BEST AVAILABLE TECHNIQUES GUIDANCE DOCUMENT ON OIL AND GAS INDUSTRY

FOREWORD

Best Available Techniques Economically Achievable (BAT) document had been prepared as a guidance notes for the nine (9) major industries in Malaysia and to support the implementation of the new Environmental Quality (Clean Air) Regulations 20xx. These documents were prepared based on the latest state-ofthe-art technologies, internationally accepted limit values but had been adjusted and tailored to local requirements.

BAT is defined as the effective methods in preventing pollution and, where generally that is not practicable, to reduce emissions from industrial activities and their impact on the environment. This definition implies that BAT not only covers the technology used but also the way in which the installation is operated, to ensure a high level of environmental protection. Implementations of BAT in any specific industrial sectors are under economically and technically viable condition.

It is hope that the technical contents of these documents will prove beneficial to the industries in their endeavour to comply with the environmental regulations and standards through more cost-efficient means. In the identification of BAT, emphasis is placed on pollution prevention techniques rather than end-of-pipe treatment. These documents will be reviewed and updated from time to time.

These documents have been prepared in consultations with the University of Malaya Consultancy Unit (UPUM), Malaysia German Technical Cooperation (GTZ) and the relevant industries/stakeholders. The Department of Environment wishes to record appreciation to representatives of the relevant industrial sectors, government agencies and individuals for their invaluable input.

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LIST OF ABREVIATIONS

| AUTO-OIL I, II | - | 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 Techniques economically achievable | | | |
| BB | - | Butane/Butylenes | | | |
| BREF | - | Best Available Technique Reference Document | | | |
| С | - | Carbon | | | |
| CAR | - | Clean Air Regulation | | | |
| Cd | - | Cadmium | | | |
| СО | - | Carbon Monoxide | | | |
| DAO | - | Deasphalted Oil | | | |
| DEA | - | Diethylamine | | | |
| DOE | - | Department of Environment | | | |
| EIA | - | Environmental Impact Assessment | | | |
| EMS | - | Environmental Management System | | | |
| ESP | - | Electrostatic Precipitators | | | |
| ETBE | - | Ethyl Tertiary Butyl Ether | | | |
| FCC | - | Fluidised-Bed Catalytic Cracker | | | |
| FCCU | - | Fluidised-Bed Catalytic Cracker Unit | | | |
| FGD | - | Flue Gas Desulphurization | | | |
| Н | - | Hydrogen | | | |
| HCI | - | Hydrogen Chloride | | | |
| HDS | - | Hydro Desulphurisation | | | |
| HC | - | Hydrocracking | | | |
| HF | - | Hydrogen Flouride | | | |
| HFO | - | Heavy Fuel Oil | | | |
| HGO | - | Heavy Gas Oil | | | |
| IPPC | - | Integrated Pollution Prevention Control | | | |
| LGO | - | Light Gas Oil | | | |
| LPG | - | Liquid Petroleum Gas | | | |

| MTBE | - | Methyl Tertiary Butyl Ether |
|------|---|---------------------------------|
| NMP | - | N-methyl pyrrolidone |
| PP | - | Propane/Propylene |
| PSA | - | Pressure Swing Adsorption |
| psia | - | pounds per square inch absolute |
| psig | - | pounds per square inch gauge |
| SCR | - | Selected Catalytic Reaction |
| SNCR | - | Selected Non-Catalytic Reaction |
| SRU | - | Sulfur Recovery Unit |
| TAME | - | Tertiary Amyl Methyl Ether |
| VGO | - | Vacuum Gas Oil |
| VOC | - | Volatile Organic Compounds |
| WWTP | - | Waste Water Treatment Plant |

1.0 PREFACE

1.1 Status of This Document

This document forms a part of a series presenting the guidance notes for selected industries in Malaysia (list given at the end of this preface) to apply best available techniques economically achievable (BAT), associated monitoring and developments in them. This series is published by the Department of Environment (DOE) in accordance to the Environmental Quality (Clean Air) Regulations 2014 (CAR 2014).

1.2 Definition of BAT

In order for the user of this document to understand the legal context of this document, the interpretation on the definition of BAT is taken from Regulation 2 – Interpretation of CAR 2014 and described as below:

"Best Available Techniques Economically Achievable" means the effective methods in preventing pollution and, where that is not practicable, generally to reduce emissions in the air from the industrial activities and their impact on the environment as a whole. In this regard:

"Techniques" includes both the technology used and the way in which the facility is designed, built, maintained, operated and decommissioned;

"Available Techniques" means those techniques that are accessible to the occupier and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and

"Best" means effective in achieving a high general level of protection of the environment as a whole;

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this document that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels "associated with best available techniques" are presented, this is to be understood to mean those levels representing the environmental performance that could be expected as a result of the application, of the techniques described, taking into account the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such.

In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of "levels associated with BAT" described above is to be distinguished from the term "achievable level" used elsewhere in this document. Where a level is described as "achievable" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

The actual cost of applying a technique will depend strongly on the specific situation such as taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific economic viability of techniques drawn from observations on existing installations.

2

The purpose of CAR 2014 is to achieve prevention and control of pollution arising from activities listed in its First Schedule. More specifically, it provides for a notification system for certain categories of industrial installations to conduct an integrated and comprehensive view of the pollution and consumption potential of their installation. The overall aim is to ensure a high level of protection of the environment as a whole based on appropriate preventative measures through the application of BAT.

1.3 Objective of This Document

The 'emission minimization principle' as cited in CAR 2014 requires that the goal of emission abatement is to achieve minimum emissions as a result of applying current BAT. Hence this guidance document is meant to provide the reference information for the permitting authorities to take into account when determining permit conditions. This document should serve as valuable input to achieve better environmental performance.

1.4 Information Sources

The information is mainly based on the European IPPC BREF document where the assessment was achieved through an iterative process involving the following steps:

- identification of the key environmental issues for the sector
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in Implementation of these techniques;

 selection of the BAT and the associate emission and/or consumption levels for this sector

1.5 How to Use This Document

It is intended that the general BAT in this document could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate BAT based conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general BAT levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or perform better. This reference document does not set legally binding standards, but they are meant to give information for the guidance of industry, the relevant government bodies and the public on achievable emission and consumption levels when using specified techniques.

The structure of the guideline document is as follows:

An overview of each particular sector in the Malaysian context is firstly covered briefly followed by process description, process optimization, sources of pollution, emission control options, recommended practices and emission values and finally emission monitoring and reporting. More often than not, trade-off judgements between different types of environmental impacts and specific site condition are the influencing factors.

Another important point to note is that BAT change over time and this guidance document needs to be reviewed and updated as appropriate.

2.0 OVERVIEW OF OIL AND GAS INDUSTRIES IN MALAYSIA

"Offshore' in the context of this Guidance document BAT refer to EIA Guidance Document for Petroleum Industries. Its define as the waters from the lowest tide level to the 200 nautical mile Exclusive Economic Zone limit.

Offshore platforms in Malaysia are typically steel jacket structures located in 10 to 80 meters of water in the South China Sea. On these steel structures is process modules that separate oil, gas and water produced from subsurface reservoirs. After separation, oil and gas are sent via sub-sea pipelines to onshore terminals for further treatment prior to sale. Produced water is typically treated at the platform to an acceptable level as approved by the DOE prior to discharge into the sea.

In other cases, after separation at the platform into gaseous and aqueous phases, the gas and liquid are sent to onshore terminals for separation and treatment of oil, gas and water. Produced water is separated from the liquid are treated at the terminals to an acceptable level.

