

Category		Title			
NFR	1.B.2.a.iv	Fugitive emissions oil – refining/storage			
SNAP	0401 040101 040102 040103 040104 040105	Processes in petroleum industries Petroleum products processing Fluid catalytic cracking — CO boiler Sulphur recovery plants Storage and handling of petroleum products in refinery Other			
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# **1 Overview**

This chapter treats emissions from the petroleum refining industry. This industry converts crude oil into more than 2 500 refined products, including liquid fuels (from motor gasoline to residual oil), by-product fuels and feedstock (such as asphalt, lubricants, gases, coke), and primary petrochemicals (for instance, ethylene, toluene, xylene). Petroleum refinery activities start with the receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and terminate with storage preparatory to shipping the refined products from the refinery (US EPA, 1995b, 2006a).

Not all processes that could result in the emissions to the air are included in this chapter:

emissions from the crude oil feed stock handling are covered by chapter 1.B.2.a.i;

- combustion processes are covered by chapter 1.A.1.b;
- emissions from flaring are covered by chapter 1.B.2.c. Incineration of ground flares is also included in chapter 1.B.2.c and not in 6.C.b, since the latter chapter focuses on solid and liquid wastes, not gases;
- emissions from asphalt (bitumen) blowing are covered by chapter 3.C;
- emissions due to loading at refinery dispatch facilities are covered by chapter 1.B.2.a.v;
- emissions due to waste water treatment in refineries and sulphur recovery are included in this chapter;
- estimating non-methane volatile organic compounds (NMVOC) emissions due to spills and accidental discharges is considered outside the terms of reference for this manual. Also, emissions from the production of primary petrochemicals are not included, even if these chemicals are produced at a petroleum refinery. Refer to Chapter 2.B Chemical industry for guidance on estimating emissions from the chemical industry.

Petroleum refineries are sources of  $SO_2$  and NMVOC emissions, and less significant sources of particulates,  $NO_x$  and CO.

# **2** Description of sources

### 2.1 Process description

The petroleum refinery industry employs a wide variety of processes. The types of processes operating at one facility depend on a variety of economic and logistic considerations such as the quality of the crude oil feedstock, the accessibility and cost of crude (and alternative feedstock), the availability and cost of equipment and utilities, and refined product demand.

Four main categories can be distinguished within the processes in a petroleum refinery:

#### 1. Separation processes

Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons plus small amounts of impurities including sulphur, nitrogen, oxygen and metals. The first phase in petroleum refining operations is the separation of crude oil into common boiling point fractions using three petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing).

#### 2. Conversion processes

Where there is a high demand for high-octane gasoline, jet fuel and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasoline and other light fractions. Cracking, coking and visbreaking processes break large petroleum molecules into smaller petroleum molecules. Polymerization and alkylation processes rearrange the structure of petroleum molecules into larger ones. Isomerisation and reforming processes rearrange the structure of petroleum molecules to produce higher-value molecules of a similar size.

#### 3. Treating processes

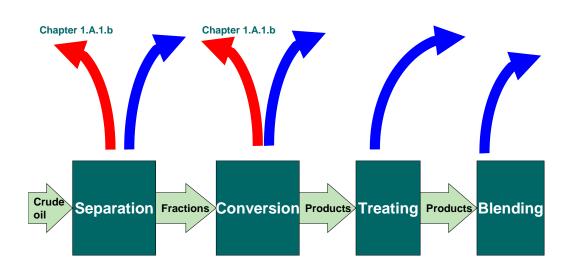
Petroleum-treating processes stabilise and upgrade petroleum products. De-salting is used to remove salt, minerals, grit, and water from crude oil feedstock prior to refining. Undesirable elements such as sulphur, nitrogen and oxygen are removed from product intermediates by hydrodesulphurization, hydro treating, chemical sweetening and acid gas removal. De-asphalting is used to separate asphalt from other products. Asphalt may then be polymerised and stabilised by blowing (see sub-sector 3.C Chemical products).

#### 4. Blending

Streams from various units are combined to produce gasoline, kerosene, gas oil and residual oil, and in some cases a few speciality items.

Figure 2-1 gives an overview of the 4 main categories described in this section.

# Figure 2-1 Process scheme for source category 1.B.2.a.iv Refining and storage. Red arrows indicate combustion emissions; these are accounted for in NFR source category 1.A.1.b Petroleum refining. Blue arrows indicate process emissions which are considered in this chapter.



Diffuse emission sources are defined as NMVOC sources not associated with a specific process but scattered throughout the refinery. Fugitive process emissions are a subset of diffuse emissions and sources include valves of all types, flanges, pump and compressor seals, pressure relief valves, sampling connections and process drains. These sources may be used, for example, in the pipelines transporting crude oil, intermediates, wastes or products.

Note that this category will actually include diffuse emissions from all such refinery sources, rather than those sources only associated with process emissions.

#### Sulphur recovery

Sulphur recovery, used at both petroleum refineries and natural gas processing plants, converts byproduct hydrogen sulphide (H<sub>2</sub>S) in sour gas streams to an elemental sulphur product. During initial stages of high-sulphur crude oil or gas processing, process and fuel gases that contain significant amounts of H<sub>2</sub>S are treated in a lean amine solution to absorb the sulphide components. The H<sub>2</sub>S is subsequently stripped to provide either a feed gas to a sulphur recovery plant or the stripped H<sub>2</sub>S may be flared or incinerated at plants where sulphur is not recovered. Further details of sulphur recovery processes are provided in subsection 0 of the present chapter.

#### Storage and handling

Storage and handling of crude oils, intermediates and products in a refinery is one part of the refining process.

Emissions arise as a result of evaporation from storage tanks and the displacement of vapour during filling.

Intermediates and products may be stored in a variety of tanks. This chapter considers the following categories of tanks:

- fixed-roof tanks
- external floating roof
- internal floating roof
- other tank types such as variable vapour space.

Pressure tanks are considered to be minor sources and are not included in this chapter.

# 2.2 Techniques

For storage and handling of products, the following storage tanks can be distinguished:

fixed roof tanks — a typical vertical fixed roof tank consists of a cylindrical steel shell with a
permanently affixed roof, which may vary in design from cone- or dome-shaped to flat. These
tanks are either freely vented or equipped with a pressure/vacuum vent, which prevents the
release of vapours during very small changes in temperature, pressure, or liquid level. This type
of tank is used for the storage of products such as kerosene, gasoil and fuel oil;

Crude oils and volatile products are stored in floating roof tanks. There are two types:

 external floating roof (EFR) tanks — an external floating roof tank typically consists of an opentopped cylindrical steel shell equipped with a roof that floats on the surface of the storage liquid. These tanks are equipped with a seal system, which is attached to the roof perimeter and contacts the ta006Ek wall. The floating roof system and seal act to reduce evaporative losses of the contents. Evaporative losses from the external floating roof design are limited to losses from the seal system and roof fittings (standing storage loss) and any exposed liquid on the tank walls (withdrawal loss);

