differences between refineries in the solvents and wavelengths used, and in the number of wavelengths measured. The oil extraction solvents have changed over the years initially because of health concerns over carbon tetrachloride and, more recently, environmental concerns regarding the Freon-CFC that replaced it. The diversity of methods used and the differences in their limits of detection and quantification have a significant influence on the comparability of data for the different refineries.

Given the low concentrations of oil now discharged from most refineries, it is possible that oil content might cease to be used as a parameter for control, which may not be advisable in Turkey. Substitute effluent control parameters could be chemical oxygen demand (COD) or total organic carbon (TOC) that provides a measure of the sum of all the organic compounds

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[9] **For Standard Analysis methods see the Annexes of Monitoring BREF and the more recent Appendix 3: List of internationally approved measuring methods for air and water pollutants of the Document "Guidance for the implementation of the European PRTR"**

that are present. However, even these can be measured using a variety of methods so that complete comparability of data may still not be possible without the adoption of a standard approach.

In Europe, during the years between 1969 and 2000, there was a continuous reduction in the amount of total oil discharged (TOD) with refinery aqueous effluents from about 44000 tonnes from 73 refineries in 1969 to 750 tonnes from 84 refineries in 2000. The ratio of oil discharged relative to the refining capacity reduced continuously from 1969 to 2008.

The methods used are still largely determined by the requirements of the authorities that monitor and regulate refinery discharges at the national and local level.

The adoption of standardised methods must be considered to be a very desirable objective. In this sense, the requirements of the Water Framework Directive[10] and the QA/QC Directive 2009/90/EC[11] must be a positive stimulus for achieving this objective.

The different methods used to determine THC include gravimetric methods, infra-red(IR) spectrometry or gas chromatography (GC). The Limit of Detection (LOD) values for the methods is in the range 0.0005 to 2 mg/l.

The use of different methods introduces systematic differences in the total oil concentrations, the inclusion or removal of intermediate sample clean-up or concentration steps. The use of different extraction media, such as Freon or n-hexane, are also likely to introduce variation in results obtained using almost the same approach. In addition, some analytical methods include work-up procedures that remove all polar hydrocarbons.

These differences in analytical approach and methods can result in reported values differing by up to 4 orders of magnitude, when compared to a data set that was analysed by a single method. It is therefore important that methods of measurement are associated with BAT-Associated Emission Levels ranges.

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[10] **EU (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal of the European Communities No. L327, 22.12.2000**

[11] **EU (2009) Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. Official Journal of the European Union No. L201, 01.08.2009**

In Europe, in 2005, 80% of the refineries reported annual average THC concentrations higher than 0.15 mg/l and lower than 6 mg/l. In comparison, the proposed range of the BAT-AELs (Table 4.18 in Chapter 4) is an annual average between 0.1 and 2.5 mg/l.

For most of the refineries, this value cannot be measured given the LOD values of the methods that are being used. Therefore, it is important to implement a method based on EN 9377-2[12] or compatible with it.

Although there is a wide range of concentrations for each class of treatment, lower average concentration of THC can be reached with biological treatments that are able to remove a part of soluble HC.

BIOCHEMICAL OXYGEN DEMAND (BOD)

BOD concentrations reported in Europe in 2005 were determined using methods whose Limit of Detection (LOD) values were in the range 0.5 to 15 mg/l.

BOD is generally measured over a 5-day period although some refineries reported a value determined over 7 days. The test is reliant upon the use of a microbial inocculum (activated sludge) obtained from a sewage treatment plant. Variation in the exposure history of the micro-organisms present in the inocculum to substances present in an effluent can have a significant effect on the result of the test.

80% refineries in Europe, in 2005, reported annual average BOD concentrations in the range to 35 mg/l.

Approximately 60% of the refineries reported annual average BOD loads that were lower than 11 g/t crude oil or feedstock processed (upper value of the current BAT range) and approximately 98% reported loads that were above 0.5 g/t (lower value of the BAT range).

The recommended method must be based in EN 1899-1[13] or APHA 5210 Standards.

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[12] **EN 9377-2 Determination of hydrocarbon oil index -- Part 2: Method using solvent extraction and gas chromatography**

[13] **EN 1899-1 Water quality. Determination of biochemical oxygen demand after n days (BODn).**

CHEMICAL OXYGEN DEMAND (COD)

Both BOD and COD are indicators of wastewater quality indicative of the impact it might have on the receiving environment. The COD test directly measures the amount of organic compounds in water. However, COD is less specific, as it measures all oxidisable organic and inorganic compounds rather than just levels of biodegradable organic matter.

COD concentrations can be determined using different methods whose Limit of Detection (LOD) values are in the range between 0.01 to 100 mg/l.

80% of the refineries in Europe in 2005 reported annual average COD concentration between 25 mg/l and 150 mg/l. In comparison, the current proposed lower and upper values of the BAT range, which are monthly averages and not annual average values, are 30 and 125 mg/l.

Approximately 80% of the refineries reported annual average COD loads that were lower than 70 g/t crude oil or feedstock processed (upper value of the current BAT range) and approximately 98% reported loads that were above 3 g/t (lower value of the current BAT range).

The recommended method must be based in ASTM D1252-06[14] or ISO 15705[15] Standards.

TOTAL NITROGEN (TN)

TN is defined as the sum of Kjeldahl (which is organic nitrogen + ammonia), nitrite and nitrate nitrogen.

Ammonia is also included in total nitrogen but many refineries measure the latter rather than ammonia. Although related, the two measurements are required for different reasons; ammonia can cause acute aquatic toxicity depending upon the pH whereas total nitrogen (TN) is a measure of the potential for eutrophication of the aquatic environment.

Dilution and seeding method with allylthiourea addition

[14] **ASTM D1252 - 06 Standard Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water**

[15] **ISO 15705 Water quality -- Determination of the chemical oxygen demand index (ST-COD) -- Small-scale sealed-tube method**

TN concentrations can be determined using different methods whose Limit of Detection (LOD) values are in the range between 0.02 to 2.1 mg/l.

80% of the refineries in Europe in 2005 reported annual average TN concentration between 3 mg/l and 35 mg/l. In comparison, the current lower and upper value of the BAT range, which are yearly averages values, are 1.5 and 25 mg/l; and the proposed BATAEL's range (Table 4.18 of Chapter 4) is between 1 and 25 mg/l.

Approximately 85% of the refineries reported annual average TN loads that were lower than 15 g/t crude oil or feedstock processed (upper value of the current BAT range) and approximately 99% reported loads that were above 0.5 g/t (lower value of the BAT range).

The recommended method must be based in EN ISO 7890[16] (EN 25663[17]/EN 26777[18]) Standards and, on the other hand, in EN 12260[19] and EN ISO 11905-1:1998[20]

TOTAL SUSPENDED SOLIDS (TSS)

TSS concentrations can be determined using different methods whose Limit of Detection (LOD) values are in the range between 0.1 to 10 mg/l.

80% of the refineries in Europe reported annual average TSS concentrations between 5 mg/l and 35 mg/l. In comparison, the current lower and upper value of the BAT range, which are annual average values, are 2 and 50 mg/l; and the proposed new BAT-AEL's range (Table 4.18 of Chapter 4) is between 5 and 25 mg/l.