Offshore oil and gas developments comply with stringent and proven worldwide safety and environmental standards established by the petroleum industry. The establishment and compliance with these self-imposed standards are due to the recognized need to protect the environment where the platform structures/pipelines will be located, the importance of protecting the safety and health of the offshore workers and need to protect the high cost of investment associated with such developments. There is no onshore oil and gas field development in Malaysia to date although a few exploration drilling campaigns have been carried out onshore.

3.0 PROCESS DESCRIPTIONS

3.1 The Purpose of Refineries

The purpose of refining is to convert natural raw materials such as crude oil and natural gas into useful saleable products such as fuels, raw materials for the petrochemical and chemical industries, specialty products such as lubricating oils, paraffin's/waxes and bitumen. In order to manufacture these products, these raw materials are processed in a number of different refining facilities. The combination of these processing units to convert crude oil and natural gas into products, including its supporting units and facilities, is called a refinery.

3.2 General Overview of the Oil Refinery Processes

Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories: fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke); finished non-fuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke); and chemical industry feedstock (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene). A general setup of an oil refinery is shown in **Figure 1**.

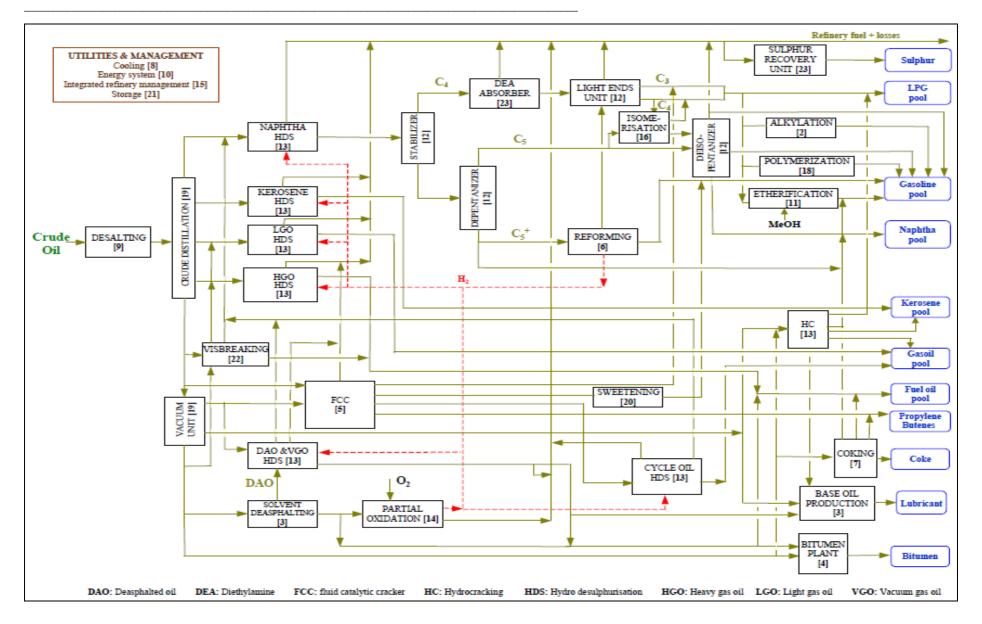


Figure 1 : General Setup of an Oil Refinery

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

- Desalting and distillation of crude oil and the subsequent distillation into its various components or fractions.
- Downstream processes combining, breaking, and reshaping.
 Downstream processes convert some of the distillation fractions into petroleum products (residual fuel oil, gasoline, kerosene, etc.) through any combination of different cracking, coking, reforming, and alkylation processes.
- Supporting operations may include, sulfur recovery, additive production, heat exchanger cleaning, blowdown systems, blending of products and storage of products

3.2.1 Crude Oil Distillation and Desalting

One of the most important operations in a refinery is the initial distillation of the crude oil into its various boiling point fractions. Distillation involves the heating, vaporization, fractionation, condensation, and cooling of feedstocks.

(a) Desalting

Before separation into fractions, crude oil usually must first be treated to remove corrosive salts. The desalting process also removes some of the metals and suspended solids which cause catalyst deactivation. Desalting involves the mixing of heated crude oil with water (about three to 10 percent of the crude oil volume) so that the salts are dissolved in the water. The water must then be separated from the crude oil in a separating vessel by adding demulsifier chemicals to assist in breaking the emulsion and/or, more commonly, by applying a high potential electric field across the settling vessel to coalesce the polar salt water droplets.

(b) Atmospheric Distillation

The desalted crude oil is then heated in a heat exchanger and furnace to about 400 °C and fed to a vertical, distillation column at atmospheric pressure where most of the feed is vaporized 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. Heavier fractions, which may not vaporize in the column, are further separated later by vacuum distillation. Within each atmospheric distillation tower, a number of side streams (at least four) of lowboiling point components are removed from the tower from different trays. Fractions obtained from atmospheric distillation include naphtha, gasoline, kerosene, light fuel oil, diesel oils, gas oil, lube distillate, and heavy bottoms. Another product produced in atmospheric distillation, as well as many other refinery processes, is the light, non-condensable refinery fuel gas (mainly methane and ethane). Typically this gas also contains hydrogen sulfide and ammonia gases. The mixture of these gases is known as acid gas. The sour gas is sent to the refinery sour gas treatment system which separates the fuel gas so that it can be used as fuel in the refinery heating furnaces. Air emissions during atmospheric distillation arise from the combustion of fuels in the furnaces to heat the crude oil, process vents and fugitive emissions. Oily sour water (condensed steam containing hydrogen sulfate and ammonia) and oil is also generated in the fractionators as shown in Figure 2.

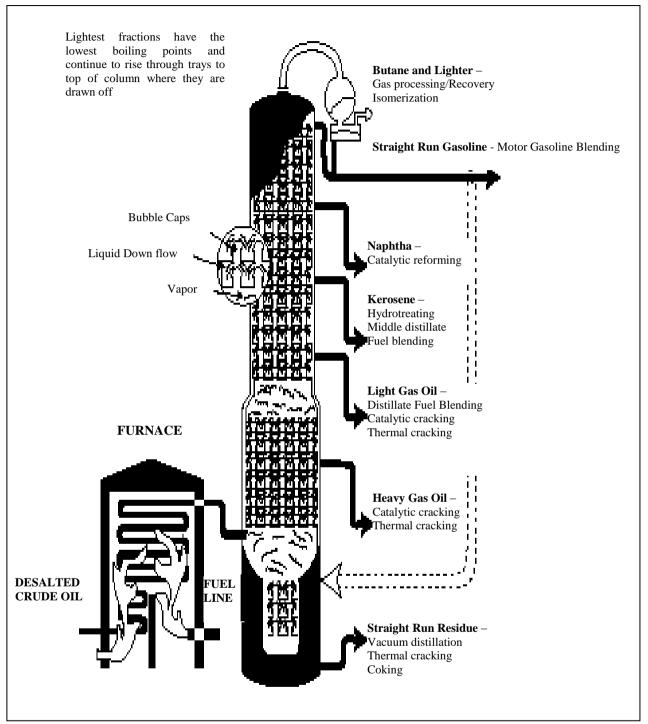


Figure 2: Crude Oil Distillation

(c) Vacuum Distillation

Vacuum distillation is simply the distillation of petroleum fractions at a very low pressure (0.2 to 0.7 psia) to increase volatilization and separation. In most systems, the vacuum inside the fractionator is maintained with steam ejectors and 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 vaporization and separation. The heavier fractions from the vacuum distillation column are processed downstream into more valuable products through either cracking or coking operations.