- internal floating roof (IFR) tanks an internal floating roof tank has a permanent fixed roof as well as an internal floating roof (deck). Fixed roof tanks that have been retrofitted with an internal deck typically have the fixed roof supported by vertical columns within the tank. External floating roof tanks which have been converted to IFR tanks by retrofitting a fixed roof over the EFR typically have a self-supporting fixed roof. A newly constructed internal floating roof tank may have either type of fixed roof. The internal floating roof may be a contact type (deck floats directly on the liquid) or a non-contact type (deck attached to pontoons which float on the liquid surface). Both types incorporate rim seals and deck fittings. Evaporation losses from decks may come from deck fittings, non-welded deck seams, and from the seal fitted in the annular space between the deck and the wall. Generally circulation vents on the fixed roof allow these emissions to freely vent, although pressure/vacuum vents may alternatively be installed;
- variable vapour space tanks these tanks are equipped with expandable vapour reservoirs to
  accommodate vapour volume fluctuations due to temperature and barometric pressure
  changes. These are normally connected to the vapour space of one, or more, fixed roof tanks.
  Lifter roof tanks (a telescoping roof) and flexible diaphragm tanks are two types of variable
  vapour space tanks, but this type of tank is rarely used at refineries. Losses occur from these
  tanks when the variable vapour space is fully filled, e.g. when vapour is displaced by liquid from
  a fixed roof tank into the variable vapour space tank.

# 2.3 Emissions and controls

#### **Process emissions**

Vacuum distillation, catalytic cracking, thermal cracking, sweetening, blowdown systems, sulphur recovery, asphalt blowing and flaring processes have been identified as being potentially significant sources of SO<sub>2</sub> and NMVOC from petroleum products processing, with a relatively smaller contribution of particulate, NO<sub>x</sub> and CO (US EPA, 2006a).

# 2.3.1.1..1 Vacuum distillation

Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high-boiling-point hydrocarbons. The topped crude is separated into common-boiling-point fractions by vaporisation and condensation in a vacuum column at a very low pressure and in a steam atmosphere. A major portion of the vapours withdrawn from the column by steam ejectors or vacuum pumps are recovered in condensers. The non-condensable portion is controlled as described below.

The major NMVOC emission sources related to the vacuum column include steam ejectors and vacuum pumps that withdraw vapours through a condenser.

Methods of controlling these emissions include venting into blowdown systems or fuel gas systems, e.g. for use in furnaces or waste heat boilers (see Chapter 1.A.1 Combustion in energy industries and NFR code 1.A.1.b Petroleum refining). These control techniques are generally greater than 99 per cent efficient in the control of hydrocarbon emissions.

# 2.3.1.1..2 Catalytic cracking

Catalytic crackers use heat, pressure and catalysts to convert heavy oils into lighter products with product distributions favouring the gasoline and distillate blending components.

Fluidised-bed catalytic cracking (FCC) processes use finely divided catalysts that are suspended in a riser with hot vapours of the fresh feed. The hydrocarbon vapour reaction products are separated from the catalyst particles in cyclones and sent to a fractionator. The spent catalyst is conveyed to a regenerator unit, in which deposits are burned off before recycling.

Moving-bed catalytic cracking processes (TCC) involve concurrent mixing of the hot feed vapours with catalyst beads that flow to the separation and fractionating section of the unit.

Aside from combustion products from heaters, emissions from catalytic cracking processes are from the catalyst regenerator. These emissions include NMVOC, NO<sub>x</sub>, SO<sub>x</sub>, CO, particulates, ammonia, aldehydes, and cyanides.

In FCC units, particulate emissions are controlled by cyclones and/or electrostatic precipitators. CO waste heat boilers may be used to reduce the CO and hydrocarbon emissions to negligible levels.

TCC catalyst regeneration produces much smaller quantities of emissions than is the case for FCC units. Particulate emissions may be controlled by high-efficiency cyclones. CO and NMVOC emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater firebox or smoke plume burner.

SOx from catalyst regeneration may be removed by passing the flue gases through a water or caustic scrubber.

### 2.3.1.1..3 Thermal cracking

Thermal cracking units break heavy oil molecules by exposing them to higher temperatures. In viscosity breaking (visbreaking), topped crude or vacuum residuals are heated and thermally topped in a furnace and then put into a fractionator. In coking, vacuum residuals and thermal tars are cracked at high temperature and low pressure with a long residence time. In Europe there are many visbreaking units; coking is less often applied.

Emissions from these units are not well characterised. In delayed coking, particulate and hydrocarbon emissions are associated with removing coke from the coke drum and subsequent handling and storage operations. Generally there is no control of hydrocarbon emissions from delayed coking, although in some cases coke drum emissions are collected in an enclosed system and routed to a refinery flare.

### 2.3.1.1..4 Sweetening

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl disulfides in the presence of a catalyst. Conversion may then be followed by an extraction step in which the disulfides are removed.

Hydrocarbon emissions are mainly from the contact between the distillate product and air in the airblowing step. These emissions are related to equipment type and configuration, as well as to operating conditions and maintenance practices.

# 2.3.1.1..5 Blowdown systems

Many of the refining process units subject to hydrocarbon discharges are manifold into a collection unit (i.e. blowdown system), comprising a series of drums and condensers, whereby liquids are separated for recycling and vapours are recovered, recycled or flared with steam injection (for flaring see chapter 1.B.2.c Venting and flaring).

#### Sulphur recovery plants

Tail gas from a Claus sulphur-recovery unit contains a variety of pollutants from direct process oxidation reactions including SO<sub>2</sub> and unreacted H<sub>2</sub>S, other furnace side reaction products such as reduced sulphur compounds and mercaptans (e.g. COS, CS<sub>2</sub>) as well as small quantities of CO and VOC. These components may be emitted directly in older or very small uncontrolled Claus plants. The quantity and composition of sulphur components in the Claus plant tail gas are directly related to the sulphur recovery efficiency which will depend on factors such as the number of catalytic stages, the concentration of H<sub>2</sub>S and other contaminants in the feed gas, the stoichiometric balance of inlet gaseous components, operating temperatures, combustion efficiencies and catalyst maintenance. Typical Claus plant efficiencies range from 94–96 % for two-stage units to 97–98.5 % for four-bed catalytic plants and, because the process is thermodynamically limited, the tail gas still contains per cent quantities of sulphur compounds which may be further treated for recovery and emission control. When feed gas flow is much lower than the dimensional flow for the Claus unit and when sour gas composition and flow is fluctuating between 80 and 90 % it can be difficult to achieve these high efficiencies. Efficiencies between 80 and 90 % have been reported for such difficult conditions.

Tail gas emission reduction from the Claus process is normally achieved by one of the three following types of control methods.