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[16] **ISO 7890 Water quality -- Determination of nitrate**

[17] **EN 25663 Water quality. Determination of Kjeldahl nitrogen. Method after mineralization with**

[17] **ISO 7890 Water quality -- Determination of nitrate**

[17] **EN 25663 Water quality. Determination of Kjeldahl nitrogen. Method after mineralization with selenium**

[18] **EN 26777 Water quality. Physical, chemical and biochemical methods. Determination of nitrite: molecular absorption spectrometric method**

[19] **EN 12260:2003: *Water quality – Determination of nitrogen – Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides***

[20] **EN ISO 11905-1:1998: *Water quality - Determination of nitrogen - Part 1: Method using oxidative digestion with peroxodisulfate***

85% of the refineries reported annual average TSS loads that were lower than 25 g/t crude oil or feedstock processed (upper value of the current BAT range) and approximately 99% reported loads that were above 1 g/t (lower value of the BAT range).

The recommended method must be based in EN 872:2005[21] or APHA 2540 Standards.

HEAVY METALS (Pb, Cd, Ni, Hg y V)

The heavy metals are usually determined through spectrophotometric methods. It is very frequent that the refinery had its own equipment for these determinations.

The standards recommended are the following:

- EN ISO 11885:2009 Water quality -- Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (valid for more than 30 elements)
- EN 13506: Water Quality - Determination of Mercury by Atomic Fluorescence Spectrometry.
- EN 12338: Water quality - Determination of mercury - Enrichment methods by amalgamation

PHENOLS

The majority of phenols present in refinery wastewater originate from the catalytic cracking process. Another possible source of phenolic compounds is losses of phenol used as a solvent in extraction.

The recommended standard is, in the determination of phenols (as C total):

ISO 18857-1 Water quality -- Determination of selected alkylphenols -- Part 1: Method for non-filtered samples using liquid-liquid extraction and gas chromatography with mass selective detection

BTEX

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[21] **EN 872:2005 Water quality. Determination of suspended solids. Method by filtration through glass fibre filters**

The new BREF for refineries is concerned about Benzene discharges, as one can see in the Table 4.18 in the Chapter 4.

The recommended standards in its determination are:

- ISO 11423-1: Water quality -- Determination of benzene and some derivatives -- Part 1: Head-space gas chromatographic method
- ISO 11423-2: Water quality -- Determination of benzene and some derivatives -- Part 2: Method using extraction and gas chromatography
- EN ISO 15680: Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

5.2.1.2 Others pollutants to be reported to E-PRTR

According to Article 5 of the E-PRTR Regulation, operators of refineries are obliged to report specific information if the applicable capacity threshold(s), Annex I to the E-PRTR Regulation, and release threshold(s), Columns 1a, b, and c of the table set out in Annex II to the E-PRTR Regulation, and/or the applicable capacity threshold(s) and off-site transfer threshold(s).

As a help, the Appendix 5 of the European Commission Document "Guidance for the implementation of the European PRTR", contains an indicative sector specific sub-list of pollutants. This list shows for all Annex I activities those air pollutants that are likely to be emitted and aids the identification of relevant pollutants at a given facility. According to this list, the pollutants to be reported by the refineries would be:

- Total Nitrogen
- Total Phosphorus
- Arsenic and compounds (as As)
- Cadmium and compounds (as Cd)
- Chromium and compounds(as Cr)
- Copper and compounds (as Cu)
- Mercury and compounds (as Hg)
- Nickel and compounds (as Ni)
- Lead and compounds (as Pb)
- Zinc and compounds (as Zn)
- Dichloromethane (DCM)
- Halogenated organic compounds (as AOX)
- PCDD + PCDF (dioxins + furans) (as Teq)
- Pentachlorobenzene
- Benzene
- Ethyl benzene
- Phenols (as total C)
- Polycyclic aromatic hydrocarbons (PAHs)
- Toluene

- Total organic carbon (TOC) (as total C or COD/3)
- Xylenes
- Chlorides (as total Cl)
- Cyanides (as total CN)
- Fluorides (as total F)
- Fluoranthene
- Benzo(g,h,i)perylene

The final amounts of the pollutants are obtained multiplying each average concentration by the year total flow discharged.

The different analytical techniques are, essentially, those are included in the Appendix 3: List of internationally approved measuring methods for air and water pollutants of the Document “Guidance for the implementation of the European PRTR” (mentioned above), which are reproduced below for the pollutants that the refineries have to report to E-PRTR.

Total nitrogen	EN 12260 -- EN ISO 11905-1
Total phosphorus	EN ISO 15681-1 -- EN ISO 15681-2 EN ISO 11885 -- EN ISO 6878
Arsenic and compounds (as As)	EN ISO 11969 -- EN 26595
Cadmium and compounds (as Cd)	EN ISO 5961 -- EN ISO 11885
Chromium and compounds (as Cr)	EN 1233 -- EN ISO 11885
Copper and compounds (as Cu)	EN ISO 11885
Mercury and compounds (as Hg)	EN 14837--EN 12338--EN 13506 According to the level of concentration
Nickel and compounds (as Ni)	EN ISO 11885
Lead and compounds (as Pb)	EN ISO 11885
Zinc and compounds (as Zn)	EN ISO 11885
Dichloromethane (DCM)	EN ISO 10301 -- EN ISO 15680
Halogenated organic compounds (as AOX)	EN ISO 9562

PCDD +PCDF (dioxins +furans) (as Teq)	ISO 18073
Pentachlorobenzene	EN ISO 6468
Benzene	ISO 11423-1-- ISO 11423-2 EN ISO 15680
Ethyl benzene	EN ISO 15680
Phenols (as total C)	ISO 18857-1
Polycyclic aromatic hydrocarbons (PAHs)	EN ISO 17993 -- ISO 7981-1 ISO 7981-2
Toluene	EN ISO 15680
Total organic carbon (TOC) (as total C or COD/3)	EN 1484
Xylenes	EN ISO 15680
Chlorides (as total Cl)	EN ISO 10304-1-- EN ISO 10304-2 EN ISO 10304-4-- EN ISO 15682
Cyanides (as total CN)	EN ISO 14403
Benzo(g,h,i)perylene	EN ISO 17993
Fluorides (as total F)	EN ISO 10304-1

5.2.2 Operation conditions and measurement techniques

The most important and relevant method to evaluate the operation conditions in the refineries are the Toxicity Studies, that allow a deep knowledge and assessment of their impacts over the receiving waters.

METHODS FOR ASSESSING TOXICITY, PERSISTENCE AND BIOACCUMULATION OF EFFLUENTS

There are essentially three reasons to conduct toxicity studies on effluents:

- To comply with regulations and identify the toxicity of the effluent;
- To investigate whether the effluent is impacting the environment and to carry out studies that are designed to confirm this and explore the type/extent of the toxicity;

- To initiate an internal assessment and toxicity identification process in the event that toxicity in the effluent is observed and requires action.

The purpose and objectives of conducting that kind of study must be clearly assessed and identified before it is undertaken. Acute (short-term) or chronic (long-term) toxicity may be tested for and, given the variability of effluents, the tests need to be designed, conducted and interpreted with great care. It is essential that the guidance available on sampling, handling of samples and conduct of the test is followed and that each step and manipulation is accurately documented. A key part of conducting a toxicity testing programme is the 'learning by doing' approach; the test programme may need to be refined and tailored as it progresses, depending on individual site conditions and objectives.