3.2.2 Refinery Downstream Processes

Certain fractions from the distillation of crude oil are further refined. These downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. **Table 1** below shows the various type of refined product with respective unit operation or processes.

Table 1: Refinery Units and Their Main Products

| $PRODUCTS \rightarrow$ | Section | LPG | Gasoline | Kerosene/ | Heating | HFO | Base | Coke/ | Special |
|------------------------|---------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------|------------------|------------------|----------------|
| REFINERY | | | | naphtha | oil/diesel | | Oil | bitumen | |
| UNITS ↓ | | | | | | | | | |
| Carbon n ^o | | | <u> </u> | | | . (| | | |
| range | | C ₃ -C ₄ | C ₄ -C ₁₂ | C ₈ -C ₁₇ | C ₈ -C ₂₅ | >C ₈ | >C ₁₅ | >C ₃₀ | |
| Alkylation | 2 | | | | | | | | |
| Base Oil | 3 | | | | | | | | wax |
| production | Ũ | | | | | | | | Wax |
| Bitumen | 4 | | | | | | | | |
| production | 4 | | | | | | | | |
| Catalytic cracker | 5 | | | | | | | | |
| Residue cracking | 5 | | | | | | | | |
| Catalytic | 6 | | | | | | | | H ₂ |
| reforming | Ũ | | | | | | | | 112 |
| Delayed coking | 7 | | | | | | | | |
| Flexicoker | 7 | | | | | | | | low joule |
| | ' | | | | | | | | gas |
| Gasification | 10 | | | | | | | | syngas |
| Etherification | 11 | | | | | | | | MTBE |
| Gas separation | 12 | | | | | | | | Refinery |
| processes | | | | | | | | | fuel gas |
| Hydrogen plant | 14 | | | | | | | | H ₂ |
| Residue | | | | | | | | | |
| Hydroconversion | 14 | | | | | | | | H ₂ |
| Hydrocracker | 15 | | | | | | | | |
| Hydrodesulphuri- | 45 | | | | | | | | |
| sation | 15 | | | | | | | | |
| Isomerisation | 17 | | | | | | | | |
| Crude | 19 | | | | | | | | |
| atmospheric | | | | | | | | | |
| distillation | | | | | | | | | |
| Vacuum | 10 | | | | | | | | |
| distillation | 19 | | | | | | | | |
| Thermal | | | | | | | | | |
| cracking/ | 22 | | | | | | | | |
| Visbreaking | | | | | | | | | |
| Sulphur recovery | 23 | | | | | | | | S |
| unit | 23 | | | | | | | | 3 |

a) Thermal Cracking/Visbreaking

Thermal cracking uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules. In thermal cracking, heavy gas oils and residue from the vacuum distillation process are typically the feed stocks. The feed stock is heated in a furnace or other thermal unit to up to 936 $^{\circ}$ C and then fed to a reaction chamber which is kept at a pressure of about 140 psig. 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 vaporize 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 as shown in **Figure 3.**

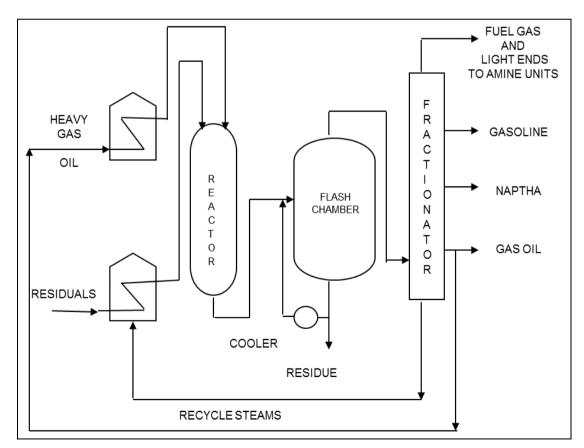


Figure 3: Simplified Thermal Cracker Flow Diagram

b) Coking

Coking is a cracking process used primarily to reduce refinery production of low-value residual fuel oils to transportation fuels, such as gasoline and diesel. Hot vapors from the coke drums, containing cracked lighter hydrocarbon products, hydrogen sulfide, 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. Steam is then injected into the full coke drum to remove hydrocarbon vapors, water is injected to cool the coke, and the coke is removed. Typically, high pressure water jets are used to cut the coke from the drum as shown in **Figure 4**.

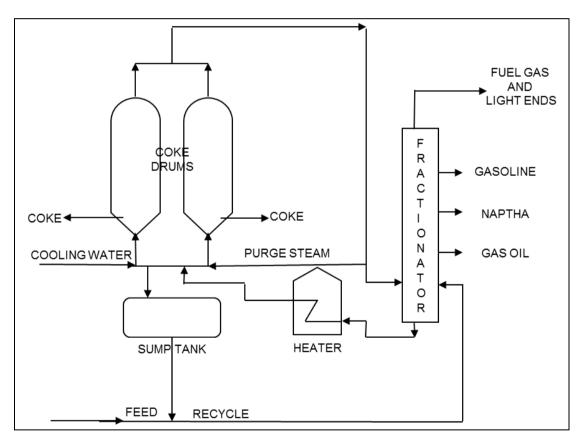


Figure 4: Simplified Coker Flow Diagram

c) Catalytic Cracking

Catalytic cracking uses heat, pressure and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. Fluidized-bed catalytic cracking units (FCCUs) are by far the most common catalytic cracking units. In the fluidized-bed process, oil and oil vapor preheated to 260 to 430 °C is contacted with hot catalyst at about 700 °C either in the reactor itself or in the feed line (riser) to the reactor. The catalyst is in a fine, granular form which, when mixed with the vapor, has many of the properties of a fluid. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in the reactor and any oil remaining on the catalyst is removed by steam stripping. The cracked oil vapors are then fed to a fractionation tower where the various desired fractions are separated and collected. The catalyst flows into a separate vessel(s) for either single or two-stage regeneration by burning off the coke deposits with air as shown in **Figure 5**.

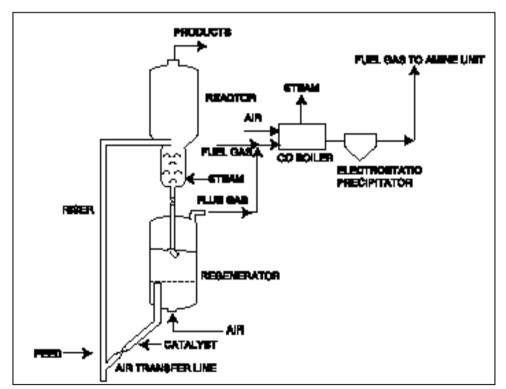


Figure 5: Simplified Catalytic Cracking Flow Diagram

d) Catalytic Hydrocracking

Catalytic hydrocracking normally utilizes a fixed-bed catalytic cracking reactor with cracking occurring under substantial pressure (1,200 to 2,000 psig) in the presence of hydrogen. The hydrogen suppresses the formation of heavy residual material and increases the yield of gasoline by reacting with the cracked products. However, this process also breaks the heavy, sulfur and nitrogen bearing hydrocarbons and releases these impurities to where they could potentially foul the catalyst. For this reason, the feedstock is often first hydrotreated to remove impurities before being sent to the catalytic hydrocracker. Sometimes hydrotreating is accomplished by using the first reactor of the hydrocracking process to remove impurities. Water also has a detrimental effect on some hydrocracking catalysts and must be removed before being fed to the reactor. The water is removed by passing the feed stream through a silica gel or molecular sieve dryer. Depending on the products desired and the size of the unit, catalytic hydrocracking is conducted in either single stage or multi-stage reactor processes. Most catalysts consist of a crystalline mixture of silica-alumina with small amounts of rare earth metals as shown in Figure 6.