- Claus reaction extension to lower temperature liquid phase: several processes are available which extend the Claus reaction into a lower temperature liquid phase, whereby enhanced conversion occurs at cooler temperatures in the catalytic stages. These processes result in overall higher sulphur recoveries (e.g. 98–99%) and correspondingly reduced sulphur compound emissions in the tail gas.
- Tail gas scrubbing: although several types of tail gas scrubber variations exist, two generic types are used to reduce sulphur emissions from the sulphur recovery process oxidation or reduction tail gas scrubbers. For example, the Wellman-Lord oxidation scrubber system is used in combination with tail gas incineration, whereby the Claus plant sulphur compounds are oxidized to SO<sub>2</sub> during combustion and this component is absorbed by sodium sulphite/bisulphite solution with associated release of the off gas. The bisulphite solution is then decomposed by boiling to produce a sodium sulphite precipitate for re-use and a regenerated SO<sub>2</sub> stream which is recycled back to the Claus process. Up to 99.9 % sulphur recovery can be accomplished with the system. In reduction scrubbers, tail gas sulphur compounds are converted by hydrogenation to H<sub>2</sub>S, which is either removed by conventional amine scrubbers for regeneration/recycle back to the Claus process.
- Tail gas incineration: Claus plant emissions may also be directly incinerated to convert the more hazardous reduced sulphur compounds to SO<sub>2</sub> under proper combustion conditions for release to the stack.

#### Diffuse emission sources

Emissions can be classified depending upon whether they can be monitored within the source (e.g. in a process vent pipe, flue or combustion unit stack) when they are called 'channelled' emissions, or whether they can only be monitored external to the source, e.g. storage tanks, oil-water separators, etc., when they are called 'diffuse' emissions. So called 'fugitive' emissions, which occur due to leaks from pressurised components, are a subset of diffuse emissions (European Commission, 2015).

# 2.3.1.1..1 Storage and handling

For all tanks, the total emission of NMVOC is the result of two types of losses. The first type of loss is the breathing or standing loss, which for fixed roof tanks is the release of vapours in the tank due to changes in meteorological conditions such as temperature and pressure, without any appreciable change in the liquid level of the tank. For floating roof tanks, the standing losses are due to vapour leakage past seals, roof fittings, etc. The majority of emissions from floating roof tanks are due to standing losses. The second type of loss is the working (including withdrawal) loss. For fixed roof tanks this results from the displacement of vapours during filling and the evaporation of product left on the tank shell during emptying. For floating roof tanks, the working loss is only due to the evaporation of product left on the tank shell when the roof level drops as product is removed from the tank (CPPI and Environment Canada 1991).

All intermediates and final products should be stored in the appropriate container: pressure vessels for gases, floating roof tanks for volatile liquids, fixed roof tanks for kerosene, distillate, fuel oil and other non-volatile liquids.

Improved operational procedures are an important part of a NMVOC emission control program. This may include such items as ensuring roof hatches, etc. are not opened unnecessarily, frequent external inspections and painting volatile product tanks a light shade to reduce the impact of solar radiation.

Vapour balancing, in which the vapours displaced during handling are collected and recovered, can have control efficiencies of 90 to 98 per cent. Vapour recovery methods include vapour/liquid absorption, vapour compression, vapour cooling and/or vapour/solid adsorption. Efficiencies as high as 90 to 98 per cent may be achieved, depending on the methods used, the design of the unit, the composition of vapours recovered, and the mechanical condition of the system (European Commission, 2005).

Other control programs involve design changes and are more specific to the tank in question, as summarised, by tank type, below.

- <u>Fixed r</u>oof tanks fixed roof tank emissions vary as a function of vessel capacity, vapour pressure of the contents, utilisation rate of the tank and atmospheric conditions. Emissions can be controlled by the installation of an internal roof and seals, with a control efficiency of 60 to 99 per cent. The control efficiency depends on the type of roof and seals installed as well as on the type of organic liquid being stored.
- External floating roof tanks efficiencies of primary seals may be improved through the installation of a secondary seal above the primary. Weather shields may be installed to provide protection of the seal systems. External floating roof tanks may also be retrofitted with a fixed roof. Losses from roof fittings can be minimised through proper design, installation, maintenance and use.

• Internal floating roof tanks — additional control of standing losses can be achieved through the installation of secondary seals. As for external floating roof tanks, losses from roof fittings can be minimised through proper design, installation, maintenance and use.

# 2.3.1.1..2 Oily-water collection and treatment

Diffuse emissions due to the evaporation of the hydrocarbons entrained in the water in process and oily-water drain systems and oil-water separators can be controlled by sealing the drain openings and fitting covers to separators.

# 2.3.1.1..3 Process fugitive emissions

Fugitive process emissions sources include valves of all types, flanges, pumps in hydrocarbon service (packed or sealed), compressor seals, pressure relief devices, open-ended lines or valves, sampling connections.

For these sources, a very high correlation has been found between mass emission rates and the type of stream service in which the sources are employed. For compressors, gases passing through are classified as either hydrogen or hydrocarbon service. For all other sources, streams are classified into one of three stream groups: gas/vapour streams, light liquid/two phase streams, and kerosene and heavier liquid streams. It has been found that sources in gas/vapour service have higher emission rates than those in heavier stream service. This trend is especially pronounced for valves and pump seals. Of these sources of NMVOC, valves are the major source type. This is due to their number and relatively high leak rate.

Normally, control of fugitive emissions involves minimising leaks and spills through equipment changes, procedure changes, and improved monitoring, housekeeping and maintenance practices.

Table 2-1         Control technologies for fugitive sources (US EPA, 2006a)							
Fugitive source	Control technology						
Pipeline valves	monitoring and maintenance programs						
Open-ended valves	installation of cap or plug on open end of valve /line						
Flanges	monitoring and maintenance						
Pump seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents						
Compressor seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents						
Process drains	traps and covers						
Pressure/relief valves	rupture disks upstream of relief and/or venting to a flare						

Applicable control technologies are summarised in the table below.

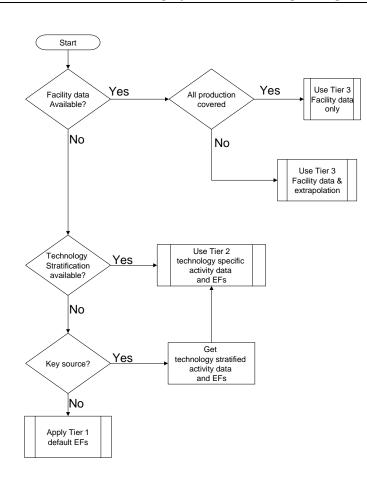
# 3 Methods

# 3.1 Choice of method

Figure 3-1 presents the procedure to select the methods for estimating emissions from the refining industry. The basic idea is:

- if detailed information is available, use it;
- if the source category is a key category, a Tier 2 or better method must be applied and detailed input data must be collected. The decision tree directs the user in such cases to the Tier 2 method, since it is expected that it is more easy to obtain the necessary input data for this approach than to collect facility level data needed for a Tier 3 estimate;
- the alternative of applying a Tier 3 method, using detailed process modelling, is not explicitly included in this decision tree. However, detailed modelling will always be done at facility level and results of such modelling could be seen as 'facility data' in the decision tree.

Figure 3-1 Decision tree for source category 1.B.2.a.iv Refining, storage



#### 3.2 Tier 1 default approach

#### 3.2.1 Algorithm

The Tier 1 approach for the refining industry uses the general equation:

$$E_{pollutant} = AR_{production} \times EF_{pollutant} \tag{1}$$

This equation is applied at the national level, using the total refined oil production as production statistics. It is also possible to use the crude oil throughput as production statistics.

