Report

Air pollutant emission estimation methods for E-PRTR reporting by refineries

2019 edition

Concawe

Air pollutant emission estimation methods for E-PRTR reporting by refineries

2019 edition

L. Hoven (Concawe Science Executive)
T. Megaritis (Concawe Research Associate)

This report was prepared by B. Smithers

ABSTRACT

This report is an update of the Concawe publication *"Air Pollutant Emission Estimation Methods for EPER and PRTR Reporting by Refineries"*. It provides algorithms to permit emission estimates to be made by refineries to meet the reporting requirements of the European Pollutant Release and Transfer Register (E-PRTR) regarding pollutant emissions to air. This edition contains new factors for the estimation of hydrogen cyanide (HCN) emissions from fluid catalytic cracking units (FCCUs). This report supersedes previous versions, as listed below:

Concawe Report 4/17
Concawe Report 3/15
Concawe Report 1/09
Concawe Report 3/07
Concawe Report 9/05R
Concawe Report 9/05

The control copy of this report is posted as an electronic document on the Concawe web-site (www.concawe.org).

There are 60 air pollutants which must be reported under the E-PRTR requirements if their respective annual emission threshold values are exceeded at a facility. All 60 pollutants are listed in **Appendix 1** of this report. Emission estimation methods are provided for 25 of those pollutants. New and updated information is summarised in **Appendix 2**.

KEYWORDS

Air pollution, refineries, E-PRTR, emission factors, sources.

INTERNET

The controlled version of this report is available as an Adobe pdf file on the Concawe website (www.concawe.org) and the latter should be checked for updates. New and updated information provided in this version is summarised in **Appendix 2**.

CONTENTS
Page

SUMMARY

With the introduction of the public domain databases of pollutant releases - EPER (European Pollutant Emission Register) and its successor E-PRTR (European Pollutant Release and Transfer Register) - there is a need for reliable and consistent emissions data in the oil industry sector.

The E-PRTR Regulation requires that annual emissions of key species are reported where those emissions exceed a minimum threshold.

This Report provides the estimation algorithms and emission factors for uncontrolled releases of air pollutants from stationary sources at oil refineries which Concawe recommends for E-PRTR reporting purposes, where measurements have not been undertaken. The emission estimation algorithms are fully referenced and the emission factors provided in a consistent metric unit base.

Concawe has previously published Report No. 9/05 (and a revised version 9/05R) *Air Pollutant Emission Estimation Methods for EPER and PRTR Reporting by Refineries*.

Report No. 9/05R was submitted to the European Commission and the European Environment Agency and is referenced as a source of sector specific calculation methods in the EU (2006) *Guidance Document for the Implementation of the European PRTR*.

It was superseded in 2007 by Report No. 3/07 *Air Pollutant Emission Estimation Methods for E-PRTR Reporting by Refineries*. This provided new and revised factors and algorithms and focused on the reporting requirements of the E-PRTR Regulations. A second updated edition of that report was published in 2009 (Report No. 1/09), a third edition in 2015 (Report No. 3/15) and a fourth edition in 2017 (Report No. 4/17).

This current report is the fifth edition of Report No. 3/07. This edition includes new factors for estimating hydrogen cyanide (HCN) emissions from fluid catalytic cracking units (FCCUs). A change log is presented in **Appendix 2**.

It is expected that future refinements to the emission factor database will be made. This document is therefore a "snapshot" of the present knowledge. Before using this report, the version number should be compared with the control copy which is posted as an electronic document on the Concawe web-site (www.concawe.org).

Concawe

1.   INTRODUCTION

The European Directive 96/61/EC on integrated pollution prevention and control (IPPC) [48] mandated the publication of a regularly updated pollutant inventory. The European Pollutant Emission Register (EPER) required the reporting of a number of pollutants, both to air and water, from all facilities listed in Annex 1 of the IPPC Directive.

The EPER requirements were succeeded by those of the European Pollutant Release and Transfer Register (E-PRTR) Regulation [52]. This implements at EU level the UNECE PRTR Protocol which was signed in 2003 in Kiev [61]. The first report of the E-PRTR was for the year 2007 with annual reporting thereafter. The E-PRTR is more extensive than EPER in a number of respects. For example, the list of pollutants has been enlarged and the amount of information required to be reported concerning emissions and transfers of pollutants has increased. Guidance on the implementation of the E-PRTR has been provided by the European Commission [51]. The list of air pollutants and their threshold values above which emissions must be reported are given in **Appendix 1**.

With regard to the data submissions for these Registers, Concawe identified three issues that require attention by the oil refining sector:

1. The data submitted should be reliable, in the sense that they represent as accurately as possible the actual pollutant emissions. Over-estimation of emissions is clearly to be avoided. Moreover, under-estimation can give a false impression of what pollution emissions levels can be reached under realistic circumstances.
2. Data should be consistent between comparable sources within the industry.
3. The sharing of best practices in terms of emission factors is important in order to improve the quality of the reporting.

To address these issues, the Concawe Air Quality Management Group initiated a review of the published emission factors for those air pollutants which may be emitted in excess of the reporting threshold values from stationary sources found at the majority of European refineries.

It was noted that there were no emission estimation guidelines for each and every one of the pollutants to air from refineries which may possibly require reporting under the regulations. Although guidance is provided in the European Environment Agency Emission Inventory Guidebook [28] for the major air pollutants, it does not give estimation methodologies for all of the E-PRTR listed pollutants.

On the other hand, for some pollutants such as non-methane volatile organic compounds (NMVOCs) there are a number of different estimation methodologies being used by European refineries e.g. protocols produced by the US EPA [36] and a number of nationally agreed methods such as that published by the UK Energy Institute [30].

Concawe, therefore, published Report No. 9/05 and its first revision No. 9/05R [16] which comprised a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants. The compendium could not be fully comprehensive as emission factors are not available in the public domain for all sources and/or pollutants. Concawe, however, considered this to be the most appropriate set of emissions factors for the refining sector.

Report No. 9/05R was superseded by Report No. 3/07 [17], which focused on the requirements of the E-PRTR and contained additional algorithms and updated emission factors. The second updated edition of that report was published in 2009 (Report No. 1/09 [19]), a third edition in 2015 (Report No. 3/15 [21]) and a fourth edition in 2017 (Report No. 4/17 [24]).

This current report is the fifth edition of Report No. 3/07 and supersedes Report 4/17. It includes new emission factors for hydrogen cyanide (HCN) from fluid catalytic cracking units (FCCUs).

This report provides the estimation algorithms which Concawe recommends for E-PRTR reporting purposes. Alternatively, where measurements have been undertaken, these can be used if considered representative. It does not consider the estimation of accidental or non-routine (e.g. due to maintenance) releases to air. The EU Guidance [51] recommends that emissions from such releases should be estimated by sites on an ad-hoc basis using whatever data are available and the most appropriate methods considered for the circumstances. This report also does not provide guidance on estimating emissions from mobile sources, e.g., transport and mobile machinery on site.

The emission factors provided are for underlined uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc. (see Section 6).

Where emission factors are available, algorithms are provided for sources found in the majority of European refineries. There are some emission sources for which estimation algorithms are not provided in this report e.g. coke calciners. Refineries should review all of the sources of air pollutants on-site and establish if there are any additional sources from those listed in this report which may require emission estimates to be made for E-PRTR reports.

Concawe has previously published reports on non-methane volatile organic compound (NMVOC) emissions from refineries and other downstream oil industry sources. However Report No. 85/54 [14] which was widely used by Industry is now out of date and is no longer available. Although marketing terminals and service stations are not subject to E-PRTR reporting requirements, for completeness this current report provides NMVOC emission estimation algorithms which are applicable to gasoline storage and handling at these facilities.

A summary of the changes to the algorithms and emission factors given in Report No. 4/17 is provided in **Appendix 2**.

2. EMISSION ESTIMATION METHODOLOGIES

There are a number of sources of emission estimation methodologies:

- Oil industry associations e.g. Concawe, API, etc.
- Oil companies that have published methods in the professional press
- National and international environmental authorities e.g. US EPA, European Environment Agency, etc.
- International organisations e.g. IPCC, etc.
- European Commission.

Methodologies published by the national and international organisations may be non-oil industry sector specific.

Only those estimation methods which are currently in the public domain were considered for inclusion in this report. The methodologies were considered in the following order of preference to determine those most representative for oil industry sources:

- Methods published by the oil industry
- Sector specific methods published by national and international authorities
- Non-sector specific methods.

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

Class M: emission data are based on measurements. Additional calculations are needed to convert the results of measurements into annual emission data. Emissions can be derived from continuous or discontinuous measurements of pollutant concentrations. Alternatively, they can be determined based on the results of short term or spot measurements.

Class C: emission data are based on calculations using activity data (e.g. fuel used, production rate) and emission factors or mass balances.

Class E: emission data are based on non-standardised estimations derived from best assumptions or expert guesses that are not based on publicly available references or good practice guidelines.

Where data are measured or calculated, the method of measurement and/or the calculation method must also be provided in the E-PRTR data submission.

The EU Guidance document [51] provides a list of the internationally approved or "equivalent" methodologies that should be used and the method names to be included in the E-PRTR submission. One of the accepted equivalent methodologies is a "European-wide sector specific calculation method, developed by industry experts, which has been delivered to the European Commission, to the European Environment Agency and the relevant international organisations". The EU Guidance document [51] references Concawe Report No. 9/05R [16] which had been submitted to the EC and EEA. This current report is a replacement for Report No. 9/05R and hence use of the algorithms in this report can be considered to be an approved calculation methodology: data could then be reported using the letters "C" and method name acronym "SSC" (sector specific calculation).

3. POLLUTANTS

There are 60 air pollutants which must be reported under the E-PRTR requirements if their respective annual emission threshold values are exceeded at a facility. All of these are shown in **Appendix 1,** with their threshold values.

The EU Guidance Document on E-PRTR Implementation [51] provides indicative lists of the pollutants likely to be emitted on a sector specific "activity" basis. In addition to having its own specific sectoral activity of "mineral oil and gas refineries", the Oil Industry also uses combustion units with ratings in excess of 50 MW. These are included in the sectoral activity classified within the PRTR Regulation [52] as "thermal power stations and other combustion installations".

Those pollutants on the sector specific indicative lists within the EU Guidance Document for these two activities are listed in **Appendix 1**.

Information was requested from the Concawe member companies concerning the emissions of air pollutants from refineries reported either internally or externally. **Appendix 1** lists those pollutants which had been estimated, by at least one of the nine companies who responded, to exceed the E-PRTR reporting thresholds.

Appendix 1 indicates that the pollutants included on the two EU indicative lists are almost identical to those on the oil industry list. The difference is the addition of trichloroethylene on the indicative list for combustion installations.

Trichloroethylene (TRI) is not a product of combustion; its major use is as an organic solvent for industrial degreasing. The inclusion of this pollutant on the sector specific indicative list for combustion installations appears to be due to an anomaly in the EPER database. Only one facility classified as "Combustion installation > 50 MW" reported emissions of TRI, but these would appear to be from the process of manufacturing rubber tyres and tubing at the site and not as a by-product of combustion. TRI has been used in refineries as a chlorinating agent in platformer units, but it is no longer an authorised substance under REACH for this application. This report, therefore, does not consider this pollutant further.

This report provides algorithms to estimate the emissions of all of the other pollutants on the indicative lists in the EU Guidance for refineries and combustion installations rated in excess of 50 MW.

Anthracene and naphthalene are two pollutants that are known to be emitted by refineries, but are not on the sector specific indicative lists. A review of the emissions of these pollutants is provided in **Appendix 3.** It is shown that, even for the largest refineries, neither anthracene nor naphthalene emissions are likely to exceed their E-PRTR reporting threshold values.

Hydrogen cyanide (HCN) is not listed in the refining sector specific indicative list. Information available from the US EPA (Environmental Protection Agency) [45], however, indicated that annual emissions from some fluid catalytic cracking units (FCCUs) could exceed the yearly E-PRTR reporting threshold. Concawe has, therefore, reviewed the information in the US EPA report [45] and data from recent tests on a number of FCCUs in the EU and developed emissions factors for the two modes of FCCU operation [25]. These factors are provided in **Section 30** of this report.

Sites should review their processes and emission sources to establish if there is the potential for any of the other E-PRTR air pollutants to be released in excess of their reporting thresholds.

4. EMISSION SOURCES

4.1. REFINERIES

This report divides the sources found within the majority of refineries, for which emission factors are available in the public domain, into the following categories:

- Combustion
- Process vents
- Storage
- Loading
- Miscellaneous

Combustion sources considered comprise:

- o Boilers
- o Furnaces
- o Fired waste heat boilers
- o CO boilers
- o Gas turbines
- o Gas engines
- o Diesel engines
- o Incinerators
- o Flares

Process sources included are:

- o Hydrogen plants
- o Fluid coking units
- o Fluid catalytic cracking units
- o Catalytic reforming units

Miscellaneous sources included are:

- o Process drains
- o Oil-water separators
- o Fugitive emissions from pressurised pipe work and components
- o Refrigeration systems
- o Use of SF_6

There are some sources which are only found in a limited number of refineries for which algorithms are not given in this report. One example is coke calcining, for which emission factors are available in an API report [1].

4.2. GASOLINE MARKETING FACILITIES

Neither marketing distribution terminals nor service stations are regulated under the terms of the IPPC Directive [48] and hence are not required to submit E-PRTR reports.

Emission estimates for distribution terminals and service stations may, however, be made by oil companies for their own environmental reporting purposes.

Emissions from distribution terminals are primarily NMVOCs due to the storage and loading of refined products, in particular gasolines. Emission estimation methods for sources of NMVOCs at terminals are provided in **Appendix 4.1.**

Some terminals have small steam raising boilers e.g. to heat heavy oil storage tanks. The algorithms provided in this report can be used to estimate combustion emissions from these facilities.

Unlike refineries and terminals, storage at service stations is in underground horizontal tanks. Emissions occur from these due to the displacement of vapours during filling and the evaporation of the stored gasoline. Emissions also occur due to the filling of automobile fuel tanks and from minor drips and spills during those operations. Estimation methods for NMVOC emissions from these sources are provided in **Appendix 4.2**.

5. EMISSION ESTIMATION ALGORITHMS

5.1. INTRODUCTION

Algorithms are provided for the E-PRTR air pollutants which may exceed their emissions reporting thresholds. The level of emissions depends upon the refinery crude throughput, the process units installed, fuels consumed, type of equipment in use, procedures in place, etc.

Algorithms are given on a pollutant by pollutant basis in **Sections 7** through **31**, in the order of the pollutant list in **Appendix 1**.

Algorithms are also provided in **Appendix 3** for two additional pollutants (anthracene and naphthalene). It is demonstrated that the emissions of neither of these pollutants are likely to exceed their E-PRTR reporting thresholds.

Estimation algorithms are given for the sources of each pollutant. A reference is provided for each method, with additional details where considered appropriate.

If no pollutant algorithm is provided for a source, it is because:

- emissions of the pollutant do not occur from that source;
- emissions are considered negligible; or
- no published algorithm has been found or considered appropriate for sources at refineries.

Table 1 indicates those sources for which pollutant algorithms are provided in this report.

Emission factors are given in scientific units to 3 significant figures i.e. 5.67E+03 is equivalent to 5670.

It should be noted that data submitted in E-PRTR reports should be expressed in kg/year and with three significant digits, e.g. 123 000, 17.9, 2.10.

Table 1   Sources for which pollutant emission estimation methodologies are provided in this report

	CH_4	CO	CO_2	HFC	N_2O	NH_3	NMVOC	NOx	SF_6	SOx	HCFC	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Dioxins	C_6H_6	PAH	Cl	HCN	PM_{10}
Boiler	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×	×	×	×			×
Furnace	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×	×	×	×			×
Gas turbine	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×			×
Gas engine	×	×	×		×		×	×		×											×	×			×
Diesel engine	×	×	×		×		×	×		×											×	×			×
Pilot or support fuel	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×			×
Incinerator	×	×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×			×
Flare	×	×	×				×	×		×		×	×	×	×	×	×	×	×		×	×			×
Hydrogen plant			×																						
Fluid coking unit			×				×					×		×	×	×	×	×	×		×				×
Fluid catalytic cracking unit		×	×		×		×	×		×		×	×	×	×	×	×	×	×		×	×		×	×
Catalytic reforming unit		×	×							×										×			×		
Process drainage							×																		
Oil-water separator							×																		
Process fugitives	×						×															×			
Loading							×																		
Storage							×																		
SCR/SNCR						×																			
Refrigeration				×		×					×														
Lab/test/HV switch gear									×																

5.2. EMISSION FACTORS DERIVED FROM MEASUREMENTS WITH DATA BELOW THE LIMIT OF DETECTION

A few emission factors were originally derived from measurements where, if the values measured were all below the limit of detection, those data points were set at the limit of detection level. Where possible, in this report these factors have been identified and the following rule used to adjust them:

- Where all data points were below the measurement detection limit, the emissions factor has been set to zero (i.e. it is considered that the source is not proven).