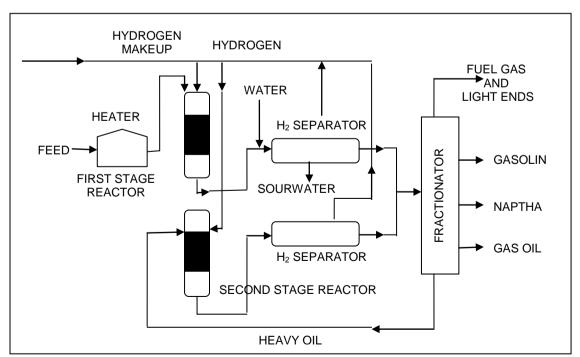


Figure 6: Simplified Two-Stage Hydrocracker Flow Diagram

e) Hydrotreating/Hydroprocessing

Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulfur, nitrogen, oxygen, halides and trace metal impurities that may deactivate process catalysts. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. The processes utilize catalysts in the presence of substantial amounts of hydrogen under high pressure and temperature to react the feedstocks and impurities with hydrogen. The reactors are nearly all fixed-bed with catalyst replacement or regeneration done after months or years of operation often at an off-site facility. In addition to the treated products, the process produces a stream of light fuel gases, hydrogen sulfide, and ammonia. The treated product and hydrogen-rich gas are cooled after they leave the reactor before being separated. The hydrogen is recycled to the reactor.

The off-gas stream may be very rich in hydrogen sulfide and light fuel gas. The fuel gas and hydrogen sulfide are typically sent to the sour gas treatment unit and sulfur recovery unit. Catalysts are typically cobalt or molybdenum oxides on alumina, but can also contain nickel and tungsten. Air emissions from hydrotreating may arise from process heater flue gas, vents, and fugitive emissions as shown in **Figure 7**.

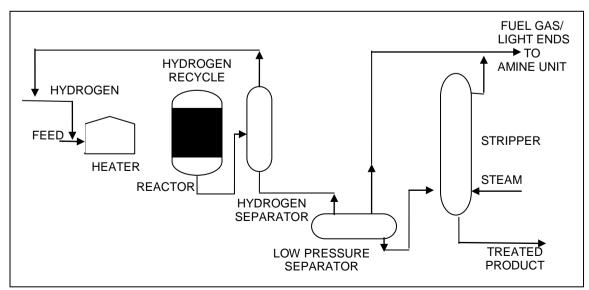


Figure 7: Simplified Hydrotreater Flow Diagram

f) Alkylation

Alkylation is used to produce a high octane gasoline blending stock from the butylenes formed primarily during catalytic cracking and coking operations, but also from catalytic reforming, crude distillation and natural gas processing. Alkylation joins an olefin and an isoparaffin compound using either a sulfuric acid or hydrofluoric acid catalyst.

g) Isomerization

Isomerization is used to alter the arrangement of a molecule without adding or removing anything from the original molecule. Typically, paraffins (butane or pentane from the crude distillation unit) are converted to isoparaffins having a much higher octane. Isomerization reactions take place at temperatures in the range of 93 to 204 °C in the presence of a catalyst that usually consists of platinum on a base material.

h) Polymerization

Polymerization 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.

i) Catalytic Reforming

Catalytic reforming uses catalytic reactions to process primarily low octane heavy straight run (from the crude distillation unit) gasoline and naphtha into high octane aromatics (including benzene). There are four major types of reactions which occur during reforming processes: Dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins to aromatics, isomerization and hydrocracking

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j) Solvent Extraction

Solvent extraction uses solvents to dissolve and remove aromatics from lube oil feed stocks, improving viscosity, oxidation resistance, color and gum formation. A number of different solvents are used with the two most common being furfural and phenol.

k) Chemical Treating

In petroleum refining, chemical treating is used to remove or change the undesirable properties associated with sulfur, nitrogen, or oxygen compound contaminates in petroleum products. Chemical treating is accomplished by either extraction or oxidation (also known as sweetening), depending upon the product. Extraction is used to remove sulfur from the very light petroleum fractions, such as propane/propylene (PP) and butane/butylenes (BB). Sweetening, though, is more effective on gasoline and middle distillate products.

I) Dewaxing

Dewaxing of lubricating oil base stocks is necessary to ensure that the oil will have the proper viscosity at lower ambient temperatures. Two types of dewaxing processes are used: selective hydrocracking and solvent dewaxing. In selective hydrocracking, one or two zeolite catalysts are used to selectively crack the wax paraffins. Solvent dewaxing is more prevalent. In solvent dewaxing, the oil feed is diluted with solvent to lower the viscosity, chilled until the wax is crystallized, and then filtered to remove the wax.

m) Propane Deasphalting

Propane deasphalting produces lubricating oil base stocks by extracting asphaltenes and resins from the residuals of the vacuum distillation unit. Propane is usually used to remove asphaltenes due to its unique solvent properties. At lower temperatures (38 to 60 °C), paraffins are very soluble in

propane and at higher temperatures (about 93 °C) all hydrocarbons are almost insoluble in propane. The propane deasphalting process is similar to solvent extraction in that a packed or baffled extraction tower or rotating disc contactor is used to mix the oil feed stocks with the solvent.

n) Base oil production

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 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.

o) Bitumen production

Bitumen is a residue derived from certain crude oils 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.

p) Etherification

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. These additives replaced the lead additives which were being phased out as required by the Auto-Oil I. 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).

q) Gas separation processes

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. (eg. Cat reformers, catcrackers and distillation units). Those systems 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.

r) Hydrogen consuming processes

Two types of processes are commonly available: hydrocracking and hydrotreatments. Both processes take place over a metal catalyst in a hydrogen atmosphere. Many of those processes are found in a refinery, normally named according to the type of feed to treat and the reaction conditions. The common denominator to those processes is that all rely on hydrogenation processes and consequently consume hydrogen.

s) Hydrogen production

The purpose of a hydrogen plant is to produce hydrogen for use in hydrocracking and other hydrogen-consuming refinery process units.

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3.2.3 Supporting Operations

Many important refinery operations are not directly involved in the production of hydrocarbon fuels but serve in a supporting role. Some of the major supporting processes are discussed below.

(a) Gas Treatment and Sulfur Recovery

Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SO_x emissions limits and to recover saleable elemental sulfur. Current methods for removing sulfur from the hydrogen sulfide gas streams are typically a combination of two processes: the Claus Process followed by the Beaven Process, Scot Process, or the Wellman-Land Process. The Claus process consists of partial combustion of the hydrogen sulfide-rich gas stream (with one-third the stoichiometric quantity of air) and then reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur as shown in **Figure 8**.