The Tier 1 emission factors assume an averaged or typical technology and abatement implementation in the country and integrate all sub-processes within the petroleum refining process.

In cases where specific abatement options are to be taken into account a Tier 1 method is not applicable and a Tier 2 ort Tier 3 approach must be used.

#### 3.2.2 Default emission factors

The Tier 1 default emission factors have been established by combining statistics:

- all emissions from oil refineries for EU-27 in 2010 that were present in E-PRTR;
- the total production statistics for EU-27 in 2010 from Eurostat.

Combining these two datasets provides a first order estimate for emission factors for all relevant pollutants. These emission factors are used as the Tier 1 estimate and are displayed in Table 3-1. The uncertainty of these factors is qualified as C.

Emissions of DCE, DCM and tetrachloroethylene may occur as emissions from petrochemical facilities located alongside refineries on refinery sites. It is good practice to derive the emission factors for these pollutants from the chemical industry European Pollutant Release and Transfer Register (E-PRTR) submissions. Further details are given in Chapter 2.B Chemical industry.

Tier 1 default emission factors							
	Code Name						
NFR Source Category	1.B.2.a.iv	Fugitive emissions oil: R	efining / s	torage			
Fuel	NA						
Not applicable         BC, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, HCB, PCB				nthene,			
Not estimated							
Pollutant	Value	Unit	95% confidence interval		Reference		
			Lower	Upper			
NO <sub>x</sub>	0.24	kg/Mg crude oil input	0.08	0.72	1)		
СО	0.09	kg/Mg crude oil input	0.03	0.26	1)		
NMVOC	0.20	kg/Mg crude oil input	0.07	0.61	1)		
SOx	0.62	kg/Mg crude oil input	0.21	1.9	1)		
NH <sub>3</sub>	0.0011	kg/Mg crude oil input	0.0004	0.0034	1)		
TSP	0.016	kg/Mg crude oil input	0.005	0.048	2)		
PM <sub>10</sub>	0.0099	kg/Mg crude oil input	0.003	0.030	1)		

Table 3-1 Tier 1 emission factors for source category 1.B.2.a.iv Ref	lefining, storage
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PM <sub>2.5</sub>	0.0043	kg/Mg crude oil input	0.001	0.013	2)
Pb	0.0051	g/MG crude oil input	0.002	0.015	1)
Cd	0.0051	g/MG crude oil input	0.002	0.015	1)
Hg	0.0051	g/MG crude oil input	0.002	0.015	1)
As	0.0051	g/MG crude oil input	0.002	0.015	1)
Cr	0.0051	g/MG crude oil input	0.002	0.015	1)
Cu	0.0051	g/MG crude oil input	0.002	0.015	1)
Ni	0.0051	g/MG crude oil input	0.002	0.015	1)
Se	0.0051	g/MG crude oil input	0.002	0.015	1)
Zn	0.0051	g/MG crude oil input	0.002	0.015	1)
PCDD/F	0.0057	µg/Mg crude oil input	0.002	0.017	1)

1) Tier 1 EFs are estimated as the emissions reported by EU-27 to E-PRTR for the year 2010 divided by the amount of 'Transformation input in Refineries' in 2010 provided by Eurostat (Supply, transformation, consumption - oil - annual data [nrg\_102a]).

2) EFs for TSP and  $PM_{2.5}$  are estimated from the Tier 1  $PM_{10}$  EF and the average TPS/PM<sub>10</sub> and  $PM_{2.5}/PM_{10}$  for Catalytic Cracking unit regenerators and Fluid coking units.

The majority of emissions from refineries are from both processes and combustion sources e.g. particulates are emitted from both the catalytic cracking process and from combustion of fuels. To avoid duplication in emission estimation, where the majority of the emissions are considered to be from combustion sources, the Tier 1 emission factors are provided in Chapter 1.A.1 Combustion in energy industries under NFR code 1.A.1.b Petroleum refining.

Care should be taken if the Tier 1 approach is used to estimate emissions for this source category, because in this case the emissions of these pollutants should not be reported in NFR source category 1.A.1.b Petroleum refining to avoid double counting.

#### 3.2.3 Activity data

To apply the Tier 1 default emission factors, the annual total throughput of each refinery is required, which can be obtained from Eurostat.

# 3.3 Tier 2 technology-specific approach

#### 3.3.1 Algorithm

Unlike in other source categories, the Tier 2 approach for the refinery sector is not similar to the Tier 1 approach. The Tier 2 approach for refineries identifies different processes in the refinery, and provides process-specific emission factors for these. The total emissions are determined by adding up all the process-specific emission factors.

To apply the Tier 2 approach, both the activity data and the emission factors need to be stratified according to the different techniques that may occur in the country. This may be done by:

- defining the production using each of the separate product and/or process types (together called 'technologies' in the formulae below) separately; and
- applying technology specific emission factors for each process type:

$$E_{pollutant} = \sum_{technologies} AR_{production technology} \times EF_{technology pollutant}$$
(2)

where:

AR<sub>production,technology</sub> = the production rate within the source category, for the specific technology,

EF<sub>technology,pollutant</sub> = the emission factor for this technology and this pollutant.

A country where only one technology is implemented will result in a penetration factor of 100 % and the algorithm reduces to:

$$E_{pollutant} = AR_{production} \times EF_{technologypollutant}$$
(3)

where:

Epollutant	=	the emission of the specified pollutant,
ARproduction	=	the activity rate for petroleum refining,
EFpollutant	=	the emission factor for this pollutant.

#### 3.3.2 Technology-specific emission factors

This section is split in two, first the process emission factors are discussed, thereafter the fugitive emission factors. The section provides the process emission factors for petroleum refineries processes, for the various techniques available for use. The majority of the factors are taken from CONCAWE (2017) and, if not specified otherwise, based on uncontrolled processes.

#### Catalytic cracking unit regenerators

The emission factors given in Table 3-2 are for partial burn without a CO boiler. For the emission factors to be used with full burn regeneration or partial burn with CO boiler, please use these emission factors combined with the relevant abatement efficiencies in subsection 0 of the present chapter.

catalytic cracking - CO boller (not installed)							
Tier 2 emission factors							
	Code	Name					
NFR Source Category	1.B.2.a.iv	Fugitive emissions oil:	Refining / st	torage			
Fuel	NA						
SNAP (if applicable)	040102	Fluid catalytic cracking	g - CO boiler				
Technologies/Practices	-	Catalytic Cracking unit regenerators Partial burn without CO boiler					
Region or regional conditions							
Abatement technologies	Cyclone s	ystems installed interna	ally within th	e regenera	tor		
Not applicable	HCB, PCB						
Not estimated	PCDD/F						
Pollutant	Value	Unit	95% cor inte	ifidence rval	Reference		
			Lower	Upper			
NO <sub>x</sub>	0.2	kg/m3 fresh feed	0.12	0.29	CONCAWE (2017)		
СО	39	kg/m3 fresh feed	24	55	CONCAWE (2017)		
NMVOC	0.63	kg/m3 fresh feed	0.38	0.88	CONCAWE (2017)		
SOx	1.4	kg/m3 fresh feed	0.85	2	CONCAWE (2017)		
NH <sub>3</sub>	0.16	kg/m3 fresh feed	0.093	0.22	CONCAWE (2017)		