The advantages of chemical and biological monitoring of receiving waters are that there is greater realism of exposure conditions and a more diverse biological community can be examined. However, field monitoring has its own limitations and complications. For example, it may be problematic, if not impossible to use as a risk-based management tool for receiving waters polluted by multiple inputs over a relatively large geographical scale. This is because of the difficulty of attributing toxicity to a particular source or it may be hard to discern subtle effects because of 'natural' biological variability. In addition, impacts from non-polluting sources such as the physical quality of the habitat will have a major impact on the biological status. It is therefore appropriate that Water Emission Analysis (WEA) and receiving water monitoring be viewed as complementary techniques that can be used singly or in combination depending upon the particular circumstances.

Common applications for receiving water monitoring studies are:

- To determine water quality status;
- To evaluate major episodic discharges to receiving streams: i.e. strong rains.
- To evaluate receiving water exposure concentrations that are equal or exceed laboratory-derived toxicity levels;
- To interpret whether laboratory responses indicate ecosystem impairment;
- To increase confidence in an assessment (to improve it) when the receiving water contains particularly sensitive or endangered species;
- To understand the effects of effluents that are known to contain components that are poorly evaluated

Field monitoring involves comparison of samples from target sites that are receiving effluent with samples taken from the same location at another time (e.g. before discharge), or with samples from a reference site not impacted by the discharge (e.g. upstream of the discharge) or with samples from a site that is presumed pristine.

Samples may be compared in terms of analyte concentrations to validate persistence and bioaccumulation modelling, either in terms of toxicity, or in terms of structure of the biological community to validate toxicity tests. Biological community structure may either be compared to reference sites or to pollution indices derived from the species typically observed in sites with similar hydrology, topography, geomorphology and a history of exposure to different types of pollution. Monitoring usually involves repeated or regular sampling of specific sites, however, for the purpose of a whole effluent assessment, limited sampling (a survey) may be sufficient. Measurement of generic water quality parameters will almost always be part of the monitoring programme.

The following techniques are available for use in fate and exposure monitoring studies:

1. Specific analyte measurement (e.g. SPMD, caged mussels, large volume *in situ* sampling);
2. Other water and sediment quality parameters;
3. Tissue analysis using for example mussels and/or fish;
4. Solid phase extraction (SPE) techniques;
5. Biomarkers;
6. Dilution studies using dyes and other markers.

1.- Specific analyte measurements

Measurement of specific effluent constituent concentrations in receiving waters, when considered together with other parameters, including suspended solids, sediment and biota analyses, allows a more complete understanding of the final environmental fate of the constituents. The fate of other constituents may also be predicted from the results of such analyses if they share similarities (e.g. in chemical structure) with those that have been studied.

Water column

The nature of water column monitoring will, to an extent, depend upon local circumstances and experience.

The following direct and indirect methods of monitoring concentrations of effluent discharge constituents have been tested and evaluated in the water column monitoring program:

- Direct water sampling (spot sampling);
- In-situ large volume water sampling (time averaging);
- Solid phase micro-extraction (SPME) techniques;
- Deployed semi-permeable membrane devices (SPMDs);
- Deployed blue mussels;
- Plankton samples.

The SPMDs and mussels together with *in-situ* sampling of seawater were identified as being capable of measuring average levels of chemical constituents present in produced waters. Furthermore, predictions using mussels, SPMDs, and modelling were found to support and complement each other and the surveys demonstrated that all are valuable tools for estimating the fate and impact of chemical contaminants present in produced waters that are discharged to marine environments.

The methods may also be applicable to programs designed to investigate the fate and effects of constituents of refinery effluents.

2.- Other water and sediment quality parameters

Physical, chemical and biological characteristics of natural environments fluctuate within and between regions. Understanding the extent of these fluctuations is important when assessing the significance of the impacts of effluent discharges. A wide range of parameters may be relevant; pH, dissolved oxygen, temperature, salinity, density, turbidity and alkalinity for the water column; and colour, smell, organic matter content and distribution of particle size for the sediment. The relevance of each needs to be considered on a case-by-case basis.

3.- Tissue analysis in mussels/fish

Analysis of the tissues of sedentary animals, such as marine mussels, in receiving water environments has been practiced for many years in effluent monitoring programs.

Analysis of tissues from caged or wild-caught invertebrates and fish can provide an indication of exposure to effluent components. Such information may be valuable in determining the potential for bioconcentration/bioaccumulation of effluent constituents in the food chain. The information may also be combined with methods designed to assess the health and fitness of indigenous populations of organisms.

4.- Solid phase (micro) extraction techniques – SP(M)E

In some receiving waters it may be possible to use indirect methods for monitoring the concentrations, fate or behaviour of effluent constituents. SPME is one example of such a method that is based on the relationship that exists between the chemicals octanol/water partition coefficient (log Kow) of a chemical substance and its potential to bio-concentrate/bioaccumulate. Partitioning of a substance onto an SPME fibre is also related to the log Kow. Exposing SPME fibres to water samples containing effluent constituents and then desorbing the bound constituents enables their molar masses to be determined using chromatography. The molar masses can then be used to determine the hydrophobicity of the constituents as an indicator of their bioaccumulation potential and their concentrations in the environment. Hydrophobicity can also be used as an indicator of their baseline (narcotic) toxicity. SPME methods are considered to be particularly relevant to receiving water studies involving refinery effluents.

5.- Biomarkers

A biomarker is defined in the context of this report as any biochemical, physiological, or histo-pathological indicator of exposure or response to a contaminant by individual organisms. The definition includes measurements made in portions of a single organism, including contaminant receptor molecules, bio-chemicals (i.e. detoxification enzymes), blood, bile, and tissues (e.g. liver, tissue).

Biomarkers have been widely used as indicators of contaminant impacts in ecosystems. However, just because a biomarker response is observed this does not necessarily imply that an adverse effect is likely to be already present or occur in the future. Biomarkers should therefore be considered to be indicators of exposure and/or that some biochemical receptor or site of potential action has responded to the presence of the contaminant.

There has been substantial progress in developing biomarker methods to assess pollution in marine benthic systems. The increasing use of biomarkers is evident when looking at water quality monitoring which has been undertaken in some areas in Europe.

The biomarker methods that have been used include:

- EROD (Ethoxy-Resorufin-O-De-ethylase) activity in flatfish. This involves measurement of enzymatic activity in response to xenobiotic compounds, present. In this case it has provided a measure of exposure to PAHs in the absence of fish mortalities;
- DNA-adduct formation studies in fish and mussels. The complexation of DNA with PAH compounds is used as an indicator of exposure;
- Scope for Growth (SFG) in mussels (*Mytilus edulis*). Measurement of energetic resources available for growth provides an indication of the physiological fitness of an organism following exposure to toxic (or other) stressors;
- Mussel immunity studies. Involves the measurement of changes in the status of the immune system resulting from exposure to toxic (or other) stressors.

Bio-monitoring is defined as the long-term tracking of water/sediment quality to evaluate historical trends in the status of freshwater and marine habitats. Species abundance and diversity monitoring, particularly of benthic and intertidal habitats, has been one of the cornerstones of bio-monitoring programs. Species diversity monitoring of open freshwater (e.g. lakes) or pelagial habitats is less frequently performed because of the difficulty inSampling these habitats, and the unrestricted movement of organisms into and out of potential zones of influence[22].

6.- Dye studies

Dye studies have been used for many years in water column monitoring studies to determine flow characteristics and patterns in water bodies and associated dispersion and dilution profiles for effluents. Dye studies are also a key tool used in validating models for predicting such behaviour.