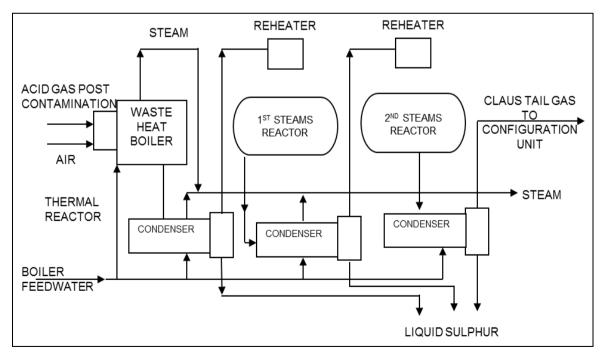


Figure 8: Simplified Claus Sulfur Recovery Flow Diagram

(b) Additive Production

A number of chemicals (mostly alcohols and ethers) are added to motor fuels to either improve performance or meet federal and state environmental requirements. The most common ethers being used as additives are methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME).

(c) Heat Exchanger Cleaning

Heat exchangers are used throughout petroleum refineries to heat or cool petroleum process streams. The heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam, or oil to transfer heat indirectly to or from the oil process stream.

(d) Blowdown System

Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system. Blowdown systems provide for the safe handling and disposal of liquid and gases that are either automatically vented from the process units through pressure relief valves, or that are manually drawn from units. Recirculated process streams and cooling water streams are often manually purged to prevent the continued build up of contaminants in the stream. Part or all of the contents of equipment can also be purged to the blowdown system prior to shutdown before normal or emergency shutdowns.

(e) Blending

Blending is the final operation in petroleum refining. It consists of mixing the products in various proportions to meet specifications such as vapor pressure, specific gravity, sulfur content, viscosity, octane number, cetane index, initial boiling point, and pour point. Blending can be carried out in-line or in batch blending tanks. Air emissions from blending are fugitive VOC's from blending tanks, valves, pumps and mixing operations.

(f) Storage Tanks

Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Finished petroleum products are also kept in storage tanks before transport off site. Storage tank bottoms are mixtures of iron rust from corrosion, sand, water, and emulsified oil and wax, which accumulate at the bottom of tanks.

3.3 General Overview of Natural Gas Plants

The overall objective of natural gas processing is to remove the treatment chemicals contaminants from the well-head stream in order to produce a methane rich gas. The main contaminants to be removed fall into the following categories:

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

The feed stock to this plants are natural gas and the products that may be separated within the natural gas plants are methane reach gas, C₂, C₃, C₄ fractions and condensates (C₅₊). The purification schematic is as shown in Figure 9 below. The purification plant consists on a gas sweetening plant where acid gases as CO_2 , H₂S, SO₂ are separated. Natural gas is considered "sour" when contains significantly greater amounts of hydrogen sulphide than those quoted for pipeline quality or when contains such amounts of SO₂ or CO_2 to make it impractical to use without purification. The H₂S must be

removed (called "sweetening" the gas) before the gas can be utilized. If H_2S is present, the gas is usually sweetened by absorption of the H_2S in an amine solution. Amine processes are the most common process used in the United States and Europe. Other methods, such as carbonate processes, solid bed absorbents, and physical absorption, are employed in the other sweetening plants. Natural gasoline, butane and propane are usually present in the gas, and gas processing plants are required for the recovery of these liquefiable constituents.

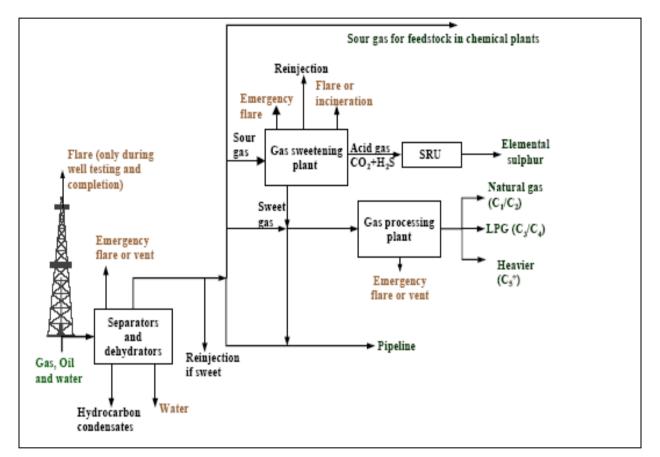


Figure 9: General Flow Diagram Of the Natural Gas Industry

4.0 PROCESS OPTIMIZATION

From Oil and gas production up to refining processes there are many design and operational features that can be incorporated to optimize operation and to prevent and control air pollution. Due to the complexity and huge variation in designs and operations, this aspect is not covered in this document.

5.0 SOURCES OF AIR POLLUTION

5.1 Overall Emission from Oil Refinery

Table 2 below shows a very brief summary of the main pollutants emitted by arefinery, with their main sources.

| Main air pollutants | Main sources |
|---|--|
| Carbon monoxide | Process furnaces and boilers Fluidised catalytic cracking regenerators CO boilers Sulphur recovery units , Flare systems Incinerators |
| Nitrogen oxides (N ₂ O, NO, NO ₂) | Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Incinerators Flare systems |
| Particulates (including metals) | Process furnaces and boilers, particularly when firing liquid refinery fuels Fluidised catalytic cracking regenerators CO boilers Coke plants Incinerators |
| Sulphur oxides | Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators CO boilers Coke calciners Sulphur recovery units (SRU) Flare system Incinerators |
| VOC | Storage and handling facilities Gas separation units Oil/water separation systems Fugitive emissions (valves, flanges, etc.) Vents Flare systems |

| Table 2: Main Air Pollutant | s Emitted by C | Dil Refineries | and Their | Main |
|-----------------------------|----------------|----------------|-----------|------|
| Sources | | | | |

Air emissions from refineries include fugitive emissions of the volatile constituents in crude oil and its fractions, emissions from the burning of fuels

in process heaters, and emissions from the various refinery processes themselves. Fugitive emissions occur throughout refineries and arise from the thousands of potential fugitive emission sources such as valves, pumps, tanks, pressure relief valves, flanges, etc. While individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources. The numerous process heaters used in refineries to heat process streams or to generate steam (boilers) for heating or steam stripping, can be potential sources of SO_x , NO_x , CO, particulates and hydrocarbons emissions. When operating properly and burning cleaner fuels such as refinery fuel gas, fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, or heaters are fired with refinery fuel pitch or residuals, emissions can be significant.

The majority of gas streams exiting each refinery process contain varying amounts of refinery fuel gas, hydrogen sulfide and ammonia. These streams are collected and sent to the gas treatment and sulfur recovery units to recover the refinery fuel gas and sulfur. Emissions from the sulfur recovery unit typically contain some H₂S, SO_x and NO_x. Other emissions sources from refinery processes arise from periodic regeneration of catalysts. These processes generate streams that may contain relatively high levels of carbon monoxide, particulates and VOCs. Before being discharged to the atmosphere, such off-gas streams may be treated first through a carbon monoxide boiler to burn carbon monoxide, and then through an electrostatic precipitator or cyclone separator to remove particulates.

The details on emission from various refining and general processes are as follows:

(a) Alkylation

Table 3 below shows emissions generated by alkylation processes.

 Table 3: Air Emissions Generated by the Alkylation Processes

| Air pollutant | Sulphuric acid | Hydrofluoric |
|---------------------------|-------------------------------|--|
| SO_2 , NO_x and other | From column heating furnaces | From column heating furnaces |
| pollutants arise from | | |
| furnaces | | |
| Hydrocarbons | May be released from pressure | May be released from pressure |
| | reliefs, storage, handling | reliefs, storage, handling operations, |
| | operations, spillages and | spillages and fugitive emissions and |
| | fugitive emissions and water | water and waste discharges |
| | and waste discharges | |
| Halogens | n.a. | Fluoride compounds may be released |
| | | from pressure reliefs, vent gas and |
| | | spillages |
| Odours | n.a. | Acid-soluble oil may be released from |
| | | process shut-down ponds during |
| | | maintenance work, particularly the |
| | | de-scaling of pipes conveying |
| | | hydrogen fluoride. This may be |
| | | odorous |

(b) Base oil production

Air emissions may arise from fugitive solvent emissions and process vents.