Table 3-2	Tier 2 emission factors for source category 1.B.2.a.iv Refining, storage, Fluid
	catalytic cracking - CO boiler (not installed)

TSP	0.7	kg/m3 fresh feed	0.05	2	Environment Australia, 1999
PM10	0.55	kg/m3 fresh feed	0.18	1.6	CONCAWE (2017)
PM <sub>2.5</sub>	0.24	kg/m3 fresh feed	0.08	0.5	1)
BC <sup>(a)</sup>	0.13	% of PM2.5	0.05	0.2	2)
Pb	0.32	g/m3 fresh feed	0.11	0.96	CONCAWE (2017)
Cd	0.063	g/m3 fresh feed	0.021	0.19	CONCAWE (2017)
Hg	0.07	g/m3 fresh feed	0.023	0.21	CONCAWE (2017)
As	0.014	g/m3 fresh feed	0.0046	0.042	CONCAWE (2017)
Cr	0.33	g/Mg coke burned	0.1	1	Bertrand & Siegell, 2002; CONCAWE (2017) <sup>(b)</sup>
Cu	0.14	g/m3 fresh feed	0.046	0.42	CONCAWE (2017)
Ni	0.61	g/m3 fresh feed	0.2	1.8	CONCAWE (2017)
Se	0.014	g/m3 fresh feed	0.005	0.042	CONCAWE (2017)
Zn	0.12	g/m3 fresh feed	0.039	0.35	CONCAWE (2017)
Benzo(a)pyrene	0.71	mg/Mg coke burned	0.4	1.4	CONCAWE (2017)
Benzo(b)fluoranthene	1.2	mg/Mg coke burned	0.6	2.4	CONCAWE (2017)
Benzo(k)fluoranthene	0.82	mg/Mg coke burned	0.4	1.6	CONCAWE (2017)
Indeno(1,2,3-cd)pyrene	0.62	mg/Mg coke burned	0.3	1.2	CONCAWE (2017)

1) Assumption that  $PM_{2.5} = PM_1 = 43 \%$  of  $PM_{10}$  in correspondence with the assumption for refining/storage based on Kupiainen & Klimont (2004)

2) Mean value of EFs from Olmez et al. (1988), Cooper et al. (1987) and Chow et al. (2004). The emission factor for BC relates to  $PM_{2.5}$  emissions after abatement in the external stack whereas the  $PM_{2.5}$  emission factor is related to emission levels before such abatement.

Note (a): For the purposes of this guidance, BC emission factors are assumed to equal those for elemental carbon (EC). For further information please refer to Chapter 1.A.1 Energy Industries.

Note (b): EF calculated from the data in Bertrand & Siegell, 2002 based on the formula in CONCAWE (2017) section 5.2

#### Catalytic reforming unit units

Table 3-3 provides emission factors for SO<sub>x</sub>, CO and PCDD/F emissions from catalytic reforming units.

Table 3-3	Tier 2 emission factors for source category 1.B.2.a.iv Refining, storage, Catalytic
	reforming units

Tier 2 emission factors						
	Code	Code Name				
NFR Source Category	1.B.2.a.iv	Fugitive emissions oil:	Refining / storage			
Fuel	NA					
SNAP (if applicable)	040102	Fluid catalytic cracking	- CO boiler			
Technologies/Practices	Catalytic r	eforming units				
Region or regional conditions						
Abatement technologies	uncontrolled					
Not applicable	NOx, CO, NH3, TSP, PM10, PM2.5, BC, Pb, Cd, Hg, As, Cr, Cu, Ni, Se, Zn, PCB, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, HCB					
Not estimated	NMVOC					
Pollutant	Value Unit 95% confidence interval Lower Upper		Reference			

CO	42	g/m³ feed	10	100	CONCAWE (2017)
SO <sub>x</sub>	4	g/m³ feed	2	10	CONCAWE (2017)
PCDD/F	0.019	ug I-TEQ/m <sup>3</sup> fresh feed	0.0019	0.19	CONCAWE (2017) *

\* Continuous regeneration mode. For semi-regenerative mode CONCAWE (2017) provide an emission factor of 6.35E-06 μg/m<sup>3</sup> feed

#### Fluid coking units

Table 3-4 provides the uncontrolled emission factors for fluid coking units. When controlled by CO or fired waste heat boiler, please refer to subsection 3.3.3.1 for abatement efficiencies.

coking units								
Tier 2 emission factors								
	Code	Code Name						
NFR Source Category	1.B.2.a.iv	Fugitive emissions oil:	Refining / st	torage				
Fuel	NA							
SNAP (if applicable)								
Technologies/Practices	Fluid coki	ng units						
Region or regional conditions								
Abatement technologies	primary c	yclone installed to abate	e particulate	es				
Not applicable	NOx, CO, NH3, TSP, PM10, PM2.5, BC, Pb, Cd, Hg, As, Cr, Cu, Ni, Se, Zn, PCB, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, HCB							
Not estimated	SOx,PCDE	D/F			_			
Pollutant	Value	Unit	95% confidence interval		Reference			
			Lower	Upper				
NMVOC	0.046	kg/m3 fresh feed	0.02	0.2	CONCAWE (2017)			
TSP	1.5	kg/m3 fresh feed	0.6	4.9	Environment Australia (1999)			
PM <sub>10</sub>	0.77	kg/m3 fresh feed	3	2.5	CONCAWE (2017)			
PM <sub>2.5</sub>	0.33	kg/m3 fresh feed	0.2	1.6	1)			
Pb	0.045	g/m3 fresh feed	0.02	0.2	CONCAWE (2017)			
Hg	0.03	g/m3 fresh feed	0.01	0.1	CONCAWE (2017)			
As	2.2	g/m3 fresh feed	1	6	CONCAWE (2017)			
Cu	0.015	g/m3 fresh feed	0.01	0.6	CONCAWE (2017)			
Ni	0.57	g/m3 fresh feed	0.2	2	CONCAWE (2017)			
Se	0.03	g/m3 fresh feed	0.01	0.1	CONCAWE (2017)			
Zn	0.045	g/m3 fresh feed	0.02	0.2	CONCAWE (2017)			

# Table 3-4Tier 2 emission factors for source category 1.B.2.a.iv Refining, storage, Fluid<br/>coking units

1) Assumption that  $PM_{2.5} = PM_1 = 43 \%$  of  $PM_{10}$  in correspondence with the assumption for refining/storage based on Kupiainen & Klimont (2004)

#### **Blowdown systems**

Gaseous emissions from refinery blowdown systems are recovered and/or flared. The emission factors for refinery flares are provided in chapter 1.B.2.c Venting and flaring.

#### Asphalt blowing

Emission factors for asphalt blowing are provided in sub-sector 3.C Chemical products.

At refineries, gaseous emissions from asphalt blowing are controlled, for example using a scrubber, and then the tail-gas is passed to a thermal oxidiser. The emission factors for thermal oxidisers are provided in chapter 1.B.2.c Venting and flaring.