Where both the averages of data points above and below the limit of detection (the 'detect' and 'non-detect' values) are provided in a reference, along with the number of data points used to derive these, a weighted value as calculated below has been used in this report.

- Weighted factor = [(average detect value × number of detect samples) + (average non-detect value × number of non-detect samples × detect ratio)] / total number of samples

where detect ratio = number of detect samples / total number of samples.

Reference: [62], Section 7.4.7

All algorithms where these adjustments have been made are identified in the text.

5.3. TREATMENT OF DATA WHERE MEAN AND MEDIAN VALUES AVAILABLE

In some references, i.e. [1], [10] and [11], both the mean and median values of pollutant emission data sets are provided. A small number of the data sets used to determine emission factors are highly skewed, resulting in mean values dominated by a few very high values that are not representative of the majority of readings. Where the mean value exceeds the median value by more than a factor of ten, the median has been considered a more realistic value and has been used in this report. In all other cases the mean value has been used.

All algorithms where the median value has been used are identified in the text.

5.4. OVERVIEW OF COMBUSTION ALGORITHMS

For many of the pollutants arising from combustion sources the published emission factors are one of the following types:

a) Mass per unit volume combusted (EF_{VOL})
b) Mass per energy consumed (EF_{NCV})

To provide a consistent approach within this report, algorithms using emissions factors based on EF_{NCV} are provided. This type of factor enables emissions to be calculated for fuels which are widely different in composition to those for which EF_{VOL} was originally determined. Where published factors are only in the form of EF_{VOL}, the values of EF_{NCV} have been calculated using default values for the fuels. Where appropriate, this is noted within the text. Details, along with the default fuel heating values used in this report, are provided in **Appendix 5.**

5.4.1. Heating Values

In the USA, the norm is to use Higher Heating Value (HHV) (or Gross Calorific Value) for a fuel, whilst in Europe the Net Calorific Value (NCV) (or Lower Heating Value - LHV) is usually quoted. In this report all heating values quoted are NCVs and all emission factors involving heat energy require the use of the corresponding fuel NCV, unless otherwise quoted.

NCV = HHV x Correction Factor for heat of vaporisation of water in the fuel

For liquid fuels:
$$NCV = HHV \times 0.95$$

For gaseous fuels:
$$NCV = HHV \times 0.9$$

Reference: [6], Section 4.2.

6. EMISSION CONTROLS

6.1. OVERVIEW

The algorithms provided in this report (with the exceptions identified in **Sections 6.2** and **6.3**) assume that <u>no</u> emission reduction control equipment (e.g. flue gas desulphurisation system, vapour recovery unit, etc.) is installed in vent lines, stacks or flues.

Calculated emissions must, therefore, take account of any emission controls. The algorithm to be used is:

Emissions reported = Uncontrolled emissions × (1 – [EFF x ONTIME] / 10 000)

where:
EFF = Average percentage efficiency of emission reduction control equipment over reporting period.
ONTIME = Percentage of the time that the emission reduction equipment is operational when required during the reporting period.

Where there are two or more emission control devices in series impacting a particular pollutant (e.g. for particulates: cyclone plus electrostatic precipitator) then the effect of each device on the pollutant emissions must be taken into account. For example, if two devices are installed, with respective efficiencies of EFF_1 and EFF_2 and operating times of $ONTIME_1$ and $ONTIME_2$, then the algorithm is:

Emissions reported = Uncontrolled emissions × {(1 – [EFF_1 x $ONTIME_1$] / 10 000) × (1 – [EFF_2 x $ONTIME_2$] / 10 000)}

For vapour recovery units (VRUs) designed to reduce NMVOC emissions from loading operations, algorithms are also provided where the average vent emission concentration is known but not the overall VRU efficiency.

6.2. PARTICULATE EMISSIONS FROM FLUID CATALYTIC CRACKING UNITS

The algorithms for emissions of particulates (PM_{10}) (see **Section 31**) and metals (see **Sections 18, 19** and **21 through 25**) from these units assume that there are cyclone systems installed inside the regenerator vessel to separate the catalyst particles from the hydrocarbon vapours. If additional cyclones or other emission abatement devices such as electrostatic precipitators are installed external to the regenerator then the effect of these additional controls to further reduce emissions must be taken into account in the reported emission level.

6.3. EMISSIONS FROM CATALYTIC REFORMING UNITS

There are limited references to emissions from catalytic reforming units (CRUs). The emission factors quoted in this report for CO and SO_X are from a paper by Bertrand et al. [11]. This paper uses combined emissions data from a number of units. As some of these units may have emission abatement controls installed, the factors may not truly represent uncontrolled emissions.

A review of the emissions for particulates and metals using the factors in reference [11] for a very high throughput CRU indicated that the estimated emissions were very small relative to other sources of these pollutants in a large refinery. No factors for these pollutants have therefore been provided.

7. METHANE (CH$_4$)

Estimation methods are provided for emissions due to:
- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Fugitive emissions from fuel gas lines
- Venting to atmosphere of uncontrolled blowdown systems

7.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 2**.

Table 2   CH$_4$ Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	6.98E-01	[6] Section 4, Table 4-7
	Refinery Fuel Oil	1.43E+00	[6] Section 4, Table 4-7
	LPG	9.63E-01	[6] Section 4, Table 4-7
	Natural Gas	1.08E+00	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[6] Section 4, Table 4-7
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	1.68E-01	[6] Section 4, Table 4-7
	Refinery Fuel Oil	3.02E+00	[6] Section 4, Table 4-7
	LPG	9.63E-01	[6] Section 4, Table 4-7
	Natural Gas	1.08E+00	[6] Section 4, Table 4-7

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces 10 MW to 100 MW	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[6] Section 4, Table 4-7
Boilers and Furnaces > 100 MW	Distillate (gas oil)	9.05E-01	[6] Section 4, Table 4-7
	Refinery Fuel Oil	8.45E-01	[6] Section 4, Table 4-7
	Natural Gas	1.08E+00	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[6] Section 4, Table 4-7
Gas Turbine[1]	Natural Gas	4.11E+00	[6] Section 4, Table 4-9
Gas Engine 4-stroke, Lean Burn	Natural Gas	5.97E+02	[6] Section 4, Table 4-9
Diesel Engine[2] Large, Stationary	Diesel Fuel	3.67E+00	[6] Section 4, Table 4-9
Incinerator Support Fuel or Flare Pilot Fuel	LPG	9.63E-01	[6] Section 4, Table 4-7
	Natural Gas	1.08E+00	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	3.26E-01	[6] Section 4, Table 4-7
	Refinery Fuel Gas - hydrogen gas content ≥ 65% v/v	2.39E-01	[6] Section 4, Table 4-7

Notes:
1. Factor derived from turbines operating at high (≥ 80%) loads.
2. Factor is derived from data from one engine with 9% CH$_4$ by weight in the exhaust gas.

7.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. low joule gas) it is recommended to use the value of EF$_{NCV}$ for natural gas from **Table 2**.

7.2. DESTRUCTION OF GASEOUS STREAMS

7.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithms in **Section 7.1**.

7.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 5.00E-00 × M × MF_{CH4}

where:
M = total mass of gas flared (in tonnes)
MF_{CH4} = mass fraction of methane in gas flared

This algorithm assumes that 0.5% of the hydrocarbons remain unburned in "well designed and operated flares, such as in refineries".

Reference: [6], Section 4.6, Figure 4-2.

7.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 2.28E-05 × Refinery Feed (in m³)

Reference: [6], Section 4.6, Table 4-11.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

7.2.2. Incineration of hydrocarbon gas streams

If the destruction efficiency of the incinerator and the mass and composition of the gas stream being combusted are known:

Mass emitted (kg) = (100 – DE) × 10 × M × MF_{NMVOC}

where:
DE = incinerator destruction efficiency (%)
M = total mass of gas incinerated (in tonnes)
MF_{NMVOC} = mass fraction of methane in gas incinerated

Otherwise, use the algorithm in **Section 7.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 7.1**.

7.3. FUEL GAS SYSTEMS

Fugitive emissions can occur from the components e.g. valves, flanges, etc., in fuel gas lines containing methane. Emissions may be determined from leak monitoring surveys where CH_4 concentrations are measured, or calculated using equipment component counts (see **Section 13.5**). Where neither of these is available, a conservative emissions estimate can be obtained from:

Mass emitted (kg) = 3.00E-01 × M × MF$_{CH4}$

where:
M = total mass of fuel gas combusted (in tonnes)
MF$_{CH4}$ = mass fraction of methane in fuel gas

Reference: [59], Section 2, Reference Table 1.

7.4. UNCONTROLLED BLOWDOWN SYSTEMS

The gaseous emissions from blowdown systems in EU refineries are recovered and/or flared.

If these controls are not operational and all of the emissions are released to atmosphere, the total hydrocarbons emissions can be conservatively estimated using the factor provided in US EPA publication AP-42 [36], Table 5.1-1. This reference states that methane comprises less than 1% by mass of the total hydrocarbon emissions.

8. CARBON MONOXIDE (CO)

Estimation methods are provided for emissions due to:
- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Partial burn regeneration of fluid catalytic cracking units (FCCUs)
- Regeneration of catalytic reforming units

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires direct measurement of CO emissions from all combustion units and from fluid catalytic cracking units.

8.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 3**.

Table 3   CO Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)[1]	1.62E+01	[38] Section 1.3, Table 1.3-1
	Refinery Fuel Oil[1,2]	6.00E+00	[26] Section 3.10.3.1
	LPG[3]	3.71E+01	[38] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[38] Section 1.4, Table 1.4-1
	Refinery Fuel Gas[4]	1.21E+01	[26] Section 3.10.3.1
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)[1]	1.62E+01	[38] Section 1.3, Table 1.3-1
	Refinery Fuel Oil[1,2]	6.00E+00	[26] Section 3.10.3.1
	LPG[3]	3.71E+01	[38] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[38] Section 1.4, Table 1.4-1
	Refinery Fuel Gas[4]	1.21E+01	[26] Section 3.10.3.1

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces > 100 MW	Distillate (gas oil)[1]	1.62E+01	[38] Section 1.3, Table 1.3-1
	Refinery Fuel Oil[1,2]	6.00E+00	[26] Section 3.10.3.1
	LPG[3]	3.47E+01	[46] SCC 10101002
	Natural Gas	3.93E+01	[38] Section 1.4, Table 1.4-1
	Refinery Fuel Gas[4]	1.21E+01	[26] Section 3.10.3.1
Gas Turbine[5]	Distillate (gas oil)[6]	1.49E+00	[37] Section 3.1, Table 3.1-1
	Natural Gas	4.80E+00	[28] Section 1.A.1, Table 3-17
Gas Engine[7] 4-stroke, Lean Burn	Natural Gas	2.66E+02	[37] Section 3.2, Table 3.2-2
Diesel Engine Large, Stationary	Diesel Fuel	3.85E+02	[37] Section 3.4, Table 3.4-1
Incinerator Support Fuel or Flare Pilot Fuel	LPG[3]	3.71E+01	[38] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[38] Section 1.4, Table 1.4-1
	Refinery Fuel Gas[4]	1.21E+01	[26] Section 3.10.3.1

Notes:
1. US EPA AP-42 [38], Table 1.3-1, note *e* states that CO emissions may increase by factors of 10 to 100 if the unit is improperly operated or not well maintained.
2. Factor derived using NCV of 40 MJ/kg from the Refinery BREF [26], Table 3.54.
3. Factor is for propane combustion.
4. Factor derived using NCV of 48.07 MJ/kg from the Refinery BREF [26], table in Annex 8.6.2, Section B.2.3.
5. Factor derived from turbines operating at high (≥ 80%) loads.
6. Factor provided in US EPA AP-42 [37] was derived using HHV of 139 MBtu/10^3 US gal.
7. Factor derived from engines operating at < 90% load.

8.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. low joule gas) it is recommended to use the value of EF$_{NCV}$ for refinery fuel gas from **Table 3**.

8.2. DESTRUCTION OF GASEOUS STREAMS

8.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithms in **Section 8.1**.

8.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 1.33E-01 × M × NCV

where:
M = mass of flare gas combusted (in tonnes)
NCV = net calorific value of the flare gas combusted (in MJ/kg)

Reference: [47], Table 13.5-2.

8.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 1.20E-02 × Refinery Feed (in m^3)

Reference: [27], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

8.2.2. Incineration of hydrocarbon gas streams

Use the algorithm in **Section 8.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 8.1**.

8.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

CO is produced during the regeneration process and depends upon its severity. Emissions from partial burn regeneration are normally controlled with a CO boiler.

It is anticipated that EU refineries will estimate CO_2 emissions from FCCUs using the algorithm in **Section 9.3**. In this case, the CO emissions will be determined from measurements of flue gas flow and CO concentration.

Where the method in **Section 9.3** is not used, CO emissions can be estimated using the following:

8.3.1. Full Burn Regeneration

CO emissions are deemed to be negligible. This assumes sufficient flue gas oxygen concentration to ensure complete conversion of CO to CO_2.

8.3.2. Partial Burn with CO Boiler

CO emissions are deemed to be negligible.

Reference: [36], Table 5.1-1.

8.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

Mass emitted (kg) = 3.92E+01 × Volume of fresh feed to unit (in m³)

Reference: [36], Table 5.1-1.

8.4. CATALYTIC REFORMING UNITS

Mass emitted (kg) = 4.16E-02 × Volume of feed to unit (in m³)

Reference: [11], Table 1. This reference uses data from a number of units with varying degrees of abatement equipment installed – see **Section 6.3**. It also provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

9. CARBON DIOXIDE (CO$_2$)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Fluid catalytic cracking unit regenerators
- Other catalyst regeneration e.g. in catalytic reforming units
- Fluid and Flexi-cokers
- Hydrogen plants

European refineries must estimate their CO$_2$ emissions under the terms of the EU greenhouse gas emission allowance trading scheme [50]. An EU guidance document [53] sets out detailed guidelines for the monitoring and reporting of CO$_2$ emissions.

9.1. COMBUSTION

EU guidance [53] specifies that CO$_2$ emissions from combustion installations be calculated by multiplying the energy content of each fuel used by an emission factor and an oxidation factor (default value equal to one). This requires the NCV of each fuel to be determined along with activity-specific emission factors.

The algorithm provided below applies the fundamental principle of complete stoichiometric combustion using the value of carbon content of the fuel. This approach reduces the emission calculation uncertainty as only carbon content has to be determined instead of values for both NCV and emission factor,

Mass emitted (kg) = 1000 × M × MF$_{CARBON}$ × CFC$_{MW}$

where:
M = mass of fuel burnt (in tonnes)
MF$_{CARBON}$ = mass fraction of carbon in fuel
CFC$_{MW}$ = Molecular weight conversion from C to CO$_2$ = (44.01/12.01) = 3.664

Thus for refinery oil and gaseous fuels:

Mass emitted (kg) = 3.664E+03 × M × MF$_{CARBON}$

9.2. DESTRUCTION OF GASEOUS STREAMS

9.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 9.1.**

9.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known, use algorithm in **Section 9.1**, where:
M = mass of flare gas burnt (in tonnes)
MF$_{CARBON}$ = mass fraction of carbon in flare gas

EU guidance [53] specifies this methodology for CO$_2$ reporting purposes by European refineries.

9.2.1.2. Flare Stream Composition Unknown

If the composition of the flare gas stream is not known, a conservative factor based on the combustion of ethane can be used:

Mass emitted (kg) = 3.93E+00 × Volume of gas flared (in m^3)

Reference: [53], Annex II, Section 2.1.1.3 (b).

9.2.1.3. Flare Stream Details Unknown

If both the mass and the composition of the flare gas stream are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 3.14E+00 × Refinery Feed (in tonne)

Reference: [57], Section 3, Table 5.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

9.2.2. Incinerators

Use algorithm in **Section 9.1**, where:
M = mass of gas incinerated (in tonnes)
MF_{CARBON} = mass fraction of carbon in gas incinerated

9.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

EU guidance [53] requires that emissions shall be calculated by a material balance approach, taking into account the state of the input air and the flue gas. Note that for CO_2 reporting, all CO in the flue gas shall be reported as CO_2.

Concawe report 10/04 [15] provides the following algorithm:

Mass emitted (kg) = (AR + SR) × (VF_{CO2} + VF_{CO}) × CON_{VOL} × TIME

where:

AR = Air blower capacity (in m^3/minute)
SR = Supplemental oxygen addition rate (in m^3/minute)
VF_{CO2} = Volume fraction of CO_2 in flue gas
VF_{CO} = Volume fraction of CO in flue gas (prior to CO boiler if installed)
CON_{VOL} = Volume conversion factor at 15 C = 44 / MCF
MCF = Molar conversion factor at 15 C = (22.4 × 288 / 273) = 23.631 m^3/kgmole
TIME = time blower operated (in minutes)

22

Thus:

Mass emitted (kg) = 1.86E+00 × (AR + SR) × (VF$_{CO2}$ + VF$_{CO}$) × TIME

Reference: [6], Section 5.2.1, equation 5-6.