IMPLICATIONS

The application of whole effluent toxicity (WET) and other WEA methods to assess control and monitor oil refinery effluents is increasing in response to EU Directives and resulting regulations:

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[22] i.e.: In the refinery of Puertollano (Spain) whose effluents go to the river (it is in the interior of the country) the biomarkers used are the amounts, in different points of the river, of the different Protozoa : **Vorticellidae**, and bdelloidea: **Rotifera.**

- The refinery survey feedback indicates that WET is used in site permits and in IPPC in particular.
- The focus to achieve 'good ecological status' under the Water Framework Directive is leading to an increase in biologically relevant monitoring. This could either be to directly assess the impact of a refinery effluent discharge (i.e. WEA) or as part of wider initiatives to assess water quality and develop River Basin Management Plans.

5.3 Soil and groundwater

Refineries often cause soil and groundwater pollution, due to potential leakages of petroleum products from underground or surface tanks and pipes at several stages of the processes.

The environmental impact that hydrocarbons pollution can cause may be extreme, pointing out the need for immediate remediation actions, as well as uptake of adequate prevention measures.

The main contaminants are, typically:

- Polycyclic Aromatic Hydrocarbons (PAH) in soil
- Benzene – Toluene – Ethylbenzene – Xylenes (BTEX) in groundwater
- Total Petroleum Hydrocabons (TPH) in soil, soil gas and groundwater
- Methyl – Tertiary - Butyl – Ether (MTBE) in groundwater
- Non-Aqueous Phase Liquids (LNAPL) stratum on the surface of the existing aquifer.

The appearance, characteristics and particularities of the existing pollution may lead the necessity to develop an appropriate program, which should be capable of providing:

- a realistic and credible picture of the pollution of the area
- the possibility of timely detection of future potential leakages,
- a useful database, on which the choice of appropriate remediation activities could be based.

MONITORING PROGRAM

Conduction of a site investigation and development of an integrated monitoring and, if necessary, remediation system are essential.

A complete monitoring programme can consist of three different, but correlating, stages:

- Stage 1: Site investigation / characterization of the existing contamination;
- Stage 2: Monitoring;
- Stage 3: Remediation.

Stage 1: Site investigation / characterization of the existing contamination

The aim of this stage is to record, as detailed and as precisely as possible, the site conditions and significant parameters that are related to the geology, the hydrology and the existing pollution levels in the refinery area.

The main activities of this stage are:

- Mapping of the refinery site including:
    - The positions of the process and storage units (including closed units; because of its probable historical pollution)
    - The flow lines of groundwater.
    - The groundwater sensitivity (the groundwater sensitivity of refinery locations in Turkey will be influenced mainly by aquifer type).

- Geological and Hydro-geological studies of the area.
- Sampling and analysis of groundwater, soil and soil air, in order to identify the type of the existing pollutants.
- Sampling and analysis of water, soil and soil air, in order to determine the concentration of each pollutant.
- Sampling and analysis of floating free phase, if exists, in order to determine its composition and possibly its origin.
- Analysis and identification of the critical points in order to implement the permanent monitoring network.

The determination of the pollutants allows the definition of the leakage points, among the different treatment stages and facilities of the refinery. This way the prevention of the observed leakages becomes feasible, limiting to a great extent the magnitude of the pollutants inflow in the soil and groundwater.

The main goals must be to obtain for pollutants:

- Current distribution map in the refinery area.
- Potential distribution map of the refinery area.

Stage 2.- Monitoring

The purpose of this stage is the continuous registration of the site and more specifically the pollution characteristics.

The need for close monitoring of the refinery area is necessary to prevent conditions that may prevail due to unexpected activities: potential leakage can lead to even greater or extended pollution of the site, changing the known pollution status of the area completely. This is the main objective of the monitoring program: the continuous knowledge of the site pollution and, therefore, the “Pollution plume”.

Therefore, continuous monitoring of the site is considered to be more than essential.

The scope of monitoring must include at least:

- Piezometers.
- Periodical sampling[23] and analysis of soil, soil gas, groundwater and free phase (if exists),
- Samples from several points of the facilities.
- Scope of these samplings.
- Image representations of the variation of the contamination in connection with space and time: graphical representation.

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[23] **For Standard Analysis methods see the Annexes of the Monitoring BREF**

- Assessment of contamination and its potential changes of position (pollution plume)

Stage 3: Remediation

If high pollution levels are detected a remediation method should be chosen based on:

- The existing components of the pollutant and their concentrations.
- The prevailing hydro-geological conditions on site.

That remediation must be done, in all cases, if the thresholds of Appendix of By-Law 25831 are exceeded.

5.4 Wastes

Integrating the wastes data in the Environmental Monitoring Plan, is a good chance to incorporate the reports that the current By-Laws, in this scope, impose to refineries.

In this sense, the reports of current Turkish By-Laws:

- 24736 Regulations on control of solid wastes
- 26952 Oil waste control
- 26739 PCB-PCT waste control
- 25755 Regulation on Hazardous waste control
- 25569 Control of waste battery and accumulators

could be integrated.

The reports could have the formats that are shown, accompanied by an example, below:

HAZARDOUS WASTES

Process	Waste description	EWR Code	Production (T/month or year)	Destination
Maintenence operations	Absorbents, filter materials (including the oil filters otherwise specified) wiping cloths, protective clothing contaminated by dangerous substances	15 02 02	---- /month ----/year	Landfill
	Volatile oily fly ash and dusr from boiler	10 01 04	---- /month ----/year	

Process	Waste description	EWR Code	Production (T/month or year)	Destination
	Packages containing dangerous substances or contaminated by those	15 01 10	---- /month ----/year	Inertization
	Other solvents and solvent mixes	14 06 03	---- /month ----/year	Recovery
	Aqueous washing liquids	12 03 01		
…	…	…	…	

NON HAZARDOUS WASTES

Process	Waste description	EWR Code	Production (T/month or year)	Destination
Cleaning units, facilities, machinery and equipment.	absorbents, filter materials, wiping cloths and protective clothing other than those mentioned in 15 02 02	15 02 03	---- /month ----/year	Landfill
	Mixed municipal waste	20 03 01	---- /month ----/year	
	other fractions not otherwise specified	20 01 99	---- /month ----/year	Inertization
	metals	20 01 40	---- /month	Recovery

Process	Waste description	EWR Code	Production (T/month or year)	Destination
	paper and cardboard	20 01 01	----/year	
…	…	…	…	

5.5 Noise

There are several kinds of equipment and operations that can produce noise in refineries. The primary and major sources of noise from operations have been associated with flaring operations. More specifically, steam injection into the flares for emissions control and smoke management purposes.

The studies indicate that the larger and newer flares perform more quietly than the older flares. The percentage of steam injection is the most significant contributor to noise from the flaring operation.

A noise monitoring network can be installed to measure the noise impact of the site on the surrounding environment and population as well as allowing the site operators to monitor, in real time, the noise being emitted from the site.

The noise monitors must be installed around the site at strategic locations, typically on the boundary of the site nearest to the local population. The number and locations will depend of different factors:

- Number, height and age of flares.
- Distance from population.
- Capacity and complexity of the refinery.

The distribution of monitoring points must be, therefore, properly balanced being, at the same time, sufficiently representative, attending the above aspects.