#### Sulphur recovery

SO<sub>2</sub> emissions from sulphur recovery can be estimated by using the Tier 2 emission factor in Table 3-5 below. It is assumed that all sulphur recovery operations are two-staged and no control technology for tail-gas cleanup is applied. Emissions of SO<sub>2</sub> would then be conservatively estimated by using the highest uncontrolled emission factor and the total amount of sulphur produced through sulphur recovery processes. This would provide an upper bound to the likely emissions, but in the absence of more detailed production information represents an acceptable estimation method to use. More detail about emissions from sulphur recovery is provided in Tier 3 by using a process model.

Table 3-5	Tier 2 emission factors for source category 1.B.2.a.iv Refining, storage, Sulphur
	recovery

Tier 2 emission factors							
Code	Name						
1.B.2.a.iv	Fugitive emissions oil:	Refining / st	torage				
NA							
040103	Sulphur recovery plan	ts					
Two-stage	ed sulphur recovery ope	erations					
no control technology for tail-gas cleanup							
NOx, CO, NH3, TSP, PM10, PM2.5, BC, Pb, Cd, Hg, As, Cr, Cu, Ni, Se, Zn, PCB,							
Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3- cd)pyrene_HCB							
112							
Value Unit 95% confidence Reference							
interval							
	Lower Upper						
140	kg/Mg sulphur produced	50	400	CONCAWE (2017)			
	Code 1.B.2.a.iv NA 040103 Two-stage no contro NOx, CO, Benzo(a)p cd)pyrene NMVOC, F Value	Code     Name       1.B.2.a.iv     Fugitive emissions oil:       NA     040103       O40103     Sulphur recovery plan       Two-staged sulphur recovery operation     Image: Sulphur recovery operation       no control technology for tail-gas     Image: Sulphur recovery operation       NOx, CO, NH3, TSP, PM10, PM2.5     Benzo(a)pyrene, Benzo(b)fluoran       cd)pyrene, HCB     Image: Sulphur recovery       NMVOC, PCDD/F     Unit	1.B.2.a.iv       Fugitive emissions oil: Refining / si         NA       040103         Sulphur recovery plants         Two-staged sulphur recovery operations         no control technology for tail-gas cleanup         NOx, CO, NH3, TSP, PM10, PM2.5, BC, Pb, Cd, Benzo(a)pyrene, Benzo(b)fluoranthene, Benz cd)pyrene, HCB         NMVOC, PCDD/F         Value       Unit         95% cor international internatinternational internation international intern	Code       Name         1.B.2.a.iv       Fugitive emissions oil: Refining / storage         NA       040103       Sulphur recovery plants         Two-staged sulphur recovery operations       Image: State St			

#### **Gasoline storage**

For depots of gasoline in refineries, refer to the Tier 3 section.

Diffuse NMVOC emissions, including those from volatile product storage and handling, drain systems/water treatment and process fugitive sources, are estimated by combining the crude oil throughput of each refinery with the emission factor provided in Table 3–6.

Tier 2 emission factors							
	Code	Name					
NFR Source Category	1.B.2.a.iv	Fugitive emissions of	il: Refining	′ storage			
Fuel	NA						
SNAP (if applicable)	0401	Processes in petrole	eum industr	ies			
Technologies/Practices	Diffuse er	nissions					
Region or regional conditions							
Abatement technologies							
Not applicable	NOx, CO, NH3, TSP, PM10, PM2.5, BC, Pb, Cd, Hg, As, Cr, Cu, Ni, Se, Zn, PCB, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, HCB						
Not estimated	SOx,PCDD	)/F					
Pollutant	Value Unit 95% confidence Reference interval						
			Lower	Upper			
NMVOC	0.2	kg/Mg crude oil throughput	0.1	0.4	Derived from E- PRTR / EUROSTAT		

# Table 3-6 Tier 2 emission factor for source category 1.B.2.a.iv Refining, storage, Diffuse emissions

Note: Emission factor derived from E-PRTR 2010 submissions from mineral oil refineries.

#### 3.3.3 Abatement

A number of add on technologies exist that are aimed at reducing the emissions of specific pollutants. The resulting emission can be calculated by replacing the technology specific emission factor with an abated emission factor as given in the formula:

$$EF_{technologyabated} = (1 - \eta_{abatement}) \times EF_{technologyunabated}$$
(4)

This section presents default abatement efficiencies for a number of abatement options, applicable in this sector.

#### Catalytic cracking unit regenerators

For catalytic cracking unit regenerators, the Tier 2 emission factors in Table 3-2 are for partial burn without a CO boiler, and with a primary cyclone installed. In

Table 3-7, abatement efficiencies for other techniques are calculated with respect to these emission factors.

Tier 2 Abatement efficiencies								
	Code	Code Name						
NFR Source Category	1.B.2.a.iv	Fugitive em	issions oil:	Refining / st	orage			
Fuel	NA							
SNAP (if applicable)	040102	Fluid cataly	tic cracking	- CO boiler				
Technologies/Practices	Catalytic cra	acking unit re	egenerators					
Abatement technology	Pollutant	Efficiency		nfidence erval	Reference			
		Default value	Lower	Upper				
Partial burn with CO boiler	со	99.5%	99%	100%	European Commission (2004)			
	NMVOC	99.5%	99%	100%	European Commission (2004)			
	NH₃	99.5%	99%	100%	European Commission (2004)			
Full burn regeneration	со	99.5%	99%	100%	European Commission (2004)			
	NMVOC	99.5%	99%	100%	European Commission (2004)			
	NH <sub>3</sub>	99.5%	99%	100%	European Commission (2004)			
Additional cyclone stage	PM <sub>10</sub>	60%	30%	90%	European Commission (2003)			
Electrostatic precipitators	PM <sub>10</sub>	95%	90%	98%	European Commission (2003)			

Table 3-7	Abatement	efficiencies	( $\eta_{abatement}$ )	for	source	category	1.B.2.a.iv	Refining,
	storage, Cat	alytic crackir	ng unit reger	nerat	tors			

Full burn regeneration and CO boilers oxidise the combustible components in the emissions, In fact, as can be seen from the Table, when using either of the two techniques, the emissions of CO, NMVOC,  $NH_3$  and  $C_6H_6$  (benzene) are considered negligible. Using either of the two techniques does not decrease emission levels for pollutants that are not listed in

#### Table 3-7.

The basic catalytic cracking regenerator design normally incorporates, inside the regenerator vessel, cyclone systems to separate the catalyst particles from the hydrocarbon vapours. Additional cyclone systems and/or electrostatic precipitators may be installed external to the regenerator to abate further the particulate emissions.

#### 3.3.4 Activity data

The crude oil throughput for each refinery is required. For calculating emissions from sulphur recovery, the amount of sulphur produced is necessary. For catalytic cracking units and cokers the total amount of fresh feed to the units is required. On a national basis the total amount of fresh feed for each type of unit can be assumed to equal the total design capacities of the catalytic cracking units and cokers installed in refineries.

