

7.4 Mineral Oil and Gas Refineries for SO₂, NO_x and dust emissions

7.4.1 Coverage

The section covers emissions from combustion processes in refineries burning non-commercial fuels or a mixture of commercial and non-commercial fuels, to Fluidised Catalytic Cracking units and to Sulphur Recovery units.

Refinery fuels are highly variable in nature and comprise both liquid and gaseous streams often used in conjunction. A significant part of the fuel used for process heaters is provided by refinery gas. Various processes contribute a large variety of compounds to the refinery gas, resulting in varying emissions. Other fuels in use in mineral oil refineries are natural gas, petroleum coke, heavy fuel oil, or other residues originating from atmospheric and vacuum distillation, fluid catalytic cracking (FCC) and thermal catalytic cracking (TCC). Refinery processes such as FCC may involve combustion of coke laid down on the catalyst and CO as well as supplementary fuel for steam raising. Use of petroleum coke as a gasification feedstock occurs but is not very common.

Many refinery units discharge through a common stack. The emissions from refineries associated with the key processes in this chapter are NO_x, SO_x and Dust.

7.4.2 Emission sources

In the following, the focus is on emissions from processes used in the production of refined products from crude oil. These include process heaters and boilers, power generation and recovery, catalytic cracking and sulphur recovery.

Process heaters and boilers

In most refining processes it is necessary to apply heat to raise the temperature of the feedstock to a required level. Fired process heaters and boilers are the main heat producers. Process heaters are mostly installed at the atmospheric distillation, before the vacuum distillation, before the FCC units and before the sulphur units. Refineries can have many process heaters, with different feedstock. [1].

Gas turbine installations are used for the transformation of thermal energy into mechanical energy. They use a steady flow of a gas (mostly air), compressed and fired with (sometimes non-commercial) gaseous or liquid fuel. Steam turbines are used to transform the steam pressure to power. Combined cycle processes combine the gas and steam turbines processes to produce power at higher efficiency than is reached with open-cycle turbines.

Integrated gasification combined cycle (IGCC) is a technique for producing steam, hydrogen and electric energy from a variety of low-grade fuel types. The gasified solid fuel is burned in the combustion chamber of the gas turbine. Emissions from IGCC are low. The technology also exists for heavy oil residue. However, this process is not yet fully commercialized, a number of demonstration units, mainly around 250 MWe size are being operated in Europe and the USA.

(Fluid) Catalytic cracking (FCC) 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. A catalytic cracking unit is usually part of a processing complex that includes a gas plant, amine treating of the light (incl. C₃/C₄) gases and treatment of various product streams. [3]

Sulphur Recovery Units (SRU) typically comprise a Claus unit and a tail gas unit. They recover elemental sulphur from the H₂S recovered in the acid gas removal section and a tail gas treatment section that maximise the overall sulphur recovery. They work by partial combustion of the hydrogen sulphide-rich gas stream and then reacting the resulting sulphur dioxide and unburned hydrogen sulphide in the presence of a catalyst to produce elemental sulphur. [3]

7.4.3 BAT, Associated Emission Levels (AEL)

7.4.3.1 SO₂

The release of sulphur dioxides is directly linked to the sulphur content of the refinery fuel gas and fuel oils used. Heavy fuel oil residues normally contain significant proportions of sulphur and nitrogen depending mainly on their source and the crude oil[2].

Various flue gas desulphurisation techniques exist with SO₂ removal efficiencies ranging from 50 to 99.99%. SO₂ is removed in general from the flue gas by means of wet scrubbers (lime/limestone, Wellman-Lord, seawater, wet gas sulphuric acid process WSA), spray dry scrubbers, application of sorbent injection and regenerative processes. By using wet lime/limestone reduction rates from 90 to 98% are achievable. With additive injection and spray dry scrubbers reduction rates above 92% are achievable. However, these efficiency figures are dependent on input concentrations, sizes of units and their specific application.

In general the reduction of the fuel consumption is considered to be BAT.

The use of low sulphur content for the overall refinery liquid fuel pool achieved for example, by hydrodesulphurisation, is considered to be BAT and FGD for large boilers/furnaces where it is cost-effective. Fuel switching is also an option.