(c) Bitumen production

The main problem with bitumen production relate to hydrogen sulphide releases from the distilled residues and sour condensates and gas produced in the blowing process. Hydrocarbons and sulphur compounds may emanate from leakages (particularly on overhead systems) and pressure relief valves and in the form of aerosol-containing liquid droplets from the venting of tanker top-loading operations.

(d) Catalytic cracking

Within a refining complex, one of the sources with major potential for atmospheric emissions is the catalytic cracking unit. Air emissions come principally from the regenerator and are mainly CO, CO₂, NO_x, particulates (mainly catalyst fines) and SO₂.

(e) Catalytic reforming

Air emissions from catalytic reforming arise from the process heater gas, fugitive emissions (hydrocarbons from pressure relief valves and leakages) and regeneration. Hydrocarbons and dust releases may arise from venting during catalyst replacement procedures and during clean-out operations.

(f) Coking processes

Air emissions from coking operations include the process heater flue gas emissions and fugitive emissions. In addition, the removal of coke from the drum (delayed coking) can release particulate and any remaining hydrocarbons to the atmosphere. The main pollutants generated as well as the sources are described below:

- hydrogen sulphide and sulphur compounds as mercaptans may be released from the sour water stream from reflux condensers.
- hydrocarbons may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling operations, spillages and waste and water discharges.
- particulate matter may be released from the kiln gas cleaning system, the rotary cooker gas cleaning system, coke handling and storage, loading operations and from the calcinatory process.

(g) Desalting

No major emissions to the air are produced during the desalting processes. Air emissions from the heating processes are expected and fugitive emissions (hydrocarbons) may be expected.

(h) Etherification

Potential releases into air are of hydrocarbons from pressure reliefs on vessels, depentaniser column overheads drum and distillation column reflux drum, methanol plant, steaming vents on scavengers and reactor catalyst.

(i) Gas separation processes

Potential releases into air are of hydrocarbons from pressure reliefs on vessels, regeneration vent gas from molecular sieves, C₁/C₂ refinery fuel gas, refrigeration system leaks, storage and handling operations. Mercury if present in the feedstock of the refinery, will concentrate in overhead sections, particularly coolers. LPG, tops and naphtha coolers are most likely involved. Steaming that contaminated equipment may give mercury emissions to atmosphere. Upon opening equipment for inspection and maintenance mercury is sometimes found. The final process in LPG production is the addition of some odorants. The odorants used are typically volatile organic sulphur compounds, i.e. mercaptans and sulphides. Potential releases into air include leaks or spillages of odorant and vapours displaced during tank filling or from thermal expansion of blanket gas. Also the products of incinerating or flaring displaced vapours if these techniques use used, including a small release of sulphur dioxide from combustion of the odorant.

(j) Hydrogen-consuming processes

Air emissions from hydrotreating may arise from process heater flue gas, vents, fugitive emissions and catalyst regeneration (CO_2 , CO, NO_x , SO_x). The off-gas stream may be very rich in hydrogen sulphide and light fuel gas. The

fuel gas and hydrogen sulphide are typically sent to the sour gas treatment unit and sulphur recovery unit. Hydrocarbons and sulphur compounds from pressure relief valves; leakages from flanges, glands and seals on pumps, compressors and valves, particularly on sour gas and sour water lines; venting during catalyst regeneration and replacement procedures or during cleaning operations.

(k) Hydrogen production

 NO_x emissions are the most important to consider. Other emissions such as SO_x or water emissions are minimal, because low-sulphur fuel is typically used and there are few emissions other than flue gas.

(I) Isomerisation

Emissions may arise from the process heater, vents and fugitive emissions. Other emissions are HCI (potentially in light ends from organic chloride added to increase catalyst activity), vents and fugitive emissions, pressure reliefs on surge drum, separators and column reflux drum, regeneration vent gas from dryers, storage and handling operations, spillage (hydrocarbons). Releases of hydrogen may occur from pressure relief on the hydrogen system. Product stabilization, however, does result in small amounts of LPG (C_3+C_4 , rich in i- C_4) and in stabilizer vent ($H_2+C_1+C_2$) products. The stabilizer vent products are usually used as fuel.

(m) Polymerisation

Potential releases into air are of hydrocarbons from pressure reliefs, storage and handling operations, spillages and water and waste discharges, and of particulate matter from catalyst fine from handling and disposal of spent catalysts. Sulphur dioxide and H₂S may arise during the caustic washing operation.

(n) Primary distillation units

Potential releases into air are from:

- Flue gases arising from the combustion of fuels in the furnaces to heat the crude oil.
- Pressure relief valves on column overheads; relief from overhead accumulator are piped to flare as well as the vent points.
- Poor containment in overhead systems, including barometric sumps and vents.
- Glands and seals on pumps, compressors and valves.
- De-coking vents from process heaters. During furnace decoking (once or twice a year) some emission of soot can occur if operation is not properly controlled in terms of temperature or steam/air injection.
- Venting during clean-out procedures.
- Some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of non-condensable light hydrocarbons and hydrogen sulphide passes through the condenser to a hot well, and is then discharged to the refinery sour fuel system or vented to a process heater, flare or other control device to destroy hydrogen sulphide. The quantity of these emissions depends on the size of the unit, the type of feedstock and the cooling water temperature. If barometric condensers are used in vacuum distillation, significant amounts of oily waste water can be generated. Oily sour water is also generated in the fractionators.

5.2 Overall Emission from Natural Gas Plants

The major emission sources in the natural gas processing industry are compressors, boilers and furnaces, acid gas wastes, fugitive emissions from leaking process equipment and, if present, glycol dehydrator vent streams. Regeneration of the glycol solutions used for dehydrating natural gas can release significant quantities of benzene, toluene, ethylbenzene and xylene, as well as a wide range of less toxic organics. Potential release routes for prescribed substances and other substances which may cause harm are shown in **Table 4** below:

| Table 4: | Releases to the Environment Associated With the Natural | |
|----------|---|--|
| | Gas Processes | |

| | H₂S | SO ₂ | NO _x | CO, CO ₂ | Organic compounds | N ₂ |
|----------------------------|--------------|-----------------|-----------------|---------------------|----------------------|----------------|
| On-shore reception | $\sqrt{*}$ | | | | | |
| Gas treatment processes | $\sqrt{*}$ | | \checkmark | \checkmark | \checkmark | |
| Acid gas processes | √* | $\sqrt{*}$ | \checkmark | \checkmark | \checkmark | |
| Nitrogen removal | $\sqrt{*}$ | | | | \checkmark | |
| Hydrocarbon removal | | | | | \checkmark | |
| Gas compression | | | \checkmark | \checkmark | | |
| Condensate treatment | | | \checkmark | \checkmark | \checkmark | |
| Field water treatment | | | | | \checkmark | |
| Flares/vents | $\sqrt{*}$ | √* | \checkmark | \checkmark | \checkmark | |
| Gas storage sites | \checkmark | \checkmark | \checkmark | \checkmark | | |
| * if sour gas is being pro | ocessed | | | | | |

6.0 BEST AVAILABLE TECHNIQUES FOR OIL AND GAS REFINERIES

A refinery consists of a number of single process units. The way these single units are built up into an integrated refinery can have a considerable effect on the emissions. In determining BAT, the environmental effects of the single units and of the whole refinery have to be considered. In this chapter BAT for refinery (oil and gas) are given both in generic and specific forms.