### 3.4 Tier 3 emission modelling and use of facility data

#### 3.4.1 Algorithm

There are two different methods to apply emission estimation methods that go beyond the technology-specific approach described above:

- detailed modelling of the process;
- using facility-level reports.

#### **Detailed process modelling**

A Tier 3 emission estimate using process details will make separate estimates for each process taking account of abatement systems installed. For example, it will use knowledge of equipment components fitted in the refinery to provide estimates of process fugitive emissions. For storage tanks, details of tank size, fittings, etc., can be used to estimate emissions on a tank by tank basis.

#### **Facility-level data**

Where facility-level emission data of sufficient quality are available (see Chapter 6, Inventory management, improvement and QA/QC in part A), it is good practice to indeed use these data. There are two possibilities:

- the facility reports cover all the refineries in the country;
- facility-level emission reports are not available for all refineries in the country.

If facility level data are covering all refineries in the country, it is good practice to compare the implied emission factors (reported emissions divided by the national refined oil product production) with the default emission factor values or technology-specific emission factors. If the implied emission factors are outside the 95 % confidence intervals for the values given below, it is good practice to explain the reasons for this in the inventory report.

If the total annual crude oil throughput from refineries in the country is not included in the total of the facility reports, it is good practice to estimate the missing part of the national total emissions from the source category, using extrapolation by applying:

$$E_{Total, pollutant} = \sum_{Facilities} E_{Facility, pollutant} + \left(National \ Production - \sum_{Facilities} Production_{Facility}\right) \times EF$$
(5)

Depending on the specific national circumstances and the coverage of the facility level reports as compared to the national crude oil throughput in refineries, it is good practice to choose the emission factor (*EF*) in this equation from the following possibilities, in decreasing order of preference:

- technology specific emission factors, based on knowledge of the types of technologies implemented at the facilities where facility level emission reports are not available,
- the implied emission factor derived from the available emission reports:

$$EF = \frac{\sum_{Facility, pollutant}}{\sum_{Facilities}} Production_{Facility}$$
(6)

• the default Tier 1 emission factor. It is good practice to choose this option only if the facility level emission reports cover more than 90 % of the total national production.

#### 3.4.2 Tier 3 emission modelling and use of facility data

#### **Process emissions**

Tier 2 estimation of emissions from catalytic cracking processes and fluid cokers uses the design capacities of these types of units to derive the value of total fresh feed.

For Tier 3, the actual fresh feed data from individual refinery process plants should be used.

#### Sulphur recovery

If allowed by the availability of activity data, the preferred methodology for estimating SO<sub>2</sub> emissions from sulphur recovery would involve either a sulphur mass balance or the measurement of emissions from each plant to develop site-specific emission factors or emissions data for all potentially significant sources.

In the mass balance approach, at minimum, the sulphur content and volumes of sulphur recovery plant feed gas materials (e.g. sour gas streams or absorption tower sulphide off-gas) are needed to define the mass of input sulphur. This may also comprise sulphur input from sour water stripping of waste-waters. In conjunction with the mass of elemental sulphur produced, the quantity of sulphur in tail gas emissions requires determination. This may be done by calculating the sulphur recovery efficiency with a knowledge of the number and type of sulphur recovery units including Claus plant catalytic stages and/or measuring the volume and sulphur content of the tail gas. Account should also be made of SO<sub>2</sub> emissions associated with catalyst regeneration, where practised on-site, as well as unaccounted losses to confirm the balance. Upon conversion to SO<sub>2</sub>, the emissions from sulphur recovery operations (expressed as kg SO<sub>2</sub> per Mg pure elemental sulphur produced) may be calculated by:

$$SO_2 \text{ emissions} (kg/Mg) = \frac{100 - \% \text{ recovery}}{\% \text{ recovery}} x 2000.$$
(7)

In instances where the tail gas is treated further by scrubbers or incinerators, the emissions may be best determined by stack testing. Emission factors could then be used to calculate emissions, as required, until such time as the process or emissions controls are significantly changed. At this time, it is good practice to derive new site-specific emission factors based on testing or mass balance determinations.

Accordingly, the most reliable emission estimation alternative is to inventory each sulphur recovery installation as a point source, using site-specific process and production information. This would ideally include site-specific information on the average percent sulphur recovery, which can be used to derive site-specific emission factors by assuming that all sulphur is released as SO<sub>2</sub>. If the sulphur recovery information is not available, it may be estimated from the number of catalytic stage and control level. See Table 3-8 below. Efficiencies in the table are for feed-gas streams with high H<sub>2</sub>S concentrations. Gases with lower H<sub>2</sub>S concentrations would have lower efficiencies. For example, a two- or three-stage plant could have a recovery efficiency of 95 % for a 90 % H<sub>2</sub>S stream, 93 % for 50 % H<sub>2</sub>S and 90 % for 15 % H<sub>2</sub>S.

Table 3-8	Modified Claus sulphur recovery plant recovery percentages (US EPA, 2006a)
-----------	--

Number of catalytic stages	Control	Average % sulphur recovery
2	Uncontrolled	93.5 (range 92-95)
3	Uncontrolled	95.5 (range 95-96)
4	Uncontrolled	96.5 (range 96-97)
2	Controlled	98.6
3	Controlled	96.8

Note. Uncontrolled emission factors are rated E, controlled emission factors have a quality rating B.

#### **Diffuse emission sources**

For Tier 2, a generic emission factor is provided for all sources of diffuse NMVOC emissions. It is recommended that where site data are available, the following estimation methodologies are used.

#### Storage emission estimation methodologies

For the types of storage tanks used to store volatile liquids at refineries, emission estimation methodologies are provided by the US EPA (2006a). These methodologies require information on the tank contents, size, shell colour, floating roof fitting types and number, etc. on a tank-by-tank basis. Emission calculation software utilizing the algorithms in the US EPA publication is available on the EPA website <u>www.epa.gov</u>, or on a CD-ROM (US EPA, 2005) but this software is now outdated and is not reliably functional on computers using modern operating systems.

#### Emissions factors for drains

The following algorithm provides an estimate for emissions from the entire refinery process drain system (CONCAWE, 2017). Drain systems on clean water (with minimal potential for contact with oil) and storm water are excluded.

Process drain openings (sumps, etc.) are normally fitted with an emission control device such as a water seal or sealed cover. An assessment needs to be made to establish how many of the drain covers are unsealed and vent directly to atmosphere.

```
Emissions (kg/hour) = 0.032 \times N (8)
where
```

N = number of unsealed covers in the refinery process drain system.

If the total number of drains is unknown, a drain count of 2.6 drains per pump in process areas can be used.

#### Emission factors for oil-water separators

For oil-water separators, emissions are dependent on the type of separator installed.

 $E(kg) = EF_{SEP} \times V_{WATER}$  (9)

where:

 $EF_{SEP}$  = emission factor for the type of separator given in Table 3-9.

 $V_{WATER}$  = volume of waste water treated by the separator (in m<sup>3</sup>).

Emissions from basins and ponds that handle clean water or storm water are considered negligible.