For catalytic cracking, SO₂ emission reduction by using a suitable combination of: hydrotreatment of the feedstock if it is economically and technically viable, Sulphur Reducing Additives (SRA), FGD of the regenerator gas with 95 – 99 % efficiency (emission target depends on uncontrolled level) is considered BAT. [3]

Wet scrubbing (for example Wellman Lord scrubbing) is one option for FGD, a suitably well designed process will normally provide an effective removal efficiency of both SO₂/SO₃ and particulates. With the inclusion of an extra treatment tower, to oxidise the NO to NO₂, NO_x can also be removed partially. [3]

Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulphide. This is typically accomplished by dissolving the hydrogen sulphide in a chemical solvent (absorption). Solvents most commonly used are amines. [3]

For sulphur recovery units (SRU), it is BAT to apply a staged SRU, including tail gas treatment with the recovery efficiency given below (based on acid gas feed to the SRU), the range depends on cost effectiveness considerations. [3]

Table 1 Emission sources and selected BAT SO_x control measures with associated emission levels in mineral oil refineries

Emission source	Combination of control measures	SO _x emission level associated with BAT ¹ (mg/Nm ³)[3]
Fuel type: refinery fuel gas		
Heaters, Boilers, Gas turbines	Use of sulphur removal techniques for fuel gas And use of monitoring	5 –20 ¹ when using fuel gas by cleaning refinery fuel gas
Fuel type: liquid fuel		

¹ As values are expressed on a dry basis, this value has to be adjusted for hydrocarbon-hydrogen mixtures. The upper value range thus increases in proportion to the fuel hydrogen content having a value of 35 at a fuel H₂ concentration of 50% v.

Heaters, Boilers	Combination of: Hydrodesulphurization Use of FGD techniques (where feasible and cost-effective)	50 – 850 for the total refinery liquid fuel pool
Catalytic cracking		
Catalytic cracking	Suitable combination of: Hydrotreatment of the feedstock if it is economically and technically viable Sulphur Reducing Additives (SRA) FGD of the regenerator gas	10-350
Sulphur Recovery Units (SRU)		
Sulphur recovery rate ²	New plants Existing plants	99.5-99.9% 98.5-99.5%
Sulphur recovery unit	Staged SRU	400-2000
¹ The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded. ² The sulphur recovery rate is the percentage of the imported H ₂ S converted to elemental sulphur as a yearly average Oxygen reference: dry basis, 3% for combustion, 15 % for gas turbines		

7.4.3.2 NO_x

Refinery NO_x emissions primarily originate from combustion units and catalytic cracking. Besides the relevance of the fuel type, NO_x emissions depend upon fuel type, on fuel nitrogen content (for liquid fuels) or hydrogen content and C3+ content (for gaseous fuels), burners and heaters design, and operating conditions.[4]

In general, the reduction of the fuel consumption and the replacement of existing burners with low-NO_x burners during major scheduled shutdowns is considered to be BAT.

For heaters and boilers burning gas fuel an application of a suitable combination of the following primary and secondary measures allowing to achieve emissions levels from 20 to 150 mg/Nm³ is considered to be BAT [3]:

- High thermal efficiency furnace/boiler designs with good control systems
- Low-NO_x burners technique
- Flue gas circulation in boilers
- SCR or SNCR

For heaters and boilers burning combinations of gas and liquid fuel (liquid fuel as majority fuel) an application of a suitable combination of the following primary and secondary measures allowing to achieve emissions levels from 55 to 300 mg/Nm³ is considered to be BAT [3]:

- Fuel with low nitrogen content

- Low-NO_x burners technique
- Flue gas circulation in boilers
- Reburning technique
- SCR or SNCR to liquid fuels heavier than gasoil type

For gas turbines an application of a suitable combination of the following primary and secondary measures allowing to achieve emissions levels from 20-75 mg/Nm³ is considered to be BAT [3]:

- Diluent injection
- Dry low NO_x combustors
- SCR

Table 2 Emission sources and selected BAT NO_x control measures with associated emission levels in mineral oil refineries