The measurements shall fulfil the By-Law 25862, based in the Regulation of Assessment and Management of Environmental Noise (2002/49/EC), according to which the environmental noise criteria for industrial plants are the following:

Article 25 — The criteria for environmental noise levels originated from industrial plants and prevention of noise are depicted below:

a) Depending on the activity that carried out in industrial plant and the time interval, the environmental noise levels that are assessed by the methods depicted in a) section of Article 20 of this regulation and represented as L_{day} and L_{night} cannot exceed the limits depicted in Table 4. These values are applied to the places stated in Annex VII List A and B, except for the entertainment places.

Table-4: Environmental Noise Criteria for Industrial Plants

Areas	L_{day} (dBA)	L_{night} (dBA)
Industrial Areas (pure industry)	70	60
Industrial and residential areas (heavily industrial)	68	58
Industrial and residential areas (heavily residential)	65	55
Rural Areas and Residential Areas	60	50

ANNEX II.1) Computation Methods

The following methods are recommended to be used for calculating the noise indicators originated from transport and industry :

a) For industrial noise: TS ISO 9613-2: ‘Acoustics -- Abatement of sound propagation outdoors, Part 2: General method of calculation’. Suitable noise-emission data (input data) for this method can be obtained from measurements carried out in accordance with one of the following methods:

ISO 8297: Acoustics -- Determination of sound power levels of multisource industrial plants for evaluation of sound pressure levels in the environment – “Engineering Method”.

TS EN ISO 3744: Acoustics -- Determination of sound power levels of noise using sound pressure engineering method in an essentially free field over a reflecting plane,

TS EN ISO 3746: Acoustics -- Determination of sound power levels of noise sources using an enveloping measurement surface over a reflecting plane.

ANNEX II.2) MEASUREMENT METHODS

a) Measurements be done in accordance with the definitions of the indicators set out in Annex I and in accordance with the principles stated in TS 9798 (ISO 1996-2) and TS 9315 (ISO 1996-1).

5.6 Environmental Monitoring and Enforcement Plan

The scope of the environmental monitoring and enforcement plan can be:

- Programme of monitoring and control of the production process
    - Parameters to control
    - Other indicators
- Rain waters management
    - Description of channelling
    - Description of regulation and storages
    - Control procedures of the level controls
    - Maintenance operations
    - Procedures under stormy conditions.
- Control of the production and management of wastes
    - Characterization of the produced wastes
    - Procedures of storage and management.
    - Temporary storages: position and logistics.
    - Documentary control.
- Description of the control of channeled emissions
    - Description of stacks
    - Description of equipment
    - Frequency and scope of sampling, regulatory controls and parallel measurements
- Monitoring and control of diffuse and fugitive emissions of Volatile Organic Compounds (VOCs)
    - Inventory
    - LDAR Programme
    - Detection and repair of leaks
    - VOCs emission control at the perimeter of the refinery

  - Odour controls
- Water discharges monitoring and control
  - Characteristics of effluents
  - Control and analysis. (Points, equipment, procedures, frequency of controls)
- Soil and groundwater monitoring
  - Geological and hydrogeological studies
  - Control points
  - Frequency and parameters to determine
- Noise
  - Mapping
  - Control
- Quality assurance and preventive/corrective maintenance of the pollution control instrumentation
  - Emissions Tasks of quality according to standard UNE EN 14181 assurance. Measurement of fuel flow.
  - Air quality stations
  - Water discharges monitoring
  - VOCs
  - Noise
  - Operational control
- Environmental emergencies plan:
  - Performance during exceptional conditions
  - Procedures in case of emergency
  - Mechanisms of information to Turkish authorities and environmental information to transmit

5.6.1 Assessment of ELVs compliance

The planning of the assessment of ELVs compliance should be fixed after the necessary approval of the Environmental Monitoring and Enforcement Plan.

5.6.2 Samplings and inspections frequencies

This planning shall integrate the frequencies of samplings and inspections.

5.6.3 Frequency and systems to report to the Environmental Authority

Annual Report

The annual report must summarize the environmental aspects of the installation during the previous year, and can include:

- Annual summary of energy consumption and consumption of natural resources, fuel and raw materials ratios
- Evaluation report on energy efficiency
- Summary report of operating hours
- Verification of compliance with the emission limit values from CEMs data, regulatory controls and self-monitoring. Includes summary of daily maximum values and comparative statistical analysis.
- Results of the tasks of quality assurance of analyzers, according to the procedure TS EN 14181.
- Performance, availability and validity of data from sensors and analyzers.
- Comparative analysis of limit values, thresholds and objectives in the air quality network. Incidents in the maintenance and performance of analyzers.

Monthly Report

The monthly report summarizes the environmental indicators of the refinery and can include:

- Report of daily concentration of pollutants and additional parameters
- Report of hourly concentrations exceeding emission limits.
- Incidents of operation with analyzers and complementary parameters
- Bubble and mass emission of SO_2, NO_x
- Daily consumption, %S, molecular weight (of gas) of different types of fuels used in each unit.
- SRUs reports.

- Measurements of parameters in the discharge authorization.
- Operating hours.
- Summary of incidents: description of periods of operation in transitional conditions in stacks, flares and sulphur recovery plants.

A protocol for the communication with the Turkish authorities must be established with the refinery, to inform about incidents that can cause environmental impacts:

- description of the incident and corrective measures
- description of the generated environmental impacts, evaluation of the relevance of the impact and the measures to be taken in the short, medium and long term for their correction.

6 EMERGING TECHNIQUES FOR THE REFINERY SECTOR

Emerging technique is a novel technique that has not yet been applied in any industrial sector on a commercial basis. This chapter contains the techniques that may appear in the near future and that may be applicable in the different process units of the refineries.

6.1 Alkylation

As described in Section 2.12 there are four process scenarios in the alkylation of parafines: sulphuric acid process, hydrofluoric acid process, soli-acid technology and ionic liquid technology. The two first processes have not experienced significant improvements but there are promising lines of investigation in the soli-acid and ionic liquid technologies.

6.1.1 Soli-acid technology

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 is similar to that used in the case of HF and H_2SO_4 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 (H_2SO_4 process) or halogens (HF process). Overall olefin conversion is almost 100% and yield and quality of the product are similar as 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.

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, neither 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.

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.

Regarding the applicability of this technique, the retrofit of conventional HF or H_2SO_4 units with a soli-acid process is impossible. AlkyClean utilises a swing reactor system, which makes that on-stream catalyst change out of catalyst is 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.

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 (REF BREF, Section 6.2.1.3).

6.1.2 Ionic liquids

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 vapour 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 (REF BREF, Section 6.2.1.4).

6.2 Base Oil production

A recently published new technology is the application of membranes for solvent recovery in the solvent extraction/dewaxing processes. Reduction in energy consumption is achieved.

6.3 Catalytic cracking

Some emerging techniques for the improvement of the environmental performance of cat crackers have reached such a degree of implementation that they have become techniques to consider in the determination of the BATs (i.e. specific low-NO_x additives, ceramic filters and wet scrubbers).

As emerging technique there is 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 for implementation are the reduction of residue (i.e. enhanced upgrading) and higher overall refinery efficiency (e.g. the elimination of high vacuum unit operation)

6.4 Catalytic reforming

The current practice of application of continuously improved catalysts (supplied by catalyst manufacturers) is expected to continue.

6.5 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. IGCC and CFB Boiler technologies are being further developed, optimized and applied with the use of coke feedstock.

6.6 Energy system

Some promising lines of investigation for the improvement of the environmental performance of the energy systems are CO_2 abatement techniques (more information in Section 6.14 on waste gas treatments) and the heat integration techniques. The search for further energy improvements is continuing, with the current focus on attractive cogeneration opportunities and more complex heat integration.