Separator type	Emission factor (EF <sub>SEP</sub> )			
	kg/m <sup>3</sup> waste water treated			
Gravity type — uncovered <sup>1</sup>	0.111			
Gravity type — covered <sup>1</sup>	0.0033			
Gravity type — covered and connected to flare <sup>1,2</sup>	0			
DAF <sup>3</sup> or IAF <sup>4</sup> — uncovered	0.004 5			
DAF <sup>3</sup> or IAF <sup>4</sup> — covered	0.00012 5			
DAF <sup>3</sup> or IAF <sup>4</sup> — covered and connected to flare	0			

#### Table 3-9 Emission factors for oil-water separators (CONCAWE, 2015)

Notes:

1. For an oil in water concentration of 880 - 3500 mg/l. For values outside of this range, refer to CONCAWE 2017

2. For flare emission estimation see chapter 1.B.2.c Venting and flaring.

3. DAF = dissolved air floatation type.

4. IAF = induced air floatation type.

5. The emission factors for these types of separator apply where they are installed as secondary treatment systems.

There are a number of complex estimation models available to calculate emissions from waste water systems. They aim to estimate average emission rates of individual species for each of the system components, collectively permitting the determination of the overall emissions from a refinery wastewater collection and treatment system.

The emission factors in Table 3-9 represent the conditions for typical inlet hydrocarbon concentration in water being treated in refinery oil-water separators. Concawe (2017) provides emission factors for other inlet conditions for gravity type separators and also for where the quantity of water treated is unknown.

The US EPA has developed a freely available computer program model called WATER9. This is Windows based and consists of analytical expressions for estimating air emissions of individual waste constituents in waste water collection, storage, treatment, and disposal facilities.

#### Process fugitive emission estimation methodologies

The methods for estimating mass emissions from process equipment leaks ranges from the use of equipment component average emission factors, which requires knowledge of pan-refinery equipment counts, to comprehensive field leak detection techniques and related emission correlations. These methods have evolved from a number of studies of the organic chemical and petroleum refining industries (US EPA, 1995a; CEN, 2008).

### 3.4.2.1..1 Average equipment component emission factors

These emissions factors are expressed as losses per equipment component per hour. CEN (2008) provides average emission factors for the different types of pressurized components in volatile product service. These are provided in Table 3–10.

Equipment type	Service	Emission factor kg/hr/source
Valves	Gas	0.0268
	Light liquid	0.0109
Pump seals	Light liquid	0.114
Compressor seals	Gas	0.636
Pressure relief valves	Gas	0.160
Flanges and non-flanged connectors	All	0.00025
Open-ended lines	All	0.0023
Sampling connections	All	0.015

# Table 3-10Average NMVOC emission factors for petroleum refineries for fugitive emissions<br/>from pressurised components (CEN, 2008)

# 3.4.2.1..2 Leak monitoring surveys

Emissions from pressurised components can be determined using leak monitoring surveys on a sample of equipment and then using methodologies depending upon the magnitude of the leak concentration.

There are two tiers of measurement methodology:

- applying average emission factors based on a leak/no leak criteria. This requires the use of monitoring equipment to measure VOC concentrations at each fitting to establish if a leak 'threshold' has been exceeded;
- applying emission correlations based on actual VOC concentration values determined at each fitting.

These surveys can be refinery-wide. Alternatively, they may be partial programs comprising either emission surveys of all components but only on some process units, or surveys on a limited range of components, e.g. valves and pumps only on light liquid duty.

Full details on the calculation of emissions are provided by the US EPA (1995a) and in the European CEN Standard (CEN, 2008).

A more recent development is the use of handheld optical imaging devices to detect leaking components, permitting surveys to be undertaken more quickly (Lev-On et al, 2007). Leak/No-Leak emission factors for use with these devices are provided in CONCAWE (2017) . Concawe (2015b) provides a recommendation for the factors to be used. Further developments are currently taking place with the technology which will provide an optical imaging device providing leak quantification.

#### 3.4.3 Activity data

Depending on the type of method being used, different activity statistics are required. For instance, for fugitive losses the NMVOC emissions depend on the amount of pressurised components.

# 4 Data quality

# 4.1 Completeness

No specific issues.

# 4.2 Avoiding double counting with other sectors

Care should be taken regarding the emissions from petroleum refinery processes. Not all processes in refineries that could result in the emissions to the air are included in this chapter:

- emissions from the crude oil feed stock handling are covered by chapter 1.B.2.a.i;
- combustion processes in refineries are covered by chapter 1.A.1.b;
- emissions from flaring are covered by chapter 1.B.2.c. Incineration of ground flares is also included in chapter 1.B.2.c and not in 6.C.b, since the latter chapter focuses on solid and liquid wastes, not gases;
- emissions from asphalt (bitumen) blowing are covered by sub-sector 3.C;
- emissions due to loading at refinery dispatch facilities are covered by chapter 1.B.2.a.v;
- emissions due to waste water treatment in refineries and sulphur recovery are included in this chapter.

# 4.3 Verification

There are more sophisticated and accurate methods to estimate fugitive process emissions (US EPA, 1995a). All of these methods involve the use of screening data, which are collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value is a measure of the concentration, in ppmv, of leaking compounds in the ambient air near the equipment in question. The EPA has detailed what is involved in an acceptable screening program in the protocol for equipment leak emission estimation manual (US EPA, 1995a).

The approaches to estimating equipment leak emissions based on screening data are:

- screening ranges approach
- EPA correlation approach, and
- unit-specific correlation approach.

In the screening value approach, it is assumed that components having screening values greater than 10 000 ppmv have a different average emission rate than components with screening values less than 10 000 ppmv.

The EPA correlation approach offers an additional refinement by providing an equation to predict mass emission rate as a function of screening value.

In the last approach, mass emissions rates are determined by bagging a specific type of equipment. The associated screening value can then be used to develop a leak rate/screening value correlation for that equipment in that process unit.

All of these methods are described in detail in the protocol document (US EPA, 1995a).

Remote sensing using optical gas imaging may be used to identify, for example, if any external floating roof storage tanks are operating outside of the performance bounds for which emission factors are valid, permitting focussed maintenance to ensure that factors can then be used for these sources for inventory purposes.

#### 4.3.1 Best Available Technique emission factors

An extensive reference document exists on the Best Available Techniques in refineries (European Commission, 2003 and European Commission, 2015). This document describes the necessary actions to achieve BAT emission levels; however no specific emission levels are given for the refinery sector in general. For more information, please refer to this document.

# 4.4 Developing a consistent time series and recalculation

No specific issues

### 4.5 Uncertainty assessment

#### 4.5.1 Emission factor uncertainties

No specific issues.

#### 4.5.2 Activity data uncertainties

No specific issues.

### 4.6 Inventory quality assurance/quality control QA/QC

No specific issues

### 4.7 Gridding

No specific issues

### 4.8 Reporting and documentation

No specific issues

# **5** References

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# 6 Point of enquiry

Enquiries concerning this chapter should be directed to the relevant leader(s) of the Task Force on Emission Inventories and Projection's expert panel on combustion and industry. Please refer to the TFEIP website (<u>www.tfeip-secretariat.org/</u>) for the contact details of the current expert panel leaders.