6.1 Generic BAT (Whole Refinery)

6.1.1 BAT for Good Housekeeping and Environmental Management

These good housekeeping/management techniques/tools often prevent emissions. BAT is to:

- (a) Implement and adhere to an Environmental Management System
 (EMS) which should include:
 - the practice of benchmarking on a continuous basis, including energy efficiency and energy conservation activities, emissions to air (SO₂, NO_x, VOC, and particulates), discharges to water and generation of waste.
 - improve stability of unit operation by applying advanced process control and limiting plant upsets, thereby minimizing times with elevated emissions (e.g. shutdowns and startups).
 - apply good practices for maintenance and cleaning.
- (b) Implement a monitoring system that allows adequate processing and emission control as specified in section 7 of this document.
- (c) Reduction of sulphur dioxide emissions. BAT is to reduce sulphur dioxide emissions by:
 - Quantifying the sulphur emissions from various refinery sources to identify the main emitters in each specific case
 - Efficient operation of the sulphur recovery unit
 - Using BAT applicable to SO_x reduction

- (d) Reduction of Nitrogen Oxides. BAT is to reduce nitrogen oxides emissions by:
 - Quantifying the NO_x emission sources in order to identify the main emitters (e.g. furnaces and boilers, the FCC regenerators and gas turbines) in each specific case.
 - Using BAT applicable to NO_x reduction in the energy system and catcracker
- (e) Reduce particulate emission by:
 - Quantifying the particulate emission sources (especially furnaces and boilers, the FCC regenerators and cokers) in order to identify the main emitters in each specific case
 - Minimizing the particulate emissions from solids handling situations (catalyst loading/unloading, coke handling, sludge transport) by applying good housekeeping and control techniques
 - Using BAT applicable to particulate reduction in the energy system, catcrackers and cokers
- (f) Reduce volatile organic carbons emissions by:
 - Quantifying VOC emission sources in order to identify the main emitters in each specific case.
 - Using a maintenance drain-out system.
 - Selecting and using low-leakage valves such as graphite-packed valves or equivalent (especially important for control valves) for lines containing product with a high vapour pressure
 - Using low leak pumps (e.g. seal-less designs, double seals, with gas seals or good mechanical seals) on product lines carrying fluid with a high vapour pressure
 - Minimizing flanges (easier to apply in the design stage), installing sealing rings on leaking flanges and use of high integrity sealing materials (fire safe) in flanges (very important for heat exchangers)
 - Blinding, plugging or capping open-ended vent and drain valves
 - Routing relief valves with high potential VOC emissions to flare

- Routing compressor vents with high potential for VOC emissions back to process and when not possible (e.g. vent compressor distance pieces) to refinery flare for destruction
- Using totally closed loop in all routine samplers (for what is understood by routine sampler) that potentially may generate VOC emissions
- Minimizing flaring
- Using BAT applicable to VOC reduction in storage and handling

6.2 BAT for Process/Activity

This section presents BAT elements for each process/activity covered in this document.

- (a) BAT for Alkylation is to use either:
 - HF alkylation and it is also BAT to reduce HF emissions to levels < 1 mg/Nm³ by scrubbing
 - Sulphuric acid alkylation and it is also BAT to minimize and regenerate spent sulphuric acid.
- (b) BAT for Base Oil Production:
 - Use triple effect evaporation systems in the solvent recovery sections of deasphalting, extraction and dewaxing process units.
 - Use N-methyl pyrrolidone (NMP) as solvent in the aromatic extraction.
 - Use hydrotreating for clean-up of the base oil streams and wax finishing if final clean-up is required
 - Apply prevention techniques for VOC emissions from solventcontaining systems (e.g. storage).
 - Apply BAT on sulphur recovery units in stand-alone lube refineries

- (c) BAT for Bitumen Production is to:
 - Reduce aerosol and VOC emissions (considered as a part of the odour abatement programme) by selecting between recovering the liquid element of the aerosol that is directed to vents from storage and during the blending/filling operations of bitumen (e.g. wet electrostatic precipitator, oil scrubbing) or incineration at a temperature over 800 °C or in process heaters.
 - Apply leakage prevention measures (as part of the waste management) to prevent waste generation
 - Apply BAT on sulphur recovery units in stand-alone bitumen refineries
 - Treat the overheads from the oxidiser for removal of air contaminants (e.g. oil, solid, VOC) (as part of the odour abatement programme). If incineration is used, the blow gas can be used in process heaters

(d) Catalytic Cracking

A catalytic cracking unit is usually part of a processing complex that includes a gas plant, amine treating of the light gases and treatment of various product streams. BAT determinations for these associated activities are dealt with in the respective parts (gas separation processes, hydrogen-consuming processes and waste gas treatments) of this section. For the catcracker itself (reactor, regenerator, fractionator, catalyst receipt, storage/loading, wet gas compressor, absorber and debutaniser) the main specific BAT determinations are given above. Solutions and measures should be considered in an integrated way with measures and solutions in other units. In this respect BAT is to:

 Include a CO-furnace/boiler for partial oxidation conditions. Under those conditions and without abatement measures associated CO emission levels are 50 - 100 mg/Nm³ and for NOx emissions are 100 – 300 mg/Nm³. Low figures for CO and NO_x are not typically achieved at the same time.

- Monitor and control O₂ (typically at 2%) for full combustion plants, resulting in a CO emission level of 50 100 mg/Nm3 and 300 600 mg NOx/Nm3 in absence of a downstream CO boiler. Low figures for CO and NOx are not typically achieved at the same time.
- Reduce NO_x emission to 40 150 mg/Nm³ (lower end is only applicable when SCR and low sulphur feedstock are used) by a suitable combination of:
- Modification of the design and operation of regenerator, especially to avoid high temperature spots. This technique may raise the CO emissions and cannot be environmentally justified if a major or complete revamp is necessary.
- Hydrotreatment of the feedstock if it is economically and technically viable. This technique is easier to implement when amine scrubbing and Claus capacities and hydrogen are available.
- Using SNCR on the regenerator flue gas, achieving a NOx reduction of 60 70 %
- Using SCR on the regenerator flue gas, achieving a NO_x reduction of 85 90%. Associated emissions of ammonia slip is 2 5 mg/Nm³. Ammonia slip concentrations may increase at the end of the catalyst life.
- Reduce particulates emissions to 10 40 mg/Nm³ (upper end of the range applicable to feedstocks with very low sulphur/metal content. Because of poor reliability of the particulates monitoring system and technical difficulties in upgrading the existing ESPs, the upper

range can be difficult to reach. In those cases 50 mg/Nm³ is seen as a more achievable level) by a suitable combination of:

- tertiary and multistage cyclones
- applying an ESP or scrubber to the FCC regenerator gas.
 Efficiencies associated with BAT range are 95 99 %
- hydrotreatment of the feedstock if it is economically and technically viable.
- selecting attrition-resistant catalyst to decrease the frequency of replacement and reduce the particulate emissions
- Reduce SO₂ emission to 10 350 mg/Nm³ (lower end of the range only achievable when both low sulphur feedstock and FGD are used) by a suitable combination of:
 - hydrotreatment of the feedstock if it is economically and technically viable
 - using DeSOx catalyst additive
 - using FGD of the regenerator gas with 95 99 % efficiency
- (e) BAT for Catalytic Reforming is to:
 - route the regenerator gas generated during the catalyst regeneration to a scrubbing system. Send the bleed stream from the scrubbing system to the WWTP.
 - optimise the amount of chlorinated promoters in the regeneration of the catalyst
 - quantify the dioxin emissions from the catalyst regenerator.
- (f) BAT for Coking Processes is to:
 - route sour gas produced from cokers to sulphur treatment
 - reduce particulate emissions (containing metals):
 - by collecting and recycling, as much as possible within the refinery the coke fines generated in the coking processes