6.7 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

6.8 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 m^3/d of methanol and 795 m^3/d of C/H_2O slurry

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 CO_2 generation is completely eliminated

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 and also smaller plot space requirement - as little as ¼ of cPSA)

6.9 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 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 challenges ahead that may probably lead to new techniques or significant improvement in the current ones.

Deep gasoline and gasoil desulphurisation 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 is a large amount of new generation catalysts that are more active and more selective. It leads to a direct impact overall process efficiency.

New process developments use less H_2 consuming technologies. Reactive adsorption at high temperature using metal oxide sorbent or alumina based adsorption is delivering promising results. Selective extraction or polar adsorption (Irvad process) are also emerging techniques to consider.

Non H_2 desulphurisation techniques

Oxidative desulphuration may be one of the most promising in this group (see Section 2.17.2) 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)

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.

6.10 Hydrocracking

Treatment of heavier feedstocks requires 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)

6.11 Isomerisation

Catalytic hydroisomerisation of long parafines to produce biofuels

This technique using the selectivity of the zeolites will improved the conversion of n-paraffins. 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 into isoparaffins having lower freezing points and still high cetane number.

Isomerization dewaxing 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. This enables fuels to flow at low temperatures. This technique is currently in operation in 8 units.

6.12 Primary distillation

Divided wall column (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-column system.

6.13 Product treatments

Biodesulphurisation of gas oil and even crude oil is still under development

Pretreatment technologies that withdraw benzene precursors from the reforming feedstock actually are facing some difficulties as, for example, 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. This technique is quite 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 H_2.

6.14 Waste gas treatments

Some developments to be mentioned are:

SO_2 removal by capture from flue-gas and conversion into liquid sulphur through regenerative process.

Biological H_2S removal.

Particulate abatement techniques by new developments including ceramic filters and a rotating particulate separator.

CO_2 abatement techniques.

Emerging techniques to enable carbon dioxide capture and storage (CCS)

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.

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 %

Technique for capturing CO_2

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 CO_2 chain.

They can be divided into three main categories:

1. Post-combustion entails separating CO_2 from the exhaust gas from the power plant using chemical cleaning. Because CO_2 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.

2. Pre-combustion: With the aid of this technology, CO_2 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 CO_2 is captured, and the new fuel is thus ‘decarbonised’ (exhaust gas contains very little CO_2). Pre-combustion requires modification of gas turbines and is considered to be a more complex technology than post-combustion

3. Oxy-fuel: 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 CO_2, and the CO_2 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 CO_2 from a power plant amount to approximately two thirds of the costs for the entire CO_2 chain, while transport and storage amount to approximately one-third.

Transport of CO_2

CO_2 must be transported from the CO_2 source to the geological structure where the CO_2 will be stored. This transport can be accomplished by pipeline or by ship. Transport is the least complicated element in the CO_2 chain, both as regards technology and the possibility of evaluating realistic costs. Anyhow, the transport of CO_2 requires substantial resources in terms of energy and costs. As CO_2 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 CO_2 to be transported. With existing technology, pipeline transport is believed to be the simplest and most cost-effective alternative.

Storage of CO_2

There is significant technical potential for storing CO_2 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 CO_2.

6.15 Waste water treatment

Emerging techniques on this issue are addressed in the CWW BREF

6.16 Other Emerging Techniques

6.16.1 Reduction of air emissions and waste water discharges, and production of biofuels through microalgae farming

The most important benefits of setting these microalgae production plants near an oil refining complex are:

- It could be used waste gas with CO_2 and other air pollutants to feed the photobioreactors. If it's the case, It could be associated nearly zero emissions of CO_2 when the biofuels are burned in the future.
- Different waste water fractions could be used either to fill the reactors or as nutrients. So less waste water is produced and less fresh water will be consumed.
- A lot of different oil refining facilities and installations could give service to the microalgae production plant (laboratory, facilities, transports…)

First of all must be explained that this is not an exclusive technique in the field of oil refining but the implementation of microalgae farms near oil refining sites could become common if the benefits of being together get optimised.

Biofuel production is turning on a very interesting alternative to fossil fuels, and the farming of microalgae is a special case because there are some advantages as compared with other biofuels.

Microalgae are unicellular organisms that make photosynthesis and present the following advantages:

- There is no influence on food markets prices. The raw materials for common biofuels used nowadays are related with food markets, but microalgae farms are not.
- There is no need to use agriculture suitable zones for microalgae farms, they could even be located in desertic places.
- During their growing, microalgae can capture CO_2 and other air pollutants.

By now, few industrial scale trials have been done and this technique has been developed in laboratories. Even for a pilot plant a lot of space is necessary.

The process consists of generation of biomass by converting light energy from the sun into chemical energy following a photosynthetic reaction:

$6CO_2 + 6H_2O + \text{light} \dashrightarrow C_6H_{12}O_6 + 6O_2$

In addition to CO2, light and water, there is a need of a presence into water of inorganic salts like nitrogen, phosphorus and iron, and it is important to maintain the temperature between 20ºC and 30ºC (it depends on the algae).

The industrial process of the pilot plant of Repsol Refinery in Tarragona is made in four stages:

- Inoculation preparation: This stage is the preparation of the growing liquid that must include a correct mixture of seawater and water with some organic content. In this mixture the alga from a laboratory is seeded and it grows by adding CO_2 and nutrients. This process is done in an inocculation photobioreactor, that is, a transparent long pipe filled with the mixture and in which it circulates at very low velocity.
- Production of algae mass: In a bigger photobioreactor the mixture is prepared like in the previous stage and filled also with the inocculation mixture prepared in the first stage. The objective is to obtain an accelerated multiplication of the algae and afterwards the growing of the algae.
- Concentration: After some time (depending on weather conditions and the type of algae) the mixture of liquid and grown algae is extracted from the photobioreactors and the algae mass must be concentrated using processes as settling, filtration or/and centrifugation. The goal at this stage is to obtain algae almost totally dried.
- Analytic control and biofuels production capacity assessment: Finally the algae are analyzed for determining some quality parameters and depending on the results the capacity of the algae to produce biofuels will be assessed.

It is important to know that there are yet a lot of algae species to investigate yet and a lot of combinations for process variables that must be tested still to improve the process. By now, productions far under 1 kg of algae per cubic meter of photobioreactor are achieved and the amount of CO_2 consumed is about 2 kg per kg of alga produced (depending on the algae used and on the absorption of CO_2 in water).

To prevent that the mixture in the photobioreactor reaches very high or very low temperatures, normally the photobioreactors are covered with external water but in a depth low enough to let the sun pass through it. The weather of the area is considered as well very important in these processes, thus the kind of algae used should be suitable for the climatic features of the area, e.g. in a Mediterranean site it is preferable to use Mediterranean algae.

6.16.2 Cultivating Plant Species with Fast Growth and High Bioenergy Potential in Open and Semi-Closed Systems with Carbon Fertilisation in a Refinery Environment

This technology attempts to demonstrate the possibility of capturing CO_2 from industrial processes through the carbon fertilisation of energy crops, obtaining biomass, which in turn can be used to produce energy.

One possible solution for reducing the amount of greenhouse gases in the atmosphere includes capturing the CO_2 primarily produced by industry and transport, and converting it into biomass through different plant species. Furthermore, this biomass can later be used to generate energy directly by combustion or as a raw material in the production of biofuels for transport use.

Other research projects have already demonstrated that carbon dioxide injected into greenhouses increases crop yield. The novelty of Repsol's pilot project at the Refinery of Puertollano is that it injects CO_2 into the greenhouses along with other impurities from the refinery processes, and uses non-food energy crops for the production of biomass.

The CO2 Funnels project aims to study the productivity of short-cycle crops, with high biomass productivity, in a Mediterranean greenhouse with carbon fertilisation.

The study aims at evaluating the flow of CO_2 into the air and soil for each crop, in different conditions. Six species are being studied: coloured Guinea grass, spurge, sorghum, camelina, triticale, Arabidopsis thaliana, under several scenarios of carbon fertilisation, from the natural atmosphere to the addition of pure CO_2 and CO_2 with impurities. Besides the effect of these gases on parameters such as production of biomass or energy value, the biological aspects of the system are being studied, including photosynthetic activity, gas exchange and the overall metabolism of the plant.

Five 400 m^2 tunnel-type greenhouses have been installed with drip irrigation systems, pipelines for CO_2 injection, sensors for monitoring temperature, humidity and CO_2 concentration, and equipment for measuring CO_2 flows in the air and soil.

GLOSSARY

Symbols	Meaning
AC	Alternative Current
API	Density unit (specific density= 141.5/(°API+131.5))
API separator	Oil/water/sludge separator (developed by American Petroleum Institute)
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
BAT	Best Available Technique
BREF	Best Available Techniques reference document
ELV	Emission Limit Value
E-PRTR	European Pollutant Release and Transfer Register
IED	Industrial Emissions Directive (Directive 2010/75/UE)
IPPC	Integrated Pollution Prevention and Control
BBU	Bitumen Blowing Unit
BFW	Boiler feed water (to produce steam)
BOD	Biological Oxygen Demand
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BTX	Benzene, Toluene, Xylene
Cat	Catalytic
Cat cracker	Catalytic cracker (typically refers to fluid catalytic cracker)
CCGT	Combined Cycle Gas Turbine
CDD/CDF	Chlorodibenzoparadioxines/furans
CDU	Atmospheric Crude Distillation Unit
CHP	Combined Heat and Power (CHP , co-generation)
COD	Chemical Oxygen Demand
Concarbon	Conradson Carbon Number
CWW BREF	Common Waste Water and Waste Gas Treatment/Management Systems for the Chemical Sector
DGF	Dissolved Gas Flotation
DS	Dissolved Solids
EIPPCB	European IPPC Bureau
EMS	Environmental Management System
ENE BREF	Energy Efficiency BREF
ETBE	Ethyl tert-butyl ether
FCC	Fluidised-bed Catalytic Cracking
FCCU	Fluidised-bed Catalytic Cracking Unit

Symbols	Meaning
FGD	Flue Gas Desulphurisation
FOE	Fuel Oil Equivalent
HC	Hydrocarbon
HFO	Heavy Fuel Oil
HVU	High Vacuum Unit
IGF	Induced Gas Flotation
IGCC	Integrated Gasification Combined Cycle
LCP BREF	Large Combustion Plants BREF
LDAR	Leakage Detection and Repair Programme
LPG	Liquified Petroleum Gas
LVGO	Light Vacuum Gasoil
PSA	Pressure-Swing Adsorption (used for purification of hydrogen)
RCC	Residue Catalytic Cracker
REF BREF	Refining of Mineral Oil and Gas BREF
RFG	Refinery Fuel Gas
RON	Research Octane Number
RSH	Mercaptan
SRU	Sulphur Recovery Unit
SS	Suspended Solids
SWS	Sour Water Stripper
TAME	Tertiary Amyl Methyl Ether
PCDD/F	Polychlorodibenzoparadioxines/furans
TCDD/F	Tetrachlorodibenzoparadioxins/furans (toxicity reference for dioxins)
TEL	Tetra ethyl lead
TGT	Tail Gas Treatment (of the sulphur recovery unit)
TML	Tethra Methyl Lead
TOC	Total Organic Carbon
TSS	Total Suspended Solids (water)
UF	Ultrafiltration
VI	Viscosity Index
VOC	Volatile Organic Compound
VR	Vacuum Residue
WWTP	Waste Water Treatment Plant

ANNEX 1 CHECK-LISTS TO BE USED IN THE ASSESSMENT OF THE PERMIT APPLICATION

CONTENTS OF THE PERMIT APPLICATION FILE			
	DESCRIPTION		**CHECK**
PROJECT REPORT	Owner of the company	Name of the company	1 ☐
		Full address	2 ☐
		VAT number	3 ☐
		Main activity	4 ☐
	Operator (if is different from the owner)	Name of the company	5 ☐
		Data of the contact person (in each work centre)	6 ☐
		Full address	7 ☐
		VAT number	8 ☐
		Main activity	9 ☐
	Description of the installation and technical characteristics		10 ☐
		Number of work centres	11 ☐
		Register number of industrial establishments	12 ☐
		National Classification of Economic Activities (NACE)	13 ☐
		Total number of workers	14 ☐
		Investments targeted to environmental improvements.	15 ☐
		Organization chart	16 ☐
		UTM coordinates	17 ☐
		Activity of Annex I of the By Law	18 ☐
		Main activity and others	19 ☐
		Nominal production/treatment capacity and size	20 ☐
		Planned date for commencing and completion of building activities (for new installations)	21 ☐
		Planned date for starting operation (for new installations)	22 ☐
		Operational time of the installation	23 ☐
	Description of the production process	Production process description, with a schematic flow chart divided into phases.	24 ☐
		Description of the phases	25 ☐
		Operational hours in each phase	26 ☐
		The methods of operation (continuous or discontinuous)	27 ☐
		Description of the equipment and the techniques used, specifying which of them are considered as Best Available Techniques (BAT)	28 ☐
	Detailed description of the natural resources, raw and auxiliary materials and products	Natural resources: - energy : use of fuel for heat and steam generation and for transport inside the enterprise not including use of fuel for production of electricity or combined power and heat, use of heat and steam from external suppliers, use of electricity, use of fuel for production of electricity and heat - power plants and boiler houses	29 ☐
		- water: quantity of water used in the process, intake of surface, ground and marine water –detailed description of intake, and indication of the cases of supply of water from outside or re-circulated	30 ☐
		Raw materials: list and quantities of raw materials, indicating hazardous or non-hazardous character	31 ☐
		Auxiliary materials: list and quantities of auxiliary materials, indicating hazardous or non-hazardous character	32 ☐
		Products and by-products: list of output products and by-products, types and quantity generated of each of them, per hour, day or year.	33 ☐

			Modelization requirements	34 ☐

	Environmental emissions and controls	Air quality	Plan for monitoring of immisions	35 ☐
		Air: Channelled emissions:	Description of the emission points	36 ☐
			Requirements and technical conditions of the focus (including operational hours)	37 ☐
			Gaseous effluents generated (air flow, temperature and pollutants emitted)	38 ☐
			Abatement equipment, specifying which ones are BAT	39 ☐
			Plan for Monitoring and Control	40 ☐
		Air: Non channelled emissions	Description of the emission points	41 ☐
			Pollutants emitted	42 ☐
			Abatement equipment, specifying which ones are BAT	43 ☐
			Plan for Monitoring and Control	44 ☐
		Noise	Description of sources (location and characterization)	45 ☐
			Acoustic study	46 ☐
			Abatement measures, specifying which ones are BAT	47 ☐
			Plan for Monitoring and Control	48 ☐
		Waste water	Description of the flow (including discharging points) and the associated process (industrial, sanitary, rainwater or other discharges)	49 ☐
			Requirements and technical conditions of discharging points	50 ☐
			Description of pollutants	51 ☐
			WWTP (specifying BAT)	52 ☐
			Monitoring and control (sampling points)	53 ☐
		Hazardous waste	Production and characterization (classification according EWC and labelling)	54 ☐
			Storage conditions	55 ☐
			Prevention on pollution measures (specifying BAT)	56 ☐
			Waste management (inside/offside treatment)	57 ☐
			Plan for minimization of waste	58 ☐
		Non hazardous waste	Characterization (classification and labelling)	59 ☐
			Prevention on pollution measures (specifying BAT)	60 ☐
			Waste management (inside/offside treatment)	61 ☐
		Packaging waste	Characterization	62 ☐
			Plan for minimization of waste	63 ☐
		Soil and groundwater protection	Safety measures for storage, specifying BAT	64☐
			Systems of drainage or collection of potentially polluted waters.	65☐
			Plan for monitoring and control	66☐
ADDITIONAL INFORMATION	Non-technical summary of the details specified in the foregoing paragraphs			67☐
	Environmental Impact Assessment (EIA) Report (for new installations, article 11 By Law 26939)			68☐
	Development plans and landscape planning report			69☐
	SEVESO report			70☐
	Identification of the information which the applicant deems to be confidential under the provisions in force			71☐
	Any other documentation evidencing compliance with the requirements under the applicable environmental legislation including, where applicable, the legislation on obligatory security or insurance required under the applicable environmental legislation			72☐
	The baseline report, that shall contain the information necessary to determine the state of soil and groundwater contamination so as to make a quantified comparison with the			73☐

	state upon definitive cessation of activities	
	Receipt of the fees paid by the operator	74☐

ANNEX 2: BREF SECTIONS TO BE TAKEN INTO ACCOUNT TO ESTABLISH THE PERMIT'S CONDITIONS

The sections indicated below correspond by default to the BREF Document for the Refining of Mineral Oil and Gas (REF BREF). Where there is reference to other relevant BREF Documents, their name is explicitly indicated.

Horizontal BREF Documents which may be mentioned in the table below
Industrial Cooling Systems (ICS)
General Principles of Monitoring (MON)
Emissions from Storage (EFS)
Economic and Cross-media Effects (ECM)
Energy Efficiency (ENE)
Common waste water and waste gas treatment / Management Systems in the Chemical Sector (CWW)

Further information on issues related to the use of commercial fuels in combustion units and the emission associated to the application of BATs can be found in the Large Combustion Plants BREF (LCP).

SUBJECT		BREF SECTION
1	Fuel consumption reduction and thermal/energetic optimization	5.1.2
BATs to reduce emissions to air		
2	Techniques to reduce dust emissions and BATAELs	5.21.1, 5.21.5
3	Techniques to reduce the SO2 emissions and BATAELs	5.21.3, 5.21.5
4	Techniques to reduce the NOx emissions and BATAELs	5.21.2, 5.21.5
5	Techniques to reduce the CO emissions and BATAELs	5.21.4
6	Techniques to reduce the VOC and odour emissions and BATAELs	5.21.6
7	Techniques to reduce other pollutants (heavy metals, aromatic compounds, methane, etc.) emissions and BATAELs	5.21.7
8	Emissions of hazardous compounds (PAH, dioxins, Chloride, etc.)	5.21.7
BATs to reduce water consumption and waste water discharges		
9	Flow and pollutant mass of waste water discharges	5.1.7, 5.22
10	BATs for waste management	5.1.8, 5.23
11	Soil and groundwater risks	
12	Environmental Management Systems. BATs for the environmental management	5.1.1, 5.1.10

ANNEX 3: COMPARISON BETWEEN BAT-AEL AND TURKISH EMISSION LIMIT VALUES

AIR EMISSIONS

For combustion and catalytic processes, reference conditions for oxygen must be given with the associated data. Usually, these values are 3% O_2 for combustion process (using liquid or gaseous fuels) and catalytic cracking and 15% O_2 for gas turbines and engines.

BAT-AEL for metals emissions are still to be determined by the technical working group of the refineries BREF and the EIPPCB.

PARAMETER	SOURCE	BAT	BAT-AEL (monthly average) (mg/Nm^3)	Current ELV in Turkey (emission limit value)
Dust	Catalytic cracking	10	New units: < 10 – 25	
			Existing units: 10-50	
	Calcining of green coke process	12	10-50	
	Combustion units	13	5 – 50 for existing units (multi-fuel)	
			5 – 25 for new units (multi-fuel)	
SO_2	Catalytic cracking	14	New units: ≤ 300	
			Existing units/full combustion: <100-800	
			Existing units/partial combustion: 100-1200	
	Combustion units	16	**RFG gas firing (3% O_2):** 5 – 35	
			Multi-fuel firing (3% O_2): 35-600 for existing units	
	Waste gas sulphur treatment: Off-gases	17	**BAT-associated sulphur recovery efficiency (*) (daily average)** Acid gas removal: Achieve	

			hydrogen sulphide (H_2S) removal in the treated RFG in order to meet gas firing BAT-AEL for BAT 16 Sulphur recovery efficiency New units: 99.5->99.9% Existing units: ≥98.5%	
NO_x	Catalytic cracking	24	< 30 – 100 For new units/all combustion mode < 100 – 300 For existing units/full combustion mode 100-400 For existing units/partial combustion mode	
	Combustion units	26	**Combustion gas turbines ($15\% \ O_2$)** 40-120 existing turbines 20 – 50 new turbines	
			Gas firing combustion with the exception of gas turbines ($3\% \ O_2$): 30 – 150 for existing units 30 – 100 for new units	
			Multi-fuel combustion with the exception of gas turbines ($3\% \ O_2$): 30 – 300 for existing units 30 – 150 for new units	

CO	Catalytic cracking (regeneration of catalyst)	28	< 100 (only for partial combustion mode)	
	Combustion units	29	≤100	
Non-methanous volatile organic compounds (NMVOC)	Loading and unloading operations	32	0.15 – 10 g/Nm^3 (hourly values concentration)	
Benzene			< 1 mg/Nm^3	
Ammonia expressed as NH_3	Waste gas treatment systems with SCR or SNCR	36	< 5 – 15 mg/Nm^3	

WATER EMISSIONS:

BAT	**Parameter**	**BAT-AEL Long term (mg/l) (yearly average)**	**ELV (emission limit value)**
40	**Total Hydrocarbon content (THC)**	0.1 – 25	
	Total suspended solids (TSS)	2 – 25	
	Chemical oxygen demand (COD)$^{(2)}$	30 – 125	
	BOD_5	No BAT-AEL	
	Total nitrogen $^{(3)}$ **(expressed as N)**	1 – 25	
	Lead, expressed as Pb	0.005 – 0.030	
	Cadmium, expressed as Cd	0.002 – 0.008	
	Nickel, expressed as Ni	0.005 – 0.100	
	Mercury expressed as Hg	0.000 1 – 0.001	
	Vanadium	No BAT-AEL	
	Penol Index	No BAT-AEL	

	Benzene, toluene Ethyl benzene, Xylene (BTEX)	Benzene: 0.001 – 0.050 No AEL for T,E ,X reporting only	