9.3.1. FCCU With CO Boiler

Mass emitted (kg) = 1.86E+00 × (AR + SR) × (VF$_{CO2}$ + VF$_{CO}$) × TIME

9.3.2. FCCU Without CO Boiler

Mass emitted (kg) = 1.86E+00 × (AR + SR) × VF$_{CO2}$ × TIME

9.4. OTHER CATALYST REGENERATION

CO_2 is produced during the catalyst regeneration in reforming and hydro-processing units.

9.4.1. Flue Gas Flow and Composition Known

EU guidance [53] specifies that the method provided in **Section 9.3** should be used.

9.4.2. Flue Gas Details Unknown

The following algorithm conservatively assumes complete stoichiometric combustion of the carbon in the coke deposited on the catalyst. In practice there will be small emissions of CO (see **Section 8.4**).

Mass emitted (in kg) = 3.66E+03 × CR × MF$_{CARB}$ × Feed

where:
CR = Mass ratio of coke produced per feed
MF$_{CARB}$ = Mass fraction of carbon in coke
Feed = Feed to unit (in tonnes)

Reference: [6], Section 5.2.4.

9.5. COKERS

There are several varieties of cokers in use in refineries, including delayed cokers, fluid cokers, and flexi-cokers.

Delayed cokers will not have CO_2 emissions, other than from their process heaters [6]. These should be calculated using the fuel combustion algorithm in **Section 9.1**.

Fluid cokers and flexi-cokers may have a CO_2 vent resulting from the coke burner.

EU guidance [53] specifies that the method provided in **Section 9.3** should be used for flexi-cokers.

For cokers where flue gas flow and composition are unknown:

Mass emitted (in kg) = 3.66E+03 × CR × MF$_{CARB}$ × Feed

where:
CR = Mass ratio of coke produced per feed
MF_{CARB} = Mass fraction of carbon in coke
Feed = Feed to unit (in tonnes)

Reference: [6], Section 5.2.3.

If the burner off-gas is burned as a low joule gas fuel, the subsequent emissions should be calculated using the fuel combustion algorithm in **Section 9.1**.

9.6. HYDROGEN PLANTS

CO_2 is produced during the hydrogen production process.

9.6.1. Feed Composition Data Known

EU guidance [53] specifies that emissions should be calculated from the carbon content of the feed gas.

Mass emitted (kg) = 3.66E+03 × MF_{CARB} × Feed

where:
MF_{CARB} = mass fraction of carbon in feed gas
Feed = Feed to unit (in tonnes)

9.6.2. Feed Composition Data Unknown

If the composition of the feed gas is not known, a conservative factor based on an ethane feed can be used:

Mass emitted (kg) = 2.90E+03 × Feed to unit (in tonnes)

Reference: [53], Annex III, Section 2.1.2.2 (b).

9.7. SOUR GAS PROCESSING

For systems that vent the waste CO_2 (e.g. amine units), emissions can be estimated by material balance using the known throughput and CO_2 concentrations of the inlet and outlet gas streams. The accuracy of this estimate is highly dependent on the consistency of the CO_2 concentration measurements. To improve the accuracy of this method, the API Compendium [6] suggests that a volume weighted-average CO_2 concentration should be determined (especially for the inlet gas) using a range of gas sample data. If the sweet gas concentration is unknown, 0% can be applied as a simplifying assumption, recognising that this will likely over-estimate the emissions.

Reference: [6], Section 5.1.5.

For sulphur recovery units that route the sulphur plant tail-gas to an incinerator, use the algorithm in **Section 9.1** (See **Section 9.2.2**).

10. HYDROFLUOROCARBONS (HFC)

Hydrofluorocarbons (HFCs) may be used as refrigerants in refinery thermal exchange equipment.

Emissions are assumed to equal the amount used during the reporting period to top-up systems to replenish losses due to uncontrolled leakage.

Mass emitted (kg) = Mass used to top-up refrigerant systems (in kg)

Usage where the systems have been fully or partially drained and refrigerants collected for recycling or destruction should not be reported.

11. NITROUS OXIDE (N_2O)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of hydrocarbon gas streams in incinerators

11.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 4**.

Table 4 N_2O Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	8.40E-01	[6] Section 4, Table 4-7
	Refinery Fuel Oil	1.60E+00	[6] Section 4, Table 4-7
	LPG	4.33E+00	[6] Section 4, Table 4-7
	Natural Gas	1.03E+00	[6] Section 4, Table 4-7
	Natural Gas (where low NO_X burners fitted)	3.00E-01	[6] Section 4, Table 4-7
	Refinery Fuel Gas	3.89E-02	[6] Section 4 Table 4-7
Gas Turbine[1]	Natural Gas	1.43E+00	[6] Section 4, Table 4-9
Gas Engine 4-stroke, Lean Burn	Natural Gas	1.00E-01	[6] Section 4, Table 4-5
Diesel Engine Large, Stationary	Diesel Fuel	6.00E-01	[6] Section 4, Table 4-5
Incinerator Support Fuel or Flare Pilot Fuel	LPG	4.33E+00	[6] Section 4, Table 4-7
	Natural Gas	1.03E+00	[6] Section 4, Table 4-7

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Incinerator Support Fuel or Flare Pilot Fuel	Refinery Fuel Gas	3.89E-02	[6] Section 4 Table 4-7

Notes:

1. Factor based on limited source tests on a single turbine with water-steam injection and operating at high (≥ 80%) loads.

11.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. low joule gas) it is recommended to use the value of EF$_{NCV}$ for refinery fuel gas from **Table 4**.

11.2. DESTRUCTION OF HYDROCARBON GAS STREAMS IN INCINERATORS

Use the algorithm in **Section 11.1** with an emission factor EF$_{NCV}$ equal to that for natural gas combustion in a furnace.

Reference: [6], Section 4.7.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 11.1**.

12.   AMMONIA (NH₃)

Estimation methods are provided for emissions from:
- Selective Non-Catalytic NO$_X$ Reduction (SNCR) systems
- Selective Catalytic NO$_X$ Reduction (SCR) systems
- Refrigeration systems
- Fluid catalytic Cracking Unit Regenerators

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires continuous, direct measurement of NH$_3$ emissions from all units equipped with SCR and SNCR.

12.1.   NO$_X$ REDUCTION SYSTEMS

Ammonia is produced as a by-product by SCR and SNCR systems installed in flues to reduce NO$_X$ emissions.

12.1.1.   SNCR

The emission algorithms are:

Mass emitted (kg) = 3.50E-01 × V$_{OIL}$

or

Mass emitted (kg) = 2.88E+02 x V$_{GAS}$

where:
V$_{OIL}$ = Volume of oil combusted in device connected to SNCR (in m^3)
V$_{GAS}$ = Volume of gas combusted in device connected to SNCR (in million m^3)

Reference: [9], Section 5.4, Table 5-5.

12.1.2.   SCR

The emission algorithms are:

Mass emitted (kg) = 1.70E-01 × V$_{OIL}$

or

Mass emitted (kg) = 1.46E+02 x V$_{GAS}$

where:
V$_{OIL}$ = Volume of oil combusted in device connected to SCR (in m^3)
V$_{GAS}$ = Volume of gas combusted in device connected to SCR (in million m^3)

Reference: [9], Section 5.4, Table 5-5.

12.2.   REFRIGERATION SYSTEMS

Ammonia may be used as a refrigerant in refinery thermal exchange equipment.

Emissions are assumed to equal the amount used during the reporting period to top-up systems to replenish losses due to uncontrolled leakage.

Mass emitted (kg) = Mass used to top-up refrigerant systems (in kg)

Usage where the systems have been fully or partially drained and refrigerants collected for recycling or destruction should not be reported.

12.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

NH_3 is produced during the regeneration process and depends upon its severity. Emissions from partial burn regeneration are normally controlled by a CO boiler.

12.3.1. Full Burn Regeneration

Emissions are deemed to be negligible

Reference: [12], Section 9.3.4.

12.3.2. Partial Burn with CO Boiler

Emissions are deemed to be negligible

Reference: [12], Section 9.3.4.

12.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

Mass emitted (kg) = 1.55E-01 × Volume of fresh feed to unit (in m^3)

Reference: [9], Section 4, Table 4.1.

13. NON-METHANE VOLATILE ORGANIC COMPOUNDS (NMVOC)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Fluid catalytic cracking unit regenerators
- Fluid cokers
- Components under pressure e.g. pumps and valves ("fugitives")
- Process drains
- Oil-water separators
- Loading of mobile containers (rail-cars, road tankers, ships and barges)
- Storage tanks
- Venting to atmosphere of uncontrolled blowdown systems
- Uncontrolled bitumen blowing

The driver for reporting VOC emissions is photochemical production of ozone. Methane has a negligible photochemical reactivity. In Europe this compound is therefore excluded from the "basket" of reactive VOCs which are collectively referred to as non-methane volatile organic compounds (NMVOC). The US EPA also considers ethane to have a significantly low reactivity. A number of emission factors developed by the EPA, therefore, are for non-(methane and ethane) VOCs. Those NMVOC emission factors provided in this section which exclude ethane emissions are identified.

13.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 5**.

Table 5   NMVOC Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.10E+00	[38] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	3.41E+00	[38] Section 1.3, Table 1.3-3
	LPG[1]	3.96E+00	[38] Section 1.5, Table 1.5-1
	Natural Gas[2]	2.58E+00	[38] Section 1.4, Table 1.4-2

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	6.47E-01	[38] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	8.45E-01	[38] Section 1.3, Table 1.3-3
	LPG[1]	3.96E+00	[38] Section 1.5, Table 1.5-1
	Natural Gas[2]	2.58E+00	[38] Section 1.4, Table 1.4-2
Boilers and Furnaces > 100 MW	Distillate (gas oil)	2.46E+00	[38] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	2.29E+00	[38] Section 1.3, Table 1.3-3
	LPG[2]	2.27E+00	[46] SCC 10101002
	Natural Gas[2]	2.58E+00	[38] Section 1.4, Table 1.4-2
Gas Turbine	Distillate (gas oil)[2,3,4]	1.86E-01	[37] Section 3.1, Table 3.1-2a
	Natural Gas	1.60E+00	[28] Section 1.A.1, Table 3-17
Gas Engine[2] 4-stroke, Lean Burn	Natural Gas	5.64E+01	[37] Section 3.2, Table 3.2-2
Diesel Engine[5] Large, Stationary	Diesel Fuel	3.71E+01	[37] Section 3.4, Table 3.4-1
Incinerator Support Fuel or Flare Pilot Fuel	LPG[1]	3.96E+00	[38] Section 1.5, Table 1.5-1
	Natural Gas[2]	2.58E+00	[38] Section 1.4, Table 1.4-2

Notes:
1. Factor is for propane combustion. Derived by subtracting the emissions factor for methane from that for total organic compounds.
2. Factor excludes ethane emissions.
3. Factor derived from turbines operating at high (≥ 80%) loads
4. Factor provided in US EPA AP-42 [37] was derived using HHV of 139 MBtu/10^3 US gal.
5. Based on data from one engine with exhaust gas TOC composition by weight of 91% NMVOCs.

13.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. refinery fuel gas, low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 5**.

13.2. DESTRUCTION OF GASEOUS STREAMS

13.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 13.1**.

13.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 5.00E-00 × M × MF$_{NMVOC}$

where:
M = total mass of gas flared (in tonnes)
MF$_{NMVOC}$ = mass fraction of NMVOC in gas flared

This algorithm assumes that 0.5% of the hydrocarbons remain unburned in "well designed and operated flares, such as in refineries".

Reference: [6], Section 4.6.

13.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 2.00E-03 × Refinery Feed (in m^3)

This factor is for total unburned hydrocarbons. Comparison with the emission factor for methane (**Section 7.2.1.2**) indicates that methane is assumed to constitute about 1% by mass of the total unburned hydrocarbons.

Reference: [27], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

13.2.2. Incineration of hydrocarbon gas streams

If the destruction efficiency of the incinerator and the mass and composition of the gas stream are known:

Mass emitted (kg) = (100 – DE) × 10 × M × MF$_{NMVOC}$

where:
DE = incinerator destruction efficiency (%)
M = total mass of gas combusted (in tonnes)
MF$_{NMVOC}$ = mass fraction of NMVOC in gas combusted

Otherwise, use the algorithm in **Section 13.1** with an emission factor EF$_{NCV}$ equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 13.1**.

13.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

NMVOCs are produced during the regeneration process. Emissions from units operating with partial burn regeneration are normally controlled with a CO boiler.

13.3.1. Full Burn Regeneration

Emissions are deemed to be negligible

13.3.2. Partial Burn with CO Boiler

Emissions are deemed to be negligible

Reference: [36], Table 5.1-1.

13.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

Mass emitted (kg) = 6.30E-01 × Volume of fresh feed to unit (in m^3)

This factor is for total hydrocarbons (THC). EPA publication AP-42 [36] states that, overall, less than 1% by mass of THC emissions is methane.

Reference: [36], Table 5.1-1.

13.4. FLUID COKERS

If the off-gas is not fed to a CO boiler, or it is not in operation:

Mass emitted (kg) = 4.60E-02 × Feed to unit (in m^3)

Reference: [31], Section 4.2.1, Table 8.

13.5. FUGITIVE EMISSIONS FROM PRESSURISED COMPONENTS

Emissions can occur due to leakage past seals on components installed in pressurised pipework or process plant e.g. valves, pumps, flanges, etc.

Emission estimates can be made by:

- Measuring the VOC concentration adjacent to potential leak points and estimating the emission flux using correlation equations or emission factors.
- Detecting leaks using optical gas imaging.
- Using average emission factors for individual types of components and their process service, where the number of components is known.
- Using a conservative overall emission factor based on refinery throughput.

Note that this section does not deal with emissions from low pressure equipment such as drains, oil-water separators, loading systems and product storage tanks. Emission estimation methodologies for these sources are provided separately – see **Sections 13.6**, **13.8** and **13.9**.

13.5.1. Leak Detection Surveys Undertaken

Leaking components can be identified either using a conventional hydrocarbon monitor to measure the VOC concentration adjacent to potential leak points or an optical gas imaging (OGI) camera can be used to visualise gas leaks remotely..

This report does not provide details of the measurement methods. Concawe Report 6/08 [18] provides a comparative review of conventional and OGI techniques for leak detection.

13.5.1.1. Conventional Hydrocarbon Monitor

This method requires the "screening" of leak sources by measuring the concentration of VOCs at the surface of each potential source using a conventional hydrocarbon monitor. The local VOC concentration ("screening value") at the surface of a leak source is converted into an emission flux using a correlation equation or emission factors.

Details of the methodologies and the calculation of emissions are provided by the US EPA [35] and in the European CEN Standard on fugitive emission estimation [13].

13.5.1.2. Optical Gas Imaging Camera

In this method emissions are estimated using a "leak" / "no-leak" criterion where the emission factor used depends on the "leak" detection sensitivity of the camera. The emission factors for each equipment type for specified camera detection limits are provided in **Table 6.** Concawe Report 6/15 [22] recommends the use of the leak/no-leak factors for 6 g/h (highlighted in **Table 6**).

The emissions can be calculated for each equipment type and service using:

Mass emitted (kg) = [(F_{LEAK} × N_{LEAK}) + ($F_{NO\text{-}LEAK}$ × $N_{NO\text{-}LEAK}$)] × TIME

where:
F_{LEAK} = Emission factor for leaking components according to the detection limit of the camera
N_{LEAK} = Number of components identified as leaking
$F_{NO\text{-}LEAK}$ = Emission factor for non-leaking components according to the detection limit of the camera
$N_{NO\text{-}LEAK}$ = Number of components identified as not leaking
TIME = Time that the equipment is in operation and pressurised (in hours).

Details of the methodology and the calculation of emissions are provided in Concawe Report 6/08 [18], Report 6/15 [22] and in a paper by Lev-On et al [55].

Table 6   Leak/No-Leak Emission Factors where optical gas imaging (OGI) is used to detect leaks

Equipment Type	Factor Type	Emission Factor for Specified OGI Leak Definition for different camera sensitivity settings kg/hr/source			
		3 g/hr	6 g/hr	30 g/hr	60 g/hr
Valves	Leak	5.50E-02	**7.30E-02**	1.40E-01	2.00E-01
	No-Leak	1.90E-05	**4.30E-05**	1.70E-04	2.70E-04
Pumps	Leak	1.40E-01	**1.60E-01**	3.10E-01	3.50E-01
	No-Leak	9.60E-05	**1.30E-04**	5.90E-04	7.50E-04
Flanges	Leak	2.90E-02	**4.50E-02**	8.80E-02	1.20E-01
	No-Leak	2.60E-06	**4.10E-06**	1.00E-05	1.40E-05
All other components	Leak	5.60E-02	**7.50E-02**	1.50E-01	2.10E-01
	No-Leak	7.00E-06	**1.40E-05**	5.10E-05	8.10E-05

Reference: [55].

Definitions of "Service"

The CEN standard [13] provides the following definitions for "service":

- Gas service: equipment which in use contains process fluid that is in the gaseous state at operating conditions.
- Light liquid service: equipment which in use contains hydrocarbon streams of which at least 20% wt has a vapour pressure in excess of 0.3 kPa at 20°C. For example, this includes automotive and aviation gasolines and crude oil. It excludes products such as kerosenes and gasoils.

13.5.2. Leak Detection Surveys Not Undertaken

13.5.2.1. Component Data Available

Where no monitoring (or only a partial survey) has been undertaken, the emissions from un-surveyed equipment can be calculated using:

Mass emitted (kg) = $F_{COMP} \times N \times TIME$

where:
F_{COMP} = Average emission factor for the particular equipment type as in **Table 7**.
N = Number of pieces of equipment grouped in the relevant category according to the equipment type, service and operation.
TIME = Time that the equipment group is in operation and pressurised (in hours).

This algorithm is conservatively high as it assumes that the product contained within the equipment components wholly comprises NMVOCs i.e. it does not account for non-NMVOC components contained within the fugitive emission. However, the non-NMVOC emissions will mainly be methane e.g. from fuel gas, and this has the lowest density of the hydrocarbons emitted. For fuel gas systems this can be compensated for; see **Section 7.3** for methane emission estimation. Moreover, the number of

equipment components in pipelines containing low concentration NMVOC streams (e.g. low joule gas) is generally a very small percentage of the total components on a refinery.

Table 7   Average Emission Factors for Components

Equipment Type	Service	Emission Factor kg/hr/source
Valves	Gas	2.68E-02
	Light Liquid	1.09E-02
Pump seals	Light Liquid	1.14E-01
Compressor seals	Gas	6.36E-01
Pressure relief valves	Gas	1.60E-01
Flanges and non-flanged connectors	All	2.50E-04
Open-ended lines	All	2.30E-03
Sampling connections	All	1.50E-02

Reference: [13]

Component counts

The count can be based on up-to-date piping and instrumentation diagrams, equipment lists, operating manuals or physical component counts. The count should include spare components if these are filled with process fluid and are pressurised.

If actual counts are not available, an extrapolation can be made from published information. An EPA report [32] cites an example of a US refinery of 52 500 m^3/day capacity having 11 500 valves, 46 500 flanges, 350 pump seals, 70 compressor seals and 100 relief valves.

Alternatively, the CFA Code of Practice [12], Section 3.4.1, Table 3-1, provides the following "average" refinery data:

Emission Source Component	Gas	Liquid
Valves per pump or compressor	133	41
Flanges per valve	4.1	4.1
Mixer seals per mixer	-	1
Pump seals per pump	-	1.35
Compressor seals per compressor	2	-

13.5.2.2.   No Component Data Available

A conservative emission factor can be used if no data on components are available:

Mass emitted (kg) = 2.00E-01 × Refinery feed (in tonnes)

Reference: [28], Chapter 1.B.2.a.iv, Table 3-6.

13.6. OILY-WATER COLLECTION AND TREATMENT SYSTEMS

Contaminated waste water systems principally comprise process drains and a water treatment facility, such as a gravity separator. The emissions from oily-water systems vary significantly with time, depending, for example, on the amount and volatility of the entrained oil, waste water temperature, flow, etc.

Emissions can be estimated for the entire system using complex models available as software packages (see **Section 13.6.1**).

Alternatively, the emissions from the process drains and the separator systems can be estimated separately (see **Sections 13.6.2** and **13.6.3**).

13.6.1. Emission Estimation Models For Entire System

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.

One such model is WATER9 which was developed by the US EPA. 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. An EPA report [34] provides the mathematical equations used in this model. However, the US EPA advises that the WATER9 model was developed using software that is now outdated and because of this the model is not reliably functional on computers using certain operating systems. The software is still freely available [39] but the US EPA is no longer providing assistance to users.

The input data demands for WATER9 are large and require considerable sampling and analyses to be undertaken. Because of this complexity the US EPA developed a simplistic refinery wastewater emission tool (RWET) [42]. The equations used in this model are provided in the EPA emissions estimation protocol [44].

13.6.2. Process Drains

The following algorithm provides an estimate for emissions from the entire refinery process drain system in oily-water service. Note that drain systems on clean water (with minimal potential for contact with oil) and storm water are excluded.

Process drains and junction boxes 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.

Mass emitted (kg) = 3.20E-02 × N × TIME

where:
N = number of <u>unsealed</u> drain openings in the refinery process drain system.
TIME = period of emission estimate in hours (for E-PRTR annual reports = 8760)

This factor excludes ethane emissions.

Reference: [12], Section 7.5.2, Table 7-3.

13.6.3. Oil-Water Separators

Emissions from separators can be determined using simple emission factors which are known to give conservatively high estimates. Alternatively, an algorithm can be used for uncovered gravity separators which requires, as a minimum, data on separator inlet flow and entrained oil concentration. Sampling and analysis thus have to be undertaken and due to the temporal variability of the input parameters the estimation accuracy will depend on the frequency of testing. A decision tree for supporting the selection of the methodology used by refineries in their estimation of annual VOC emissions from uncovered primary oil-water separator systems based on the results of the field campaigns reported in Concawe Report 5/14 [20] is provided in **Figure 1**.

13.6.3.1. Gravity Separator - where separator inlet monitoring data available

An estimate for the emissions from uncovered API type separators is provided by:

Mass emitted (kg) = 1.00E-04 × D × V × (5.74 × T_{AMB} – 5.15 × T_{DP} +38.6 × T_{WW} + 33.6) × TIME

where:
D = liquid density of evaporated hydrocarbons (kg/m^3). If unknown, Concawe Report 5/14 [20] provides a default average value of 745 kg/m^3
V = flow rate of hydrocarbons entering the separator (m^3/h). Calculated from data on waste water flow and concentration of hydrocarbons in the waste water.
T_{AMB} = ambient water temperature (°C)
T_{DP} = 10% distillation point (°C). If unknown, RIVM/MNP Handbook [58] provides a default average value of 150°C
T_{WW} = Waste water temperature (°C)
TIME = period of emission estimate in hours (for E-PRTR annual reports = 8760)

Reference: [56], developed in reference [58], Section 5.2.

Where a cover is fitted to a gravity separator, the emissions abatement efficiency can be assumed to be 97%. Reference [12], Section 7.5.2, Table 7-3.

13.6.3.2. Simple Algorithms

a) Where the quantity of water treated is unknown

Mass emitted (kg) = 2.00E-02 × A × TIME

where:
A = exposed water area of separator (m^2)
TIME = period of emission estimate in hours (for E-PRTR annual reports = 8760)

b) Where the quantity of water treated is known

Mass emitted (kg) = EF_{SEP} × VOL_{WATER}

where:
EF_{SEP} = Emission factor for the type of separator given in **Table 8**.
VOL_{WATER} = Volume of waste water treated by the separator (in m^3).

Table 8   Emission Factors for Oil-Water Separators

SEPARATOR TYPE	EMISSION FACTOR (EF$_{SEP}$)[1] kg/m³ waste water treated
Gravity type – uncovered	
Oil in water concentration <880 mg/l	2.25E-02
Oil in water concentration 880 - 3500 mg/l	1.11E-01
Oil in water concentration >3500 mg/l	6.00E-01
Gravity type – covered[2]	
Oil in water concentration <880 mg/l	6.75E-04
Oil in water concentration 880 - 3500 mg/l	3.30E-03
Oil in water concentration >3500 mg/l	1.80E-02
Gravity type – covered and connected to flare	0
DAF[3] or IAF[4] – uncovered[5]	4.00E-03
DAF or IAF – covered[5]	1.20E-04
DAF or IAF – covered and connected to flare	0

Notes:

1. These factors exclude ethane emissions
2. Where the complete system has a tightly sealed cover installed with an assumed vapour retention efficiency of 97%. For other types of cover an efficiency of 90% can be assumed. For partly covered systems guidance is provided in Concawe Report 5/14 [20].
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.

Reference: [20], Section 6.5 and [12], Section 7.5, Table 7-3.

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

For ponds temporarily storing oily-water, use the emission factor for an uncovered, gravity type separator from **Table 8**.

Concawe

Figure 1   Decision tree for guidance in determining emissions from uncovered systems
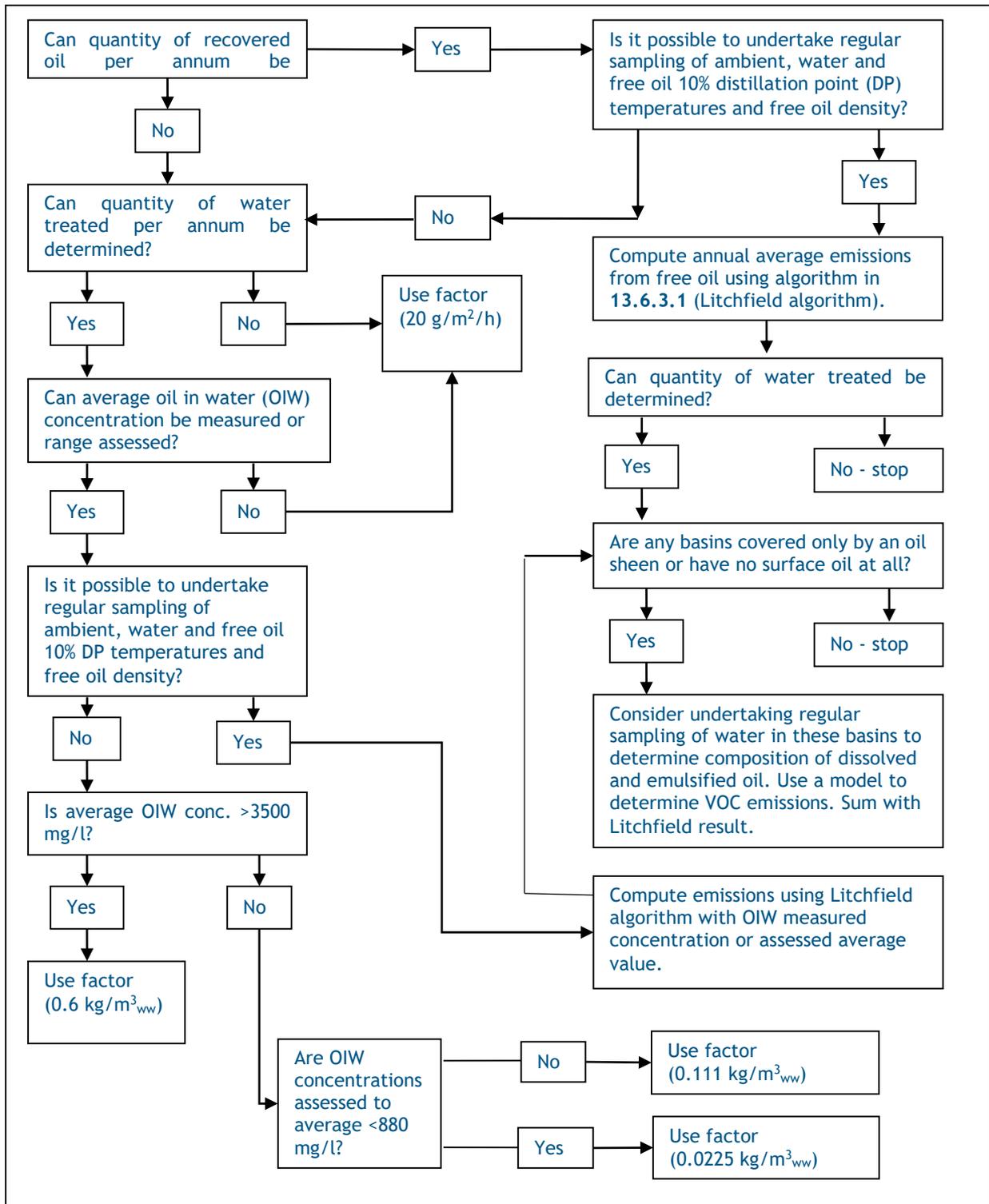
13.7. COOLING WATER TOWERS

Emissions from cooling water towers are considered negligible as sound refinery engineering practice ensures that oil is prevented from entering these systems.

Guidance on estimating emissions if a heat exchanger oil leak has occurred and monitoring data are unavailable is provided in the CFA Code of Practice [12], Section 7.9.5.

13.8. LOADING OF MOBILE CONTAINERS

Emissions from the loading of mobile containers (i.e. road tankers, rail tank cars, barges and marine tankers) depend upon the type of container being loaded and the degree of saturation of the vapour in the cargo tank. For example, uncontrolled emissions from road tankers depend upon the mode of loading (i.e. top loading with a drop pipe through an open hatch or bottom loading through pipework connected on the tanker) and if the tanker delivers product to a facility with a "vapour balancing" system installed. In this type of system, the vapours displaced from the storage tank being filled by the tanker are fed back into the tanker compartment to "balance" the off-loaded product. The tanker thus returns to the loading facility with the compartments filled with vapour.

Emissions from loading can be controlled with a vapour recovery unit (VRU) or thermal oxidiser. Algorithms for VRUs are given below. Emissions from thermal oxidisers can be calculated using the algorithms listed in this report for incinerators.

13.8.1. Uncontrolled Emissions

Mass emitted (kg) = $EF_{LOAD} \times VOL_{LOAD} \times TVP$

where:
EF_{LOAD} = Emission Factor from **Table 9**, depending on loading mode.
VOL_{LOAD} = Volume of product loaded (in m^3).
TVP = True Vapour Pressure of product at loading temperature (in kPa).

Reference: [30], Section 2.

For gasolines, TVP can be calculated from:

$$TVP = RVP \times 10^{[(7.047E\text{-}06 \times RVP + 1.392E\text{-}02) \times TEMP + (2.311E\text{-}04 \times RVP - 5.236E\text{-}01)]}$$

where:
RVP = Reid Vapour Pressure (in kPa)
TEMP = product loading temperature (in degrees Centigrade)

Reference: [30], Annex 1.

Table 9   NMVOC Emission Factors for Loading of Mobile Containers

LOADING MODE	EMISSION FACTOR EF_{LOAD} kg/m^3/kPa
Road Tanker, Bottom Loading No Vapour Balancing during Previous Off-Loading	8.60E-03
Road Tanker, Top Loading No Vapour Balancing during Previous Off-Loading	9.40E-03
Road Tanker, Bottom or Top Loading Vapour Balancing during Previous Off-Loading	2.28E-02
Rail Tanker, Top Loading	1.08E-02
Rail Tanker, Bottom Loading[1]	1.05E-02
Marine tanker - typical cargo tank condition[2]	3.91E-03
Barge - typical cargo tank condition[2]	7.45E-03

Notes:

1. During the top loading of rail tankers emissions occur from the open loading hatch both before and after loading [30]. As there is no open hatch during bottom loading of a rail tanker, this factor assumes no pre- or post-loading emissions.
2. These factors are for typical cargo tank vapour conditions. For other situations (e.g. tank gas freed or ballasted, previous cargo non-volatile, etc.) specific emission factors are provided in EPA-publication AP-42 [36], Table 5.2-2 for the loading of gasoline with a TVP of 55 kPa. These factors should be pro-rated for the value of the TVP of the product loaded.

13.8.2.   Emissions Controlled with a Vapour Recovery Unit (VRU)

VRUs may be fitted with a continuous emissions monitor (CEM) or the recovery efficiency may be known from tests.

13.8.2.1.   VRU Fitted with a CEM

Mass emitted (kg) = 1.00E-03 × $MEAS_{CONC}$ × VOL_{LOAD} × (1 – TVP / 100)

where:
$MEAS_{CONC}$ = Measured VRU vent concentration (in g/m^3)
VOL_{LOAD} = Volume of product loaded (in m^3)
TVP = True Vapour Pressure of product at loading temperature (in kPa)

Reference: [30], Section 2.2.

13.8.2.2.   VRU Efficiency Known

Emissions should be calculated using the algorithm in **Section 6.1**.

13.9.   STORAGE TANKS

Emissions from storage tanks comprise two components:

- Working loss; emissions due to the tank being filled (displacing vapours above the product stored) or emptied (evaporation of product "clingage" on tank internal walls)

- Standing losses: emissions due to the expansion of the vapour space in fixed roof tanks due to vapour temperature or pressure changes and leakage past equipment (e.g. seals, still wells, etc.) fitted to floating roofs.

13.9.1. Floating Roof Tanks

Floating roof tanks can be of the following types:
- External floating roof (EFR)
- EFR fitted with domed cover
- Internal floating roof (IFR)
  - fitted with open vents in the fixed roof
  - fitted with vents in the fixed roof which can be connected to a control device e.g. pressure/vacuum valves, a vapour recovery unit, etc.

For all of these tank types except IFR tanks which are not freely vented, use the latest edition of the API MPMS, Chapter 19.2 [7]. For IFR tanks fitted with vents which can be closed, guidance is provided in an API report [5] which shows that emissions from closed-vent internal floating roof tanks are approximately 5% less than emissions from internal floating roof tanks with open vents.

Methodologies to estimate the emissions when the roof has landed on its legs and is no longer floating on the product are provided in an API report [3].

13.9.2. Vertical Fixed Roof Tanks (VFRT)

For these tanks, use the latest edition of the API MPMS Chapter 19.1 [8].

13.9.2.1. VFRTs Connected to a Vapour Holding Tank (VHT)

A vapour holding tank comprises a fixed roof tank containing a flexible diaphragm. Where connected to a storage tank, a correctly sized VHT stores any emissions from the tank due to the rise in vapour temperature during the day, and then releases these vapours back to the tank as it cools at night. The VHT, therefore, controls the "standing losses".

Emissions, therefore, can be assumed to equal only the "working losses".

13.9.3. Aboveground Horizontal Tanks

For these tanks, use the latest edition of EPA publication AP-42 [41], Section 7.1.3.1.

13.9.4. Underground Tanks

Use the algorithms for service station storage tanks provided in **Appendix 4.2**.

13.9.5. Tank Cleaning

Guidance on the estimation of evaporative emissions during tank cleaning is provided in an API report [4].

13.9.6. Storage Tanks - General Comments

EPA publication AP-42, Chapter 7 [41] normally contains the latest versions of the API references [3], [7] and [8]. Emission calculation software (TANKS) utilising the

algorithms in reference [41] is available from the US EPA via their website, https://www.epa.gov /chief. The US EPA advise that this software is now outdated and is not reliably functional on computers using modern operating systems and therefore it is no longer providing assistance to users. Commercial software is, however, now available.

It should be noted that some options are provided in the algorithms in the API and EPA references [3], [5], [7], [8] and [41] to cover the state of equipment; e.g. degrees of rust on tank internal shells, tightness of floating roof seals, etc. Users of the algorithms, therefore, must ensure that the factors utilised to derive emissions for a particular tank are appropriate. In particular, the API states that the algorithms are only 'applicable to properly maintained equipment under normal working conditions'

13.10. UNCONTROLLED BLOWDOWN SYSTEMS

The gaseous emissions from blowdown systems in EU refineries are recovered and/or flared.

If these controls are not operational and all of the emissions are released to atmosphere, the total hydrocarbons emissions can be conservatively estimated using the factor provided in the EPA publication AP-42 [36], Table 5.1-1.

13.11. UNCONTROLLED BITUMEN BLOWING

The gaseous emissions from bitumen blowing in EU refineries are controlled, for example using scrubbers and incinerators.

Where these controls are not operational and all of the emissions are emitted to atmosphere, the emissions can be estimated using the factor in the 2005 edition of the EEA Guidebook [27], Activities 040101 & 040102, Section 8.2.1, Table 8.2.

14. NITROGEN OXIDES (NOx)

Estimation methods are provided for emissions of NO_X from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Fluid catalytic cracking unit regenerators

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires monitoring of NO_X emissions, using the techniques and frequencies specified, from all combustion units and from fluid catalytic cracking units.

14.1. COMBUSTION IN BOILERS AND FURNACES

NO_X emissions from combustion comprise two components:

- Thermal NOx; this is the thermal fixation of molecular nitrogen and is generally a function of flame temperature, residence time and oxygen concentration in the flame zone

- Fuel NOx; this is the result of the direct oxidation of the nitrogen in liquid fuels or the non-inert nitrogen containing species in gaseous fuels.

The following methodology is outlined in more detail, with an example, in a paper by Takacs et al [60].

Total NOx Emissions = Thermal NOx + Fuel NOx

Thermal NOx

Thermal NOx Mass emitted (kg) = 1.00E-03 × TNF × M × HHV

where:
TNF = Thermal NOx factor (in g/GJ)
M = Mass of fuel combusted (in tonnes)
HHV = Higher heating value of the fuel combusted (in MJ/kg)
For liquid fuels
        HHV = 1.05 × NCV
For gaseous fuels
        HHV = 1.11 × NCV
where NCV = Net calorific value (in MJ/kg)

TNF = F_{BASE} × F_{H2} × $F_{CONTROL}$ × $F_{PREHEAT}$ × F_{H_2O} × F_{LOAD} × F_{BURN}

F_{BASE} is the base fuel factor. This accounts for differences in flame temperature due to fuel composition and is therefore dependent on the type of fuel burnt. Values for different fuels are given in **Table 10.**

Table 10   Values for F_{BASE}

FUEL	F_{BASE} (g/GJ) (HHV)
Methane, Natural Gas, LPG	56
Refinery Fuel Gas	69
Low Joule Gas	30
Refinery Fuel Oil, Distillates	56

F_{H2} is the adjustment factor for the amount of hydrogen gas in the fuel.

For all liquid fuels, methane, natural gas and LPG: F_{H2} = 1.0

For other refinery gaseous fuels, values for F_{H2} are given for some hydrogen concentrations in **Table 11**. These can be used to extrapolate for other compositions.

Table 11   Values for F_{H2}

FUEL	H_2 CONCENTRATION % v/v	F_{H2}
Refinery Fuel Gas	0 - 23	1.00
	33	1.04
	43	1.09
	63	1.25
	83	1.46
Low Joule Gas	0 - 14.7	1.00
	24.7	1.04
	34.7	1.09
	54.7	1.25
	74.7	1.46

$F_{CONTROL}$ is the adjustment factor for at-the-source control technologies, including burner type. Values are given in **Table 12**.

Table 12   Values for $F_{CONTROL}$

CONTROL TECHNOLOGY		$F_{CONTROL}$
None		1.00
Low NOx burner, staged fuel		0.33
Low NOx burner, staged air		0.60
Ultra-low NOx burner		0.30
Flue Gas Recirculation	0%	1.00
	5%	0.60
	10%	0.40
	15%	0.30
	20%	0.20

$F_{PREHEAT}$ is the adjustment factor for the average air preheat temperature. Values are given in **Table 13**.

Table 13   Values of $F_{PREHEAT}$

AIR PREHEAT TEMPERATURE Degrees C	$F_{PREHEAT}$
< 38	1.00
38	1.00
93	1.10
149	1.32
204	1.60
260	1.86

F_{H_2O} is the adjustment factor for the moisture content of the combustion air. Values are given in **Table 14**.

Table 14   Values of F_{H_2O}

MOISTURE CONTENT kg H_2O / kg dry air	F_{H_2O}
0	1.00
0.01	0.79
0.02	0.67
0.03	0.53
0.04	0.41
0.05	0.29

F_{LOAD} is the adjustment factor for the loading of the combustion unit. For dual fuel firing, the load is calculated using the total thermal input. Values are given in **Table 15**.

Table 15   Values of F_{LOAD}

LOAD (% of design)	F_{LOAD}
40	0.55
60	0.70
80	0.85
100	1.00

F_{BURN} is the adjustment factor for the burner intensity, a measure of the heat release per volume of burner space. There is no precise measure for burner intensity. Where no combustion unit information on intensity is available, in general high intensity burners are used for packaged boilers and pyrolysis furnaces and low intensity burners are used for all other fired heaters and boilers. Where furnace (radiant cell) volume is known, then the classification can be ascertained from:

- High intensity is > 700 KW/m^3
- Low intensity is < 30 kW/m^3

Values for F_{BURN} are given in **Table 16**.

Table 16   Values for F_{BURN}

BURNER INTENSITY	F_{BURN}
High	1.8
Low	1.0

Fuel NO$_X$

Fuel NO$_X$ Mass emitted (kg) = 1.00E-03 × FNF × M × HHV

where:
FNF = Fuel NO$_X$ factor (in g/GJ)
M = Mass of fuel combusted (in tonnes)
HHV = Higher Heating Value of the fuel combusted (in MJ/kg)

FNF = (1.00E+04 × MP$_{NITROGEN}$ × CFN$_{MW}$ × F$_{N2CONTENT}$) / HHV

where:
MP$_{NITROGEN}$ = Mass Percentage of Nitrogen in the fuel combusted
CFN$_{MW}$ = Molecular weight conversion from N to NO$_2$ = 46 / 14 = 3.286
F$_{N2CONTENT}$ = Adjustment factor for nitrogen content. Values are given in **Table 17**.

Table 17   Values for F$_{N2CONTENT}$

FUEL NITROGEN % m/m	F$_{N2CONTENT}$	
	Uncontrolled Burner	**Low-NOx burner with staged air**
< 0.05	1.00	1.00
0.05	0.87	0.86
0.1	0.78	0.75
0.3	0.53	0.43
0.5	0.38	0.30
1.0	0.32	0.25[1]

Notes:
1. Reference: [54] - value corrected from that published in reference [60].

Combining the above equations:

Fuel NO$_X$ Mass emitted (kg) = 32.86 × MP$_{NITROGEN}$ × F$_{N2CONTENT}$ × M

where:
MP$_{NITROGEN}$ = Mass Percentage of Nitrogen in the fuel combusted (see note below).
F$_{N2CONTENT}$ = Adjustment factor for nitrogen content. Values are given in **Table 17**.
M = Mass of fuel combusted (in tonnes)

Note: the mass percentage of nitrogen in gaseous fuels only relates to the nitrogen bound in the combustible components in the fuel (e.g. ammonia) and does not apply to molecular nitrogen (N$_2$) where present as a gaseous fuel component.

Reference: [60].

14.2.   GAS TURBINES

14.2.1.   Natural Gas Combustion

Mass emitted (kg) = 1.53E-01 × M × NCV

where:

M = mass of fuel gas burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [37], Table 3.1-1. Factor derived from turbines operating at high loads (≥ 80%).

14.2.2. Distillate Oil Combustion

Mass emitted (kg) = 3.98E-01 × M × NCV

where:
M = mass of distillate oil burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [37], Table 3.1-1. Factor derived from turbines operating at high loads (≥ 80%).

14.3. GAS ENGINES (4 STROKE, LEAN BURN)

Mass emitted (kg) = 4.05E-01 × M × NCV

where:
M = mass of fuel gas burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [37], Table 3.2-2. Factor derived from engines operating at < 90% load.

14.4. DIESEL ENGINES (LARGE, STATIONARY)

Mass emitted (kg) = 1.45E+00 × M × NCV

where:
M = mass of diesel fuel burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

Reference: [37], Table 3.4-1.

14.5. COMBUSTION OF AUXILIARY AND PILOT FUELS

Auxiliary fuels are used to support combustion in, for example, CO boilers and incinerators. Pilots are used to initiate combustion in flares.

Mass emitted (kg) = 6.22E-02 × M × NCV

where:
M = mass of auxiliary/pilot fuel burnt (in tonnes)
NCV = net calorific value of the fuel burnt (in MJ/kg)

This assumes emissions are equivalent to burning natural gas with dry combustion air in an uncontrolled furnace – see **Section 14.1**.

Reference: [60].

14.6. DESTRUCTION OF GASEOUS STREAMS

14.6.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 14.5**.

14.6.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known:

Mass emitted (kg) = 3.25E-02 × M × NCV

where:
M = mass of flare gas burnt (in tonnes)
NCV = net calorific value of the flare gas burnt (in MJ/kg)

Reference: [47], Table 13.5-1.

14.6.1.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 5.40E-02 × Refinery Feed (in m^3)

Reference: [27], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

14.6.2. Incineration of hydrocarbon gas streams

Use the algorithms in **Section 14.1**, assuming that the 'fuel' is low joule gas and that $F_{CONTROL}$, $F_{PREHEAT}$, F_{LOAD} and F_{BURN} all have a value of 1.0.

For emissions from the combustion of the auxiliary gas fuel used to support incinerator combustion, use the algorithm in **Section 14.5**.

14.7. FLUID CATALYTIC CRACKING UNIT REGENERATORS

For CCU regenerators, both with and without CO boilers:

Mass emitted (kg) = 2.04E-01 × Volume of fresh feed to unit (in m^3)

Reference: [36], Section 5.1, Table 5.1-1.

15. SULPHUR HEXAFLUORIDE (SF$_6$)

Emissions of sulphur hexafluoride (SF$_6$) may occur due to its use as a tracer gas or from leaks from high voltage electrical equipment where this gas is used as an insulator.

Emissions are assumed to equal the amount used and not recovered during test procedures and/or the mass used to top-up or refill equipment.

Mass emitted (kg) = Mass used (in kg)

16. OXIDES OF SULPHUR (SOx)

The E-PRTR requires estimates of the total oxides of sulphur (SO_2 and SO_3) reported as SO_2.

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Fluid catalytic cracking unit regenerators
- Catalytic reforming units

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires monitoring of SO_X emissions, using the techniques and frequencies specified, from all combustion units, fluid catalytic cracking units and sulphur recovery units.

16.1. COMBUSTION

For all fuel combustion, the following algorithm applies:

Mass emitted (kg) = $1000 \times M \times MF_S \times SF_{MW}$

where:
M = mass of fuel burnt (in tonnes)
MF_S = mass fraction of sulphur in fuel
SF_{MW} = Molecular weight conversion from S to SO_2 = 64/32

This assumes that all the sulphur in the fuel is converted to SO_2.

For refinery oil and gaseous fuels:

Mass emitted (kg) = $2.00E+03 \times M \times MF_S$

Reference: [31], Section 4.1.1.1.

16.2. DESTRUCTION OF GASEOUS STREAMS

16.2.1. Flares

The following algorithms are for emissions from the combustion of the flare gas. For emissions from the combustion of the pilot gas fuel used to initiate flare combustion, use the algorithm in **Section 16.1**.

16.2.1.1. Flare Stream Details Known

If the mass and composition of the flare stream are known, use algorithm in **Section 16.1**, where:
M = mass of flare gas burnt (in tonnes)
MF_S = mass fraction of sulphur in flare gas

16.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used. This assumes that a flare gas recovery system is not installed:

Mass emitted (kg) = 7.70E-02 × Refinery Feed (in m³)

Reference: [27], Activity 090203, Section 8, Table 2.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

16.2.2. Incinerators

For the incineration of gas streams, including that from a sulphur plant if the gas composition is known, use the algorithm in **Section 16.1**, where:
M = mass of gas incinerated
MF_S = mass fraction of sulphur in gas incinerated

For emissions from the combustion of the auxiliary gas fuel used to support incinerator combustion, also use the algorithm in **Section 16.1**.

16.2.2.1. Sulphur Plant Tail Gas Incinerator

For a sulphur plant, if the composition of the gas stream is unknown, emissions can be determined from the sulphur balance across the plant.

Mass emitted (kg) = [(100 - ERC$_{EFF}$) / ERC$_{EFF}$] × PROD × SF$_{MW}$ × 1000

where:
ERC_{EFF} = recovery efficiency (in %)
PROD = sulphur production (in tonnes)
SF_{MW} = Molecular weight conversion from S to SO_2 = 64/32

Reference: [43], Section 8.13, Table 8.13-1.

16.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

For CCU regenerators, the emissions can be determined using coke sulphur content data. If these are not available, a less accurate emission factor can be used.

Where DeSO$_X$ catalyst additive is used, the abatement effect of this on the emissions should be taken into account using the algorithm in **Section 6.1** with the value of EFF being the SO$_X$ percentage removal efficiency.

The following emission estimation algorithms are applicable both with and without CO boilers.

16.3.1. Coke sulphur content known

Mass emitted (kg) = 2.00E+03 × M × MF$_{SFEED}$ × MF$_{SCOKE}$

where:
M = mass of feed to unit (in tonnes)

MF_{SFEED} = mass fraction of sulphur in feed
MF_{SCOKE} = mass fraction of sulphur in coke

Reference: [12], Section 15.3.1.4.

16.3.2. Coke sulphur content not known

Mass emitted (kg) = 1.41E+00 × Volume of fresh feed to unit (in m^3)

Reference: [36], Section 5.1, Table 5.1-1.

16.4. CATALYTIC REFORMING UNITS

Mass emitted (kg) = 3.63E-03 × Volume of feed to unit (in m^3)

Reference: [11], Table 1. This reference uses data from a number of units with varying degrees of abatement equipment installed – see **Section 6.3**.

17. HYDROCHLOROFLUOROCARBONS (HCFC)

Hydrochlorofluorocarbons (HCFCs) may be used as refrigerants in refinery thermal exchange equipment.

Emissions are assumed to equal the amount used during the reporting period to top-up systems to replenish losses due to uncontrolled leakage.

Mass emitted (kg) = Mass used to top-up refrigerant systems (in kg)

Usage where the systems have been fully or partially drained and refrigerants collected for recycling or destruction should not be reported.

18. ARSENIC (As)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

18.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 18**.

Table 18 As Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.81E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	3.98E-03	[38] Section 1.3, Table 1.3-11
	Natural Gas	1.20E-04	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	3.52E-04	[23]
Gas Turbine	Distillate (gas oil)	2.30E-06	[28] Section 1.A.1 Table 3.18
	Natural Gas	1.20E-04	[28] Section 1.A.1 Table 3.17
Gas Engine 4-stroke, Lean Burn	Natural Gas	5.00E-05	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.20E-04	[28] Section 1.A.1, Table 4-6

Notes:

1. It is recommended that, where available, the arsenic content of the fuel oil is used to estimate emissions, making the assumption that all of the arsenic is emitted to atmosphere.

18.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 18.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 18.1.**

18.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 1.39E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

18.4. FLUID COKERS

Mass emitted (kg) = 2.16E-03 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [31], Section 4.2.3, Tables 10 and 11.

19. CADMIUM (Cd)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators

19.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 19**.

Table 19 Cd Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	1.20E-03	[38] Section 1.3, Table 1.3-11
	Natural Gas	2.50E-07	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	2.19E-03	[23]
Gas Turbine	Distillate (gas oil)	1.20E-06	[28] Section 1.A.1 Table 3.18
	Natural Gas	2.50E-07	[28] Section 1.A.1 Table 3.17
	Refinery Fuel Gas[3]	2.52E-03	[1], [2][2]
Gas Engine 4-stroke, Lean Burn	Natural Gas	3.00E-06	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	2.50E-07	[28] Section 1.A.1, Table 4-6

Notes:
1. It is recommended that, where available, the cadmium content of the fuel oil is used to estimate emissions, making the assumption that all of the cadmium is emitted to atmosphere.
2. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.
3. Factor derived from gas turbines without duct burners.

19.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 19.1**, with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 19.1**.

19.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 6.25E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

20. CHROMIUM (Cr)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators

20.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 20**.

Table 20   Cr Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	1.48E-02	[1], [2][2]
	Natural Gas	7.60E-07	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	6.69E-03	[23]
Gas Turbine	Distillate (gas oil)	2.80E-04	[28] Section 1.A.1 Table 3-18
	Natural Gas	7.60E-07	[28] Section 1.A.1 Table 3-17
	Refinery Fuel Gas[3]	6.26E-03	[1], [2][2]
Gas Engine 4-stroke, Lean Burn	Natural Gas	5.00E-05	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	7.60E-07	[28] Section 1.A.1, Table 4-6

Notes:

1. It is recommended that, where available, the chromium content of the fuel oil is used to estimate emissions, making the assumption that all of the chromium is emitted to atmosphere.
2. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.
3. Factor derived from gas turbines without duct burners.

20.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 20.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 20.1**.

21. COPPER (Cu)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

21.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 21**.

Table 21   Cu Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	2.72E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	1.19E-02	[1], [2][2]
	Natural Gas	7.60E-08	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	3.29E-03	[23]
Gas Turbine	Distillate (gas oil)	1.70E-04	[28] Section 1.A.1 Table 3-18
	Natural Gas	7.60E-08	[28] Section 1.A.1 Table 3-17
	Refinery Fuel Gas[3]	1.97E-02	[1], [2][2]
Gas Engine 4-stroke, Lean Burn	Natural Gas	1.00E-05	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	7.60E-08	[28] Section 1.A.1, Table 4-6

Notes:
1. It is recommended that, where available, the copper content of the fuel oil is used to estimate emissions, making the assumption that all of the copper is emitted to atmosphere.
2. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.
3. Factor derived from gas turbines without duct burners.

21.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 21.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 21.1**.

21.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 1.39E-04 × Volume of fresh feed to unit (in m³)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

21.4. FLUID COKERS

Mass emitted (kg) = 1.50E-05 × Volume of fresh feed to unit (in m³)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [31], Section 4.2.3, Tables 10 and 11.

22. MERCURY (Hg)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

22.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 22**.

Table 22   Hg Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	Not Detected[1]	[1], [2][2]
	Natural Gas	1.00E-04	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	3.72E-04	[23]
Gas Turbine	Distillate (gas oil)	5.30E-05	[28] Section 1.A.1 Table 3-18
	Natural Gas	1.00E-04	[28] Section 1.A.1 Table 3-17
	Refinery Fuel Gas[3]	7.31E-03	[1], [2][2]
Gas Engine 4-stroke, Lean Burn	Natural Gas	1.00E-04	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.00E-04	[28] Section 1.A.1, Table 4-6

Notes:
1. Compound was not detected. Emission factor stated in reference [1] represents the detection limit. For the purposes of this report the emission factor is considered to be zero as the source is not proven (See **Section 5.2** of this report).
2. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.
3. Factor derived from gas turbines without duct burners

22.2.   DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 22.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 22.1**.

22.3.   FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 6.95E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

22.4.   FLUID COKERS

Mass emitted (kg) = 3.00E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [31], Section 4.2.3, Tables 10 and 11.

23. NICKEL (Ni)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires monitoring, at the specified frequencies, of nickel emissions from all combustion units firing liquid fuels and from fluid catalytic cracking units.

23.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 23**.

Table 23   Ni Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.36E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	7.73E-01	[23]
	Natural Gas	5.10E-07	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	7.37E-03	[23]
Gas Turbine	Distillate (gas oil)	2.30E-06	[28] Section 1.A.1 Table 3-18
	Natural Gas	5.10E-07	[28] Section 1.A.1 Table 3-17
	Refinery Fuel Gas[2]	7.93E-02	[1], [2][3]
Gas Engine 4-stroke, Lean Burn	Natural Gas	5.00E-05	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	5.10E-07	[28] Section 1.A.1, Table 4-6

Notes:
1. It is recommended that, where available, the nickel content of the fuel oil is used to estimate emissions, making the assumption that all of the nickel is emitted to atmosphere.
2. Factor derived from gas turbines without duct burners.
3. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.

23.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 23.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 23.1**.

23.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 6.12E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

23.4. FLUID COKERS

Mass emitted (kg) = 5.70E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [31], Section 4.2.3, Tables 10 and 11.

24. LEAD (Pb)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

24.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 24.**

Table 24   Pb Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	4.07E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	4.56E-03	[38] Section 1.3, Table 1.3-11
	Natural Gas	1.50E-06	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	1.61E-03	[23]
Gas Turbine	Distillate (gas oil)	6.90E-06	[28] Section 1.A.1 Table 3-18
	Natural Gas	1.50E-06	[28] Section 1.A.1 Table 3-17
	Refinery Fuel Gas[2]	1.36E-02	[1], [2][3]
Gas Engine 4-stroke, Lean Burn	Natural Gas	4.00E-05	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.50E-06	[28] Section 1.A.1, Table 4-6

Notes:
1. It is recommended that, where available, the lead content of the fuel oil is used to estimate emissions, making the assumption that all of the lead is emitted to atmosphere.
2. Factor derived from gas turbines without duct burners.
3. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.

24.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 24.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support incineration, also use the algorithm in **Section 24.1**.

24.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 3.20E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

24.4. FLUID COKERS

Mass emitted (kg) = 4.50E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [31], Section 4.2.3, Tables 10 and 11.

25. ZINC (Zn)

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

25.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 25**.

Table 25   Zn Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	1.81E-03	[38] Section 1.3, Table 1.3-10
	Refinery Fuel Oil[1]	4.93E-02	[1], [2][2]
	Natural Gas	1.50E-06	[28] Section 1.A.1, Table 4-6
	Refinery Fuel Gas	1.70E-02	[23]
Gas Turbine	Distillate (gas oil)	4.40E-04	[28] Section 1.A.1 Table 3-18
	Natural Gas	1.50E-06	[28] Section 1.A.1 Table 3-17
	Refinery Fuel Gas[3]	2.38E+00	[1], [2][2]
Gas Engine 4-stroke, Lean Burn	Natural Gas	2.91E-03	[28] Section 1.A.1 Table 4-7
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.50E-06	[28] Section 1.A.1, Table 4-6

Notes:
1. It is recommended that, where available, the zinc content of the fuel oil is used to estimate emissions, making the assumption that all of the zinc is emitted to atmosphere.
2. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures.
3. Factor derived from gas turbines without duct burners.

25.2.   DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 25.1** with an emission factor EF_{NCV} equal to that for fuel gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support flaring or incineration, also use the algorithm in **Section 25.1**.

25.3.   FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = 1.18E-04 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in FCCU vents. It is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

Reference: [31], Section 4.2.3, Tables 10 and 11.

25.4.   FLUID COKERS

Mass emitted (kg) = 4.50E-05 × Volume of fresh feed to unit (in m^3)

This algorithm has been derived from speciation data for total particulate matter in fluid coker vents.

Reference: [31], Section 4.2.3, Tables 10 and 11.

26. DIOXINS AND FURANS (PCDD AND PCDF)

Dioxins and furans are only produced during combustion processes under specific conditions and where chlorine is present. Estimation methods are provided for emissions from:

- Combustion of fuel oil
- Catalytic reforming units

The emission factors for each of the 17 isomers of PCDD and PCDF have been multiplied by the Toxic Equivalence Factor (TEF) in **Table 26** to give the emission factor in g I-TEQ (Toxic Equivalent to the most toxic isomer 2,3,7,8-CDD).

26.1. COMBUSTION OF FUEL OIL

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g I-TEQ/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 26**

Table 26 Emission Factors for PCDD and PCDF from Fuel Oil Combustion

ISOMER	I-TEF	Emission Factor lb/MMBtu (HHV)	Emission Factor g I-TEQ/GJ (NCV)
Dioxin 4D 2378	1	Not detected	0[1]
Dioxin 5D 12378	0.5	Not detected	0[1]
Dioxin 6D 123478	0.1	Not detected	0[1]
Dioxin 6D 123678	0.1	2.50E-12	1.13E-10
Dioxin 6D 123789	0.1	2.50E-12	1.13E-10
Dioxin 7D 1234678	0.01	2.12E-11	9.59E-11
Dioxin 8D	0.001	5.10E-10	2.31E-10
Furan 4F 2378	0.1	5.54E-12	2.51E-10
Furan 5F 12378	0.05	Not detected	0[1]
Furan 5F 23478	0.5	Not detected	0[1]
Furan 6F 123478	0.1	2.48E-12	1.12E-10
Furan 6F 123678	0.1	1.86E-12	8.42E-11
Furan 6F 123789	0.1	Not detected	0[1]
Furan 6F 234678	0.1	3.74E-12	1.69E-10
Furan 7F 1234678	0.01	9.79E-12	4.43E-11
Furan 7F 1234789	0.01	Not detected	0[1]
Furan 8F	0.001	4.86E-11	2.20E-11
TOTAL			**1.24E-09**

Notes:
1. Compound was not detected. The emission factor stated in reference [1] is based on the detection limit. For the purposes of this report, the emission factor is considered to be zero as the source was not proven (See **Section 5.2** of this report).

Reference: [1].

26.2. CATALYTIC REFORMING UNIT REGENERATORS

There are very few data available for the emissions from these units. The US EPA [40] provides emission factors derived from tests on units with different modes of catalyst regeneration – continuous and semi-regenerative.

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires direct measurement of PCCD/F emissions, at the frequency specified, from catalytic reformers.

26.2.1. Continuous Regeneration Mode

Mass emitted (kg I-TEQ) = 1.91E-11 × Volume of feed to unit (in m^3)

Reference: [40], Table 5-9.

26.2.2. Semi-Regenerative Mode

Mass emitted (kg [40]-TEQ) = 6.35E-15 × Volume of feed to unit (in m^3)

Reference: [40], Table 5-9.

27. BENZENE (C_6H_6)

Benzene is emitted as a constituent of VOC evaporative or leakage (fugitive) emissions and from the combustion of flare streams, fuels e.g. in boilers and furnaces, and coke in FCCU regenerators and cokers.

Combustion emissions are typically negligible compared to fugitive emissions.

Fugitive emissions are diffuse in a large facility like a refinery. Although those from pressurised equipment can be determined from speciation data for each stream in the refinery and leak monitoring surveys, this requires considerable effort and does not cover emissions from systems such as tanks, drains, oil-water separators, etc. One measurement technique is to monitor occasionally the composition of NMVOCs in the ambient air at the fence line to determine the average benzene mass fraction.

Where this technique is not undertaken, an estimation method for fugitives is provided using a default value for the mass fraction of benzene. For completeness, algorithms are also provided for the minor sources.

27.1. SPECIATED FENCELINE NMVOC DATA AVAILABLE

In general, VOC fugitive sources are numerous but individually small e.g. from valves, drain systems, etc. To determine the benzene emitted by a facility, one approach is to take occasional ambient air samples at regular points around the boundary fence and establish the average benzene mass fraction of the NMVOCs measured. Care must be taken in the positioning of the samplers to ensure that they are not located near to local emission sources that may skew the results. Full details of a methodology are given in an EI Protocol [29].

The mass of benzene emitted by the facility is then calculated from:

Mass emitted (kg) = SUMCALC$_{NMVOC}$ × MF$_{BENZENE}$

where:
SUMCALC$_{NMVOC}$ = sum of the individual calculated masses of NMVOCs emitted (in kg) within the facility, as per **Section 13**.
MF$_{BENZENE}$ = Mass fraction of benzene (from fence line monitoring survey).

27.2. NO SPECIATED FENCELINE NMVOC DATA AVAILABLE

Where fence line monitoring is not undertaken, a value of MF$_{BENZENE}$ = 1.72% mass can be used.

Mass emitted (kg) = 1.72E-02 × SUMCALC$_{NMVOC}$

where:
SUMCALC$_{NMVOC}$ = sum of the individual calculated masses of NMVOCs emitted (in kg) within the facility, as per **Section 13**.

Reference: [12], Section 15.5.3.3, Table 15-7.

27.3. ESTIMATION BY SOURCE

For completeness, algorithms are provided below for combustion sources and uncontrolled blowdown systems. The emission from the following combustion sources are typically negligible compared to fugitive sources:

- Combustion of fuels
- Destruction of gaseous streams in flares and incinerators
- Fluid catalytic cracking unit regenerators
- Fluid cokers

If some or all of the following algorithms are used, then the emissions are:

Mass emitted (kg) = Sum of emissions using algorithms below + Sum of emissions from all other sources using algorithms in Section 27.1 or 27.2

27.3.1. Combustion of Fuels

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table 27**.

Table 27   Benzene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Refinery Fuel Oil	6.47E-04	[38] Section 1.3, Table 1.3-9
	Natural Gas	9.84E-04	[38] Section 1.4, Table 1.4-3
	Refinery Fuel Gas	2.13E-03	[1][1]
Gas Turbine[2]	Distillate (Gas Oil)[3]	2.49E-02	[37] Section 3.1, Table 3.1-4
	Natural Gas	5.73E-03	[37] Section 3.1, Table 3.1-3
Gas Engine 4-stroke, Lean Burn	Natural Gas	2.10E-01	[37] Section 3.2, Table 3.2-2
	Refinery Fuel Gas	6.21E-01	[1], [2][4]
Diesel Engine Large, Stationary	Distillate (Gas Oil)	3.22E-01	[1], [2][4]
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	9.84E-04	[38] Section 1.4, Table 1.4-3

Notes:
1. Factor represents the median value as the ratio of mean to median value > 10. See **Section 5.3**.
2. Factor derived from turbines operating at high (≥ 80%) loads.
3. Factor provided in reference [37] derived using HHV of 139 MBtu/10^3 US gal.
4. Reference [1] is base document, but reference [2] provides the same emission factors to more significant figures

27.3.2. Destruction of Hydrocarbon Gas Streams

The following algorithms are for emissions from the combustion of the flare or incinerator gas. For emissions from the combustion of the pilot gas fuel used to support flaring or incineration, use the algorithm in **Section 27.3.1**.

27.3.2.1. Flare Stream Details Known

If the mass and composition of the flare hydrocarbon gas stream are known:

Mass emitted (kg) = 5.00E-00 × M × MF$_{BENZ}$

where:
M = total mass of gas flared (in tonnes)
MF$_{BENZ}$= mass fraction of benzene in gas flared

This algorithm assumes that 0.5% of the hydrocarbons remain unburned in "well designed and operated flares, such as in refineries".

Reference: [6], Section 4.6.

27.3.2.2. Flare Stream Details Unknown

If the mass and composition are not known and a flare gas recovery system is not installed, a conservative factor based on refinery feed can be used:

Mass emitted (kg) = 1.66E-06 × Refinery Feed (in m^3)

Reference: Emission factor derived from [27], Activity 090203, Section 8, Table 2, and [31], Section 4.22, Table 9.

If a flare gas recovery system is installed it can be considered to be an emissions control device. The equation in **Section 6.1** can be used (with EFF = flare gas recovery system efficiency) to adjust the emissions estimate obtained from the algorithm above.

27.3.2.3. Incinerators

If the destruction efficiency of the incinerator and the mass and composition of the hydrocarbon gas stream are known:

Mass emitted (kg) = (100 – DE) × 10 × M × MF$_{BENZENE}$

where:
DE = incinerator destruction efficiency (%)
M = total mass of gas incinerated (in tonnes)
MF$_{BENZENE}$ = mass fraction of benzene in gas incinerated

Otherwise, use the algorithm in **Section 27.3.1** with an emission factor EF$_{NCV}$ equal to that for natural gas combustion in a furnace.

27.3.3. Fluid Catalytic Cracking Unit Regenerators

27.3.3.1. Full Burn Regeneration

Emissions of NMVOCs, and hence benzene, are considered negligible.

27.3.3.2. Partial Burn with CO Boiler

Emissions of NMVOCs, and hence benzene, are considered negligible.

Reference: [36], Table 5.1-1.

27.3.3.3. Partial Burn without CO Boiler

If the off-gas is not fed to a CO boiler, or it is not in operation:

Mass emitted (in kg) = 8.04E-04 × Mass of coke burned (in tonnes)

Reference: [10], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

27.3.4. Fluid Cokers

27.3.4.1. Emissions Controlled with CO or Fired Waste Heat Boiler

Emissions of NMVOCs, and hence benzene, are considered negligible.

Reference: [36], Table 5.1-1.

27.3.4.2. Non-Controlled Emissions

If the off-gas is not fed to a CO or fired waste heat boiler, or it is not in operation:

Mass emitted (in kg) = 1.75E-04 × Feed to unit (in m^3)

This assumes that benzene makes up 0.38% by mass of the VOCs in the vented gas.

Reference: [31], Section 4.2.1, Table 8 and Section 4.2.2, Table 9.

27.3.5. Uncontrolled Blowdown System

The gaseous emissions from blowdown systems in EU refineries are recovered and/or flared.

If these controls are not operational and all of the emissions are released to atmosphere, the benzene emissions can be conservatively estimated using the factor provided in EPA publication AP-42 [36], Table 5.1-1 to determine total hydrocarbon (THC) emissions and assuming that benzene makes up 0.38% by mass of the THCs in the blowdown gas (reference [31], Section 4.2.2, Table 9).

28. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

The E-PRTR requires the total emissions of the four PAHs listed below:
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Indeno(1,2,3-cd)pyrene

Estimation methods are provided for emissions from:
- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Fluid catalytic cracking unit regenerators

Speciated values are provided for the four individual PAHs in addition to the summation of the emission factors.

Emission factors for total PAH emissions are available for the combustion of distillate fuel in gas turbines (reference [37], Section 3.1, Table 3.1-15) and for flare gas (reference [31], Section 4.2.2, Table 9). These factors are not reproduced in this report as E-PRTR requires the emissions to be reported of only the four compounds listed above.

28.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Sections 28.1.1** to **28.1.5**.

28.1.1. Refinery Fuel Oil Combustion in Boilers and Furnaces

Table 28   PAH Emission Factors for Fuel Oil Combustion

PAH	EF$_{NCV}$ g/GJ
Benzo(a)pyrene	0[1]
Benzo(b)fluoranthene	3.670E-06
Benzo(k)fluoranthene	0[1]
Indeno(1,2,3-cd)pyrene	0[1]
Total	3.67E-06

Note:
1. Compound was not detected. The emission factor stated in reference [1] represents the detection limit. The emission factor is thus considered to be zero as the source is not proven (see **Section 5.2**).

For CO boilers and fired waste heat boilers, the algorithm should only be applied to the support fuel fired.

Reference: [1], [2].

28.1.2. Gas Combustion in Boilers and Furnaces

28.1.2.1. Natural Gas

The emission factors for all four of the PAHs stated in EPA publication AP-42 [38], Table 1.4-3 represent detection limit values. The emission factors are thus considered to be zero as the source is not proven (See **Section 5.2** of this report).

28.1.2.2. Refinery Fuel Gas

Table 29   PAH Emission Factors for Refinery Fuel Gas Combustion in Boilers and Furnaces

PAH	EF_{NCV} g/GJ
Benzo(a)pyrene	6.688E-07[1]
Benzo(b)fluoranthene	1.137E-06[1]
Benzo(k)fluoranthene	6.306E-07[1]
Indeno(1,2,3-cd)pyrene	6.306E-07[1]
Total	3.07E-06

Note:
1.   Ratio of mean to median value > 10. Median value used. See **Section 5.3**.

For CO boilers and fired waste heat boilers, the algorithm should only be applied to the support fuel fired.

Reference: [1], [2].

28.1.3. Gas Combustion in Gas Turbines

Table 30   PAH Emission Factors for Gas Combustion in Gas Turbines

PAH	EF_{NCV} g/GJ^1
Benzo(a)pyrene	0^2
Benzo(b)fluoranthene	1.576E-06
Benzo(k)fluoranthene	1.113E-06
Indeno(1,2,3-cd)pyrene	8.360E-07
Total	3.53E-06

Notes:
1. Emission factors for gas turbine without duct burners.
2. No data available.

Reference: [1], [2].

28.1.4. Gas Combustion in Gas Engines

Table 31   PAH Emission Factors for Gas Combustion in Gas Engines

PAH	EF_{NCV} g/GJ^1
Benzo(a)pyrene	1.615E-05
Benzo(b)fluoranthene	1.486E-04
Benzo(k)fluoranthene	2.408E-04
Indeno(1,2,3-cd)pyrene	5.446E-05
Total	4.60E-04

Note:
1. Emission factors for 4-stroke, lean-burn gas engine.

Reference: [1], [2].

28.1.5. Distillate Oil Combustion in Diesel Engines

Table 32   PAH Emission Factors for Distillate Oil Combustion in Diesel Engines

PAH	EF_{NCV} g/GJ[1]
Benzo(a)pyrene	1.127E-04
Benzo(b)fluoranthene	4.888E-04
Benzo(k)fluoranthene	9.640E-05
Indeno(1,2,3-cd)pyrene	1.815E-04
Total	**8.79E-04**

Notes:
1. Emission factors for large stationary engine with stack gas oxygen concentration < 13%.

Reference: [1], [2].

28.1.6. Incinerator Support Fuel and Flare Pilot Fuel

Use values of EF_{NCV} provided in **Section 28.1.2**.

28.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

If the destruction efficiency of the flare or incinerator and the mass and composition of the gas stream are known:

Mass emitted (kg) = (100 – DE) × 10 × M × MF$_{PAH}$

where:
DE = flare or incinerator destruction efficiency (%)
M = total mass of gas flared or incinerated (in tonnes)
MF_{PAH} = mass fraction of PAH in gas flared or incinerated

Otherwise, use the algorithm in **Section 28.1**, with values of EF_{NCV} provided in **Section 28.1.2.2**.

28.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = EF$_{FCC}$ × Mass of coke burned (in tonnes)

where:
EF_{FCC} = emission factor from **Table 33**

Table 33   PAH Emission Factors for CCU Regenerators

PAH	EF$_{FCC}$
Benzo(a)pyrene	7.072E-07
Benzo(b)fluoranthene	1.223E-06
Benzo(k)fluoranthene	8.212E-07
Indeno(1,2,3-cd)pyrene	6.238E-07
Total	3.38E-06

Reference: [10], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2**.

29. CHLORINE AND INORGANIC CHLORINE COMPOUNDS

The E-PRTR requires estimates of the emissions of chlorine and inorganic chlorine compounds reported as HCl.

The major source of these pollutants is the catalytic reforming unit.

29.1. CATALYTIC REFORMING UNITS

The source of these compounds is the reactivation of the catalyst in the catalytic reforming unit. The catalyst is reactivated, following the burning off of coke deposits, using chlorine, chlorinated compounds or a chlorinated solvent. The emissions can be abated, for example using a caustic or water wash system, chloride trap or driers where HCl is present in water vapour.

A review of data from units without flue gas abatement systems installed indicate that for very high throughput units the emissions may be greater than the E-PRTR reporting threshold of 10 000 kg/year. For units with abatement systems the emissions were below the threshold value.

There are emission factors related to reformer feed rate for both chlorine and HCl available in a paper by Bertrand et al [11], Table 1. This reference uses combined data from reformer units both with and without flue gas abatement systems installed. Due to the corresponding very wide scatter of emissions data, the emission factor for HCl has a variance between the median and average values of four orders of magnitude.

It is not possible, therefore, to provide reliable emission factors for uncontrolled emissions from the reformer catalyst reactivation process.

The uncontrolled emissions could be estimated from knowledge of the mass of chlorine or chlorinated compound injected, the efficiency of the reactivation process and any conversion of the compound that takes place during the activation process.

For reporting purposes, the calculated mass emitted needs to be converted to equivalent mass of HCl. This is obtained by multiplying the mass of chlorinated compound emitted by the ratio of the molecular weight of HCl to the molecular weight of the compound.

30. HYDROGEN CYANIDE (HCN)

Hydrogen cyanide is formed during the combustion of coke in fluid catalytic cracking unit (FCCU) regenerators and emissions depend upon the mode of operation.

30.1. FLUID CATALYTIC CRACKING UNIT REGENERATORS

30.1.1. Full Burn Regeneration

Mass emitted (kg) = 5.80E-01 × Mass of coke burned (in tonnes)

Reference: [25], Table 5.

30.1.2. Partial Burn with CO Boiler

Mass emitted (kg) = 4.20E-02 × Mass of coke burned (in tonnes)

Reference: [25], Table 5.

31. PARTICULATE MATTER WITH DIAMETER <10 μM (PM$_{10}$)

Estimation methods are provided for emissions of PM$_{10}$ due to:
- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Fluid catalytic cracking unit regenerators
- Fluid cokers

PM$_{10}$ from industrial sources is defined by the UNECE Task Force on Emission Inventories and Projections as particulate matter which is measured after passing through a size selective inlet with a 50% efficiency cut-off at 10 μm aerodynamic diameter. Emission factors derived from US EPA reference sources are for 'filterable' particulate matter i.e. collected on or prior to a filter of an EPA Method 5 (or equivalent) sampling train.

Note that the Refinery BREF [26], Section 5.1.4, BAT 4 requires monitoring of "dust" (i.e. total suspended particulate) emissions, using the techniques and frequencies specified, from all combustion units and from fluid catalytic cracking units.

31.1. COMBUSTION OF FUELS

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table 34**.

Table 34   PM$_{10}$ Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Boilers and Furnaces < 10 MW (for CO Boilers and Fired Waste Heat Boilers only applies to the support fuel firing)	Distillate (gas oil)	3.49E+00	[38] Section 1.3, Table 1.3-7
	Refinery Fuel Oil	1.50E+01	[28] Section 1.A.1, Table 4-4
	LPG[1]	9.89E-01	[38] Section 1.5, Table 1.5-1
	Natural Gas	8.90E-01	[38] Section 1.4, Table 1.4-2

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	3.23E+00	[38] Section 1.3, Table 1.3-6
	Refinery Fuel Oil	1.50E+01	[28] Section 1.A.1, Table 4-4
	LPG[1]	9.89E-01	[38] Section 1.5, Table 1.5-1
	Natural Gas	8.90E-01	[38] Section 1.4, Table 1.4-2
Boilers and Furnaces > 100 MW	Distillate (gas oil)	3.23E+00	[46] SCC 10100501
	Refinery Fuel Oil	1.50E+01	[28] Section 1.A.1, Table 4-4
	LPG[2]	7.84E-01	[46] SCC 10101002
	Natural Gas	8.90E-01	[38] Section 1.4, Table 1.4-2
Gas Turbine[3]	Distillate (gas oil)[4]	1.95E+00	[37] Section 3.1, Table 3.1-2a
	Natural Gas	2.00E-01	[28] Section 1.A.1, Table 3-17
Gas Engine 4-stroke, Lean Burn	Natural Gas	3.68E-02	[37] Section 3.2, Table 3.2-2
Diesel Engine Large, Stationary	Diesel Fuel	2.24E+01	[37] Section 3.4, Table 3.4-2
Incinerator Support Fuel or Flare Pilot Fuel	LPG[1]	9.89E-01	[38] Section 1.5, Table 1.5-1
	Natural Gas	8.90E-01	[38] Section 1.4 Table 1.4-2

Notes:

1.   Factor is for both butane and propane combustion
2.   Factor is for propane combustion
3.   Factors based on combustion turbines using water-steam injection.
4.   Factor provided in reference [37] derived using HHV of 139 MBtu/10^3 US gal.

Estimation of PM_{10} emissions from measurement of 'dust' (total suspended particulates (TSP))

Where measurements of TSP are made for dual-fired combustion units, the mass of PM_{10} can be derived from:

Mass emitted of PM_{10} = 7.50E-01 × mass of TSP

based on an emission factor for TSP from RFO combustion of 20 g/GJ [28].

31.1.1. Other Fuels

In the absence of specific emission factors for other gaseous fuels (e.g. refinery fuel gas, low joule gas) it is recommended to use the value of EF_{NCV} for natural gas from **Table 34.**

31.2. DESTRUCTION OF HYDROCARBON GAS STREAMS

For flare and incinerator hydrocarbon gas streams, use the algorithm in **Section 30.1** with an emission factor EF_{NCV} equal to that for natural gas combustion in a furnace.

For emissions from the combustion of the auxiliary fuel used to support flaring or incineration, also use the algorithm in **Section 30.1.**

31.3. FLUID CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (in kg) = 5.49E-01 × Feed to unit (in m³)

Reference: [31], Section 4.2.1, Table 8.

This algorithm is for a unit with cyclone systems installed inside the regenerator vessel – see **Section 6.2.**

31.4. FLUID COKERS

Mass emitted (in kg) = 7.65E-01 × Feed to unit (in m³)

Reference: [31], Section 4.2.1, Table 8.

Concawe

32.   REFERENCES

1.   API (1998) Air toxics emission factors for combustion sources using petroleum-based fuels. Volume 1: Development of emission factors using API/WSPA approach. Publication No. 348. Washington DC: American Petroleum Institute

2.   API (2002) Comparison of API and EPA toxic air pollutant emission factors for combustion sources. Publication No. 4720. Washington DC: American Petroleum Institute

3.   API (2005) Evaporative loss from storage tank floating roof landings. Technical Report 2567. Washington DC: American Petroleum Institute

4.   API (2007) Evaporative loss from the cleaning of storage tanks. Technical Report 2568. Washington DC: American Petroleum Institute

5.   API (2008) Evaporative loss from closed-vent internal floating-roof storage tanks. Technical Report 2569. Washington DC: American Petroleum Institute

6.   API (2009) Compendium of greenhouse gas emissions estimation methodologies for the oil and natural gas industry. Washington DC: American Petroleum Institute

7.   API (2012) Manual of petroleum measurement standards. Chapter 19.2: Evaporative loss from floating-roof tanks. 3rd edition. Washington DC: American Petroleum Institute

8.   API (2017) Manual of petroleum measurement standards. Chapter 19.1: Evaporative loss from fixed-roof tanks. 5th edition. Washington DC: American Petroleum Institute

9.   Battye, R. et al (1994) Development and selection of ammonia emission factors. Washington DC: US Environmental Protection Agency

10.   Bertrand, R.R. and Siegell, J.H. (2002) Emission of trace compounds from catalytic cracking regenerators. *Environmental Progress 21, 3, 163-167*

11.   Bertrand, R.R. and Siegell, J.H. (2003) Emission of trace compounds from catalytic reforming units. *Environmental Progress 22, 1, 74-77*

12.   Canadian Fuels Association (2017) Code of practice for developing an emission inventory for refineries and terminals, Rev. 16. Ottawa: Canadian Fuels Association

13.   CEN (2008) Fugitive and diffuse emissions of common concern to industry sectors – measurement of fugitive emission of vapours generating from equipment and piping leaks. Standard No. EN 15446: 2008. Brussels: Comité Européen de Normalisation

14.   CONCAWE (1985) Hydrocarbon emissions from gasoline storage and distribution systems. Report No. 85/54. Brussels: CONCAWE

15.   CONCAWE (2004) Guidance document for application of the EU Commission's guidelines for monitoring and reporting of GHG emissions. Report No. 10/04. Brussels: CONCAWE

16.   CONCAWE (2006) Air pollutant emission estimation methods for EPER and PRTR reporting by refineries (revised). Report No. 9/05R. Brussels: CONCAWE

17.   CONCAWE (2007) Air pollutant emission estimation methods for E- PRTR reporting by refineries. Report No. 3/07. Brussels: CONCAWE

18.   CONCAWE (2008) Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions. Report No. 6/08. Brussels: CONCAWE

19.   CONCAWE (2009) Air pollutant emission estimation methods for E- PRTR reporting by refineries, 2009 edition. Report No. 1/09. Brussels: CONCAWE

20.   CONCAWE (2014) Methods for estimating VOC emissions from primary oil-water separator systems in refineries. Report 5/14. Brussels: CONCAWE

21.   CONCAWE (2015) Air pollutant emission estimation methods for E- PRTR reporting by refineries, 2015 edition. Report No. 3/15. Brussels: CONCAWE

22.   CONCAWE (2015) Techniques for detecting and quantifying fugitive emissions – results of comparative field studies. Report No. 6/15. Brussels: CONCAWE

23.   CONCAWE (2016) Emission factors for metals from combustion of refinery fuel gas and residual fuel oil. Report No. 9/16. Brussels: CONCAWE

24.   CONCAWE (2017) Air pollutant emission estimation methods for E- PRTR reporting by refineries, 2017 edition. Report No. 4/17. Brussels: CONCAWE

25.   CONCAWE (2019) An overview of HCN emissions from FCCU's and their potential impacts on human health. Report No. 1/19. Brussels: CONCAWE

26.   EC (2015) Best available techniques (BAT) reference document for the refining of mineral oil and gas. Report EUR 27140 EN. Seville: European Commission.

27.   EEA (2005) EMEP/CORINAIR emission inventory guidebook – 2005, 3rd edition. Copenhagen: European Environment Agency

28.   EEA (2016) EMEP/EEA air pollutant emission inventory guidebook. Copenhagen: European Environment Agency

29.   EI (2004) Protocol for the determination of the speciation of hydrocarbon emissions from oil refineries. London: Energy Institute

30.   EI (2010) Protocol for the estimation of VOC emissions from petroleum refineries and gasoline marketing operations, 2nd edition. London: Energy Institute

31.   Environment Australia (1999) National pollutant inventory – emission estimation technique manual for petroleum refining. Canberra: Environment Australia

32.   EPA (1980) Assessment of atmospheric emissions from petroleum refining. Report No. EPA-600/2-80-075a. Washington DC: US Environmental Protection Agency

33.   EPA (1985) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Appendix A: Miscellaneous data and conversion factors. Research Triangle Park NC: US Environmental Protection Agency

34.   EPA (1994) Air emissions models for waste and wastewater. Report EPA-453/R-94-080A. Research Triangle Park NC: US Environmental Protection Agency

35.   EPA (1995) Protocol for equipment leak emission estimates. Report No. EPA-453/R-95-017. Research Triangle Park NC: US Environmental Protection Agency

36.   EPA (1995/2008/15) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 5: Petroleum industry. Research Triangle Park, NC: US Environmental Protection Agency

37.   EPA (1996/2000) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 3: Stationary internal combustion sources. Research Triangle Park NC: US Environmental Protection Agency

38.   EPA (1996/8/2008/10) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 1: External combustion sources. Research Triangle Park, NC: US Environmental Protection Agency

39.   EPA (2006) Emissions factors software and tools. WATER9 version 3.0. North Carolina: US Environmental Protection Agency

40.   EPA (2006) An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995 and 2000. Report EPA/600/P-03/002F. Research Triangle Park NC: US Environmental Protection Agency

41.   EPA (2006/12) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 7: Liquid storage tanks. Research Triangle Park NC: US Environmental Protection Agency

42.   EPA (2011) Refinery wastewater emissions tool spreadsheet. Research Triangle Park NC: US Environmental Protection Agency

43.   EPA (2015) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 8: Inorganic chemical industry, Section 18.3 Sulfur recovery. Research Triangle Park NC: US Environmental Protection Agency

44.   EPA (2015) Emissions estimation protocol for petroleum refineries – Version 3.0. Research Triangle Park NC: US Environmental Protection Agency

45.   EPA (2015) Review of emissions test reports for emissions factors development for flares and certain refinery operations. Research Triangle Park NC: US Environmental Protection Agency

46.   EPA (2016) WebFIRE. Research Triangle Park NC: US Environmental Protection Agency

47.   EPA (2018) AP 42, fifth edition: Compilation of air pollutant emission factors. Vol. 1: Stationary point and area sources. Chapter 13: Miscellaneous sources, Section 13.5 Industrial flares. Research Triangle Park NC: US Environmental Protection Agency

48.   EU (1996) Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. Official Journal of the European Communities No. L257, 10.10.1996

49.   EU (2000) Regulation (EC) No. 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer. Official Journal of the European Communities No. L244, 29.09.2000

50.   EU (2003) Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC. Official Journal of the European Communities No. L275, 25.10.2003

51.   EU (2006) Guidance Document for the implementation of the European PRTR. Brussels: European Commission, Directorate General for Environment

52.   EU (2006) Regulation (EC) No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC. Official Journal of the European Communities No. L33, 04.02.2006

53.   EU (2007) Commission decision of 18 July 2007 establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council (2007/589/EC). Official Journal of the European Communities No. L229, 31.08.2007

54.   ExxonMobil (2006) Private communication with the chairman of the CONCAWE Special Task Force STF-69

55.   Lev-On, M. et al (2007) Derivation of new emission factors for quantification of mass emissions when using optical gas imaging for detecting leaks. J Air Waste Manag Assoc 57, 9, 1061-1070

56.   Litchfield, D. K. (1971) Controlling odors and vapors from API separators. Oil and Gas Journal, November 1, 1971, 60-62

57.   Martin, J. et al (2003) Testing flare emission factors for flaring in refineries. US EPA 12th International emissions inventory conference, San Diego, April 29 – May 1, 2003

58.   RIVM/MNP (2004) Diffuse emissies en emissies bij op- en overslag. Handboek emissiefactoren. Rapportagereeks Milieu Monitor No.14. Bilthoven: Dutch National Institute for Public Health and the Environment

59.   SEPA (2017) Scottish pollutant release inventory reporting. Sector guidance note, 2017 – petroleum, incineration, paper and wood production and processing, cement and lime, production and processing of metals, combustion, chemicals. Edinburgh: Scottish Environment Protection Agency

60.   Takacs, T. J. et al (2004) Method estimates NO_X from combustion equipment. *Oil & Gas Journal 102, 23, 48-52*

61.   UNECE (2003) Protocol on pollutant release and transfer register. Geneva: United Nations Economic Commission for Europe

62.   VROM (2003) Handreiking validatie milieujaarverslagen. The Hague: Ministerie van VROM

APPENDIX 1 E-PRTR AIR POLLUTANTS

Table A1.1 lists the air pollutants that must be reported under the E-PRTR Regulation if annual emissions exceed the threshold values shown. It indicates those pollutants on the sector specific indicative lists in the EU Guidance Document [51] which are considered "likely" to be emitted by refineries and combustion installations (> 50 MW). It also shows those pollutants which have been estimated by at least one refinery to exceed the E-PRTR reporting threshold.

Table A1.1   List of E-PRTR Air Pollutants

POLLUTANT	REPORTING THRESHOLD kg/year	POLLUTANT ON INDICATIVE LIST Ref [51], Appendix 5		POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED PRTR THRESHOLDS
		Mineral Oil and Gas Refineries	Combustion Installations (> 50 MW)	
Methane (CH_4)	100 000	X	X	X
Carbon monoxide (CO)	500 000	X	X	X
Carbon dioxide (CO_2)	100 000 000	X	X	X
Hydrofluorocarbons (HFCs)	100	X	X	X
Nitrous oxide (N_2O)	10 000	X	X	X
Ammonia (NH_3)	10 000	X	X	X
Non-methane volatile organic compounds (NMVOCs)	100 000	X	X	X
Nitrogen oxides (NO_X)	100 000	X	X	X
Perfluorocarbons (PFCs)	100	-	-	-
Sulphur hexafluoride (SF_6)	50	-	X	X
Sulphur oxides (SO_X)	150 000	X	X	X
Hydrochlorofluorocarbons (HCFCs)	1	X	X	X
Chlorofluorocarbons (CFCs)	1	-	-	-[1]
Halons	1	-	-	-[1]
Arsenic + compounds	20	X	X	X
Cadmium + compounds	10	X	X	X
Chromium + compounds	100	X	X	X
Copper + compounds	100	X	X	X
Mercury + compounds	10	X	X	X
Nickel + compounds	50	X	X	X
Lead + compounds	200	X	X	X
Zinc + compounds	200	X	X	X

POLLUTANT	REPORTING THRESHOLD kg/year	POLLUTANT ON INDICATIVE LIST Ref [51], Appendix 5		POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED PRTR THRESHOLDS
		Mineral Oil and Gas Refineries	Combustion Installations (> 50 MW)	
Aldrin	1	-	-	-
Chlordane	1	-	-	-
Chlordecone	1	-	-	-
DDT	1	-	-	-
1,2-dichloroethane	1000	-	-	-
Dichloromethane	1000	-	-	-
Dieldrin	1	-	-	-
Endrin	1	-	-	-
Heptachlor	1	-	-	-
Hexachlorobenzene	10	-	-	-
1,2,3,4,5,6-hexachlorocyclohexane	10	-	-	-
Lindane	1	-	-	-
Mirex	1	-	-	-
PCDD + PCDF (dioxins and furans) (as TEQ)	0.0001	-	X	X
Pentachlorobenzene	1	-	-	-
Pentachlorophenol	10	-	-	-
Polychlorinated biphenyls (PCBs)	0.1	-	-	-
Tetrachloroethylene	2000	-	-	-
Tetrachloromethane	100	-	-	-
Trichlorobenzenes	10	-	-	-
1,1,1-trichloroethane	100	-	-	-
1,1,2,2-tetrachloroethane	50	-	-	-
Trichloroethylene	2000	-	X [2]	-
Trichloromethane	500	-	-	-
Toxaphene	1	-	-	-
Vinyl chloride	1000	-	-	-
Anthracene	50	-	-	- [3]
Benzene	1000	X	X	X
Ethylene oxide	1000	-	-	-
Naphthalene	100	-	-	- [3]

POLLUTANT	REPORTING THRESHOLD kg/year	POLLUTANT ON INDICATIVE LIST Ref [51], Appendix 5		POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED PRTR THRESHOLDS
		Mineral Oil and Gas Refineries	Combustion Installations (> 50 MW)	
Di-(2-ethyly hexyl) phthalate	10	-	-	-
Polycyclic aromatic hydrocarbons (PAHs) [4]	50	X	X	X
Chlorine + inorganic compounds (as HCl)	10 000	X	X	X
Asbestos	1	-	-	-
Fluorine + inorganic compounds (as HF)	5000	-	-	-
Hydrogen cyanide (HCN)	200	-	-	X
Particulate matter < 10 micron diameter (PM$_{10}$)	50 000	X	X	X
Hexabromobiphenyl	0.1	-	-	-
TOTALS of 60 E-PRTR air pollutants		*22*	*25*	*25*

Notes:
1. These halocarbons have been banned under EU Regulations [49] and would not be used to top-up existing equipment.
2. Trichloroethylene is not a product of combustion. The inclusion of this pollutant in the indicative sector specific list of air pollutants for thermal power stations and other combustion installations in reference [51] appears to be due to an anomaly in the EPER database.
3. The possible magnitude of emissions of anthracene and naphthalene are reviewed in **Appendix 3**.
4. Benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene.

APPENDIX 2   UPDATES IN EMISSION ALGORITHMS AND FACTORS

The following changes in emission algorithms and factors have been made from the predecessor CONCAWE report No. 4/17 [24].

Nitrogen Oxides

Revised emission factor for:
- Flares.

HCN

New emission factors for:
- FCCU regenerators

APPENDIX 3   ANTHRACENE AND NAPHTHALENE

Anthracene and naphthalene are pollutants known to be emitted by refineries, but neither is included on the sector specific indicative lists in the EU E-PRTR Guidance [51]. Emission estimation methods for these two pollutants are provided in this Appendix. It is demonstrated that emissions of neither pollutant are likely to exceed their respective E-PRTR reporting threshold, even at the largest of refineries.

A3.1   ANTHRACENE

Estimation methods are provided for emissions from:
- Combustion of fuels
- Fluid catalytic cracking units

A3.1.1   Combustion of Fuels

Mass emitted (kg) = (EF_{NCV} × M × NCV) / 1000

where:
EF_{NCV} = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF_{NCV} are provided in **Table A3.1**.

Reference: [1].

Table A3.1   Anthracene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Furnaces and Boilers	Refinery Fuel Oil	9.37E-07	[1], [2][1]
	Gas	2.26E-06	[1], [2][1]
Gas Turbine[2]	Gas	1.64E-05	[1], [2][1]
Gas Engine 4-Stroke, Lean-Burn	Refinery Fuel Gas	1.17E-04	[1], [2][1]
Diesel Engine Large, Stationary[3]	Distillate (Gas Oil)	5.43E-04	[1], [2][1]

Notes:
1. Reference [1] is base document, but reference [2] provides emission factors to more significant figures.
2. Factor derived from gas turbines without duct burners.
3. Factor for stack oxygen concentration < 13%

A3.1.2 Fluid Catalytic Cracking Unit Regenerator

Mass emitted (kg) = 3.06E-06 × Mass of coke burned (in tonnes)

Reference: [10], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

A3.1.3 Emissions from a Very Large Refinery

To establish if anthracene could be emitted in excess of the E-PRTR reporting threshold, emissions have been calculated for a very large refinery. The fuel consumed at the refinery is assumed to be 8.4E+07 GJ/year, of which 3.6E+07 GJ is due to fuel oil use. The same refinery has a FCCU with a capacity of 2.9E+06 m^3/year, with a resultant coke burn of about 140 000 t/year.

- Fuel oil combusted = 3.6E+07 GJ/year
- Fuel gas combusted = 4.8E+07 GJ/year
- FCCU coke combusted = 1.4E+05 tonnes/year

The emissions from this very large refinery would be:

Emissions from oil and gas combustion
= [(9.37E-07 × 3.6E+07) + (2.26E-06 × 4.8E+07)] × 1.0E-03 = 1.42E-01 kg
Emissions from coke burn = 3.06E-06 × 1.4E+05 = 4.28E-01 kg

Total emissions = 0.57 kg/year

These emissions are significantly less than the E-PRTR reporting threshold of 50 kg/year.

A3.2 NAPHTHALENE

Estimation methods are provided for emissions from:
- Combustion of fuels
- Fluid catalytic cracking units

A3.2.1 Combustion of Fuels

Mass emitted (kg) = (EF$_{NCV}$ × M × NCV) / 1000

where:
EF$_{NCV}$ = Emission factor (in g/GJ)
M = mass of fuel combusted (in tonnes)
NCV = net calorific value of the fuel combusted (in MJ/kg)

Values for the emission factor EF$_{NCV}$ are provided in **Table A3.2**.

Reference: [1].

Table A3.2   Naphthalene Emission Factors for Combustion Sources

SOURCE	FUEL	EF$_{NCV}$ g/GJ	REF
Furnaces and Boilers	Refinery Fuel Oil	1.83E-04	[1], [2][1]
	Gas	1.86E-04	[1], [2][1]
Gas Turbine	Distillate (Gas Oil)[2]	1.58E-02	[37], Section 3.1, Table 3.1-4
	Gas[3]	3.48E-04	[1], [2][1]
Gas Engine 4-Stroke, Lean-Burn	Refinery Fuel Gas	5.54E-02	[1], [2][1]
Diesel Engine Large, Stationary[4]	Distillate (Gas Oil)	5.75E-02	[1], [2][1]

Notes:
1. Reference [1] is base document, but reference [2] provides emission factors to more significant figures.
2. Factor derived from turbines operating at high (≥ 80%) loads.
   Factor provided in reference [37] derived using HHV of 139 MBtu/10^3 US gal.
3. Factor derived from gas turbines without duct burners.
4. Factor for stack oxygen concentration < 13%

A3.2.2   Fluid Catalytic Cracking Unit Regenerator

Mass emitted (kg) = 5.59E-05 × Mass of coke burned (in tonnes)

Reference: [10], Table 1. This reference provides data on the number of data points both above and below the limit of detection. The emission factor is a weighted value using both sets of data – see **Section 5.2** of this report.

A3.2.3   Emissions from a Very Large Refinery

To establish if naphthalene could be emitted in excess of the E-PRTR reporting threshold, emissions have been estimated for the very large refinery described in **Section A3.1.3**.

- Fuel oil combusted = 3.6E+07 GJ/year
- Fuel gas combusted = 4.8E+07 GJ/year
- FCCU coke combusted = 1.4E+05 tonnes/year

The emissions from this refinery would be:

Emissions from combustion
= [(1.83E-04 × 3.6E+07) + (1.86E-04 × 4.8E+07)] × 1.0E-03 = 1.55E+01 kg
Emissions from FCCU coke burn = 5.59E-05 × 1.4E+05 = 7.83E+00 kg

Total emissions = 23.3 kg/year

These emissions are less than the E-PRTR reporting threshold of 100 kg/year.

APPENDIX 4   NMVOC EMISSIONS FROM GASOLINE MARKETING FACILITIES

Neither marketing distribution terminals (i.e. road tanker gasoline loading facilities which are not located on a refinery site) nor service stations are regulated under the terms of the IPPC Directive [48] and hence are not required to submit data for the E-PRTR.

Algorithms are provided in this Appendix, however, as emission estimates for distribution terminals and service stations may be made by oil companies for their own environmental reporting purposes.

A 4.1   DISTRIBUTION