- by proper handling and storing of coke including construction of wind breaks around the green coke pit or storing it in completely enclosed facilities
- by covering the conveyor belts and de-pressurising with filters
- by enclosing loading areas, keeping them under negative pressures and exhausting the collected air through bag filters or by using dust extraction incorporated with the loading equipment
- Reduce emission to 10 50 mg/Nm³ by applying ESP and/or cyclones and/or filters from the different flue gases containing particulates
- Reduce SO₂ emissions from the calcination flue gas to 25 to 300 mg/Nm³ by applying FGD techniques (efficiency >90 %).
- (g) BAT for Desalting is to:
 - Use multistage desalters for new facilities.
- (h) BAT for Etherification is to:
 - Apply heat integration either in the unit itself or within the refinery
- (i) BAT for the Gas Separation Processes is to:
 - preventing any release of odorant to any environmental medium during storage and handling (e.g. blanket storage)
 - reduce VOC fugitive emissions
- (j) BAT for Hydrogen consuming Processes is to:
 - route off-gases containing H₂S to amine systems and SRU
 - use on-stream catalyst replacement for high-metal feedstocks
 - promote catalyst regeneration options in co-operation with the catalyst suppliers/manufacturers where possible

- (k) BAT for Hydrogen Production is to:
 - recover hydrogen from the gasification processes of heavy fuel oil and coke if the technology is applied in the refinery
 - use PSA purge gas as fuel gas within the refinery
- (I) Isomerisation is to:
 - use other catalytic systems (e.g. zeolite)
 - Optimize the use of chlorinated organic compounds used in maintaining the catalyst activity
- (m) BAT for Natural Gas Plants is to:
 - apply generic BAT including good housekeeping and Environmental Management and BAT related to reduction of air, water and solid emissions
 - apply BAT for Waste Gas Treatments
 - use as fuel preferably gas that is of saleable quality (typically less than 5 mg of H₂S/Nm³)
 - consider, particularly for large carbon dioxide flows, alternatives to direct releases of CO₂
- (n) BAT for Polymerisation is to:
 - optimise the catalyst consumption
 - properly manage the unused on-site catalyst for disposal or re-use off site
- (o) BAT for Primary Distillation Units

The main refinery process is the Atmospheric Crude Distiller. In fact, it is a complex process, normally including a desalter, a gas plant, hydrotreaters, amine treaters, a sour water stripper and sometimes also an integrated high-vacuum unit. So the respective BAT as determined for the specific processing units (gas plants, hydrotreaters etc.) needs to be observed. BAT is to:

- maximize the use of liquid ring vacuum pump and surface condensers in place of some stage steam jet ejectors on the vacuum tower overhead.
- apply advanced process control to optimize energy utilization
- (p) BAT for Visbreaking is to:
 - apply deep thermal conversion, hydrovisbreakers or soaker visbreakers
 - sweeten the gas from visbreaking
 - treat gas and effluent water because of the presence of sulphur compounds
 - reduce the coke formation. It may be reduced by controlling the sodium content in the visbreaker feedstock or by using additives that decelerate the coke-formation.
- (q) BAT for sulphur recovery units (SRU)is to:
 - apply a staged SRU, including tail gas treatment with a recovery efficiency of 99.5 % to 99.9 % (based on acid gas feed to the SRU).
 - use state-of-the-art control and monitoring systems.

7.0 RECOMMENDED EMISSION VALUES

Control of air emissions normally include the capture and recycling or combustion of emissions from vents, product transfer points, storage tanks and other handling equipments. Boilers, heater, other combustion devices, cokers and catalytic units may require particulate matter control. The following features can be incorporated for new refineries

(a) New refineries should be designed such that fugitive VOC emissions from the process units can be reduced to 0.05% of the throughput, with

total VOC emissions of less than 1 kg per ton of crude (or 0.1% of throughput).

- (b) Vapor recovery systems to be fixed to control losses of VOCs from storage tanks and loading areas should achieve 90–100% recovery.
- (c) Plant operators should aim at using fuel with less than 0.5% sulfur (or an emissions level corresponding to 0.5% sulfur in fuel). High-sulfur fuels should be directed to units equipped with SO_x controls. Fuel blending is another option. A sulfur recovery system that achieves at least 97% (but preferably over 99%) sulfur recovery should be used when the hydrogen sulfide concentration in tail gases exceeds 230 mg/Nm³.

The total release of sulfur dioxide should be below 0.5 kg per ton for a hydro skimming refinery and below 1 kg per ton for a conversion refinery.

8.0 EMISSION MONITORING

The monitoring system should allow adequate processing and emission control. And therefore some elements of a monitoring system could include:

- continuous monitoring of pollutants for high volume flows with a high variability in pollutant concentrations
- periodic monitoring or the use of emission relevant parameters for flows with a low variability
- regular calibrating of measurement equipment
- periodic verification of measurement by simultaneous comparative measurements.

In order to have a good idea of the emissions generated by an installation, the emissions need to be quantified. This will give to the refinery the possibility to know where the actions to reduce a certain pollutant may be more economical. Typically higher emissions at high concentrations are more economic to be abating that lower emissions at low concentrations.

In many refineries the bubble concept is applied for some air pollutants. Where the concept is to consider the refinery as a whole and to sum up concentrations and volumes of all the emission sources. From this is calculated the average concentration of the pollutants regardless of the source or stack. SO_2 , NO_x , particulate matter, and CO are typically monitored in continuous (on-line or predictive) in the refineries. **Table 5** below shows the locations where the main air pollutants are typically continuous monitored in a refinery.

| Parameter | Location where normally is measured | | | | |
|--------------------|--|--|--|--|--|
| | Combustion processes burning fuel oil | | | | |
| | FCCU regenerators | | | | |
| Particulate matter | Coking processes and petroleum coke calciners and coolers | | | | |
| | Gasification units | | | | |
| | Catalyst regeneration (e.g. reforming) | | | | |
| | FCCU regenerators | | | | |
| | Sulphur recovery units (i.e. from tail gas incinerators) | | | | |
| Sulphur dioxido | Incinerators or furnaces used to burn sour gas or liquid fuels | | | | |
| Sulphur dioxide | Bitumen production units | | | | |
| | Gasification units | | | | |
| | Coking processes | | | | |
| Oxides of nitrogen | Combustion processes | | | | |
| | FCCU regenerators | | | | |
| | Gasification units | | | | |
| | Coking processes | | | | |
| | FCCU regenerators (for partial combustion type units if CO release | | | | |
| Carbon monoxide | is significant). | | | | |
| | Combustion processes | | | | |

 Table 5: Locations Where the Main Air Pollutants are Typically

 Monitored In A Refinery.

REFERENCES

 European Integrated Pollution Prevention and Control Bureau (EIPPCB), (February 2013). Best Available Techniques (BAT) Reference Document for Mineral Oil and Gas Refineries. Joint Research Centre, Institute of Prospective Technological Studies, EIPPCB.