Emission source	Combination of control measures	NO _x emission level associated with BAT ¹ (mg/Nm ³) [3]
Fuel type: refinery fuel gas		
Heaters, Boilers	<ul style="list-style-type: none"> - high thermal efficiency designs with good control systems - low-NO_x burners technique - flue gas circulation in boilers - SCR or SNCR. 	20 – 150 ²
Gas turbines burning either gas or light liquid fuels	<ul style="list-style-type: none"> - diluent injection - dry low NO_x combustors - SCR 	20 – 75 (lower levels for natural gas and higher levels for small gas turbines and RFG)
Fuel type: heavy liquid fuel firing (majority fuel)		
Heaters, Boilers	<ul style="list-style-type: none"> - liquid fuel with low nitrogen content - low-NO_x burners technique - flue gas circulation in boilers - SCR or SNCR to liquid fuels heavier than gasoil type 	55 – 300 ²
Catalytic cracking		
Catalytic cracking	CO-furnace/boiler for partial oxidation conditions	100-300
	for full combustion plants	300-600
	Combination of (if economically viable): modification of the design and operation of regenerator, hydrotreatment of feedstock, SCR, SNCR	40-150
¹ The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded. ² in the EU-BREF, several split views exist about BAT AELs Oxygen reference: dry basis 3% for combustion, 15 % for gas turbines		

7.4.3.3 Dust

The main emission sources of particulate matter in refining are process heaters and boilers firing liquid heavy fuel oil, catalytic cracker regenerators, coke plants, incinerators, decoking and soot blowing of heaters and the flare.

The emission levels of particulate matter depend on various parameters such as fuel type, burner design, and oxygen concentration at the outlet of the radiant section and can vary widely.

The particulate matter emissions from furnace and boilers burning heavy fuel oil consist of a mix of ash, soot and unburned carbon. Mineral matter is a natural component of crude oil and becomes ash during combustion of heavier fuel oils. Soot and unburned carbon result from imperfections in the combustion process.

The size of the particulate matter from heaters and boilers burning heavy fuel oil is in the order of 1 µm. Particulate matter removal techniques mainly used are ESPs. An application of a suitable combination of the following techniques is considered to be BAT for the reduction of particulate matter:

- Reduction of the fuel consumption
- Maximizing the use of gas and low ash content liquid fuels
- Improved atomisation on the liquid fuels
- The use of ESP or filters in the flue gas of heaters and boilers when burning heavy liquid fuel [3]

Table 3 Emission sources and selected BAT dust control measures with associated emission levels in mineral oil refineries

Emission source	Combination of control measures	Dust emission level associated with BAT ¹ (mg/Nm ³)
Fuel type: heavy liquid fuel (majority fuel)		
Heaters, boilers	By a combination of <ul style="list-style-type: none"> - Reduction of the fuel consumption - Maximizing the use of gas and low ash content liquid fuels - Steam atomisation on the liquid fuels - Use of ESP or filters 	5 – 20 [3] (split view industry: 5-50)
FCC regenerators	process integrated measures, ESP, mechanical filters, third stage cyclones, scrubbers level) by a suitable combination of:	10-40 ² [5]
<p>¹ The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.</p> <p>² If technical difficulties in upgrading the existing ESPs, the upper range can be difficult to reach. In those cases 50 is seen as a more achievable value [3]</p> <p>Oxygen reference: dry basis, 3% for combustion, 15 % for gas turbines</p>		

7.4.4 Emerging techniques

Emerging techniques in the field of SO₂ emission reduction are SO₂ capture from flue gas and subsequent conversion into liquid sulphur as well as biological H₂S removal [3].

7.4.5 References used in chapter 7.4

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[2] Environment Agency: Guidance for the gasification, liquefaction and refining sector, 2003

[3] European commission: Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries, Integrated Pollution Prevention and Control (IPPC), February 2003

[4] O. Rentz, S. Nunge, M. Laforsch, T. Holtmann: Technical Background Document for the Actualisation and Assessment of UN/ECE Protocols related to the Abatement of the Transboundary Transport of Nitrogen Oxides from Stationary Sources, Task Force on the Assessment of Abatement Options/Techniques for Nitrogen Oxides from Stationary Sources, Karlsruhe, September 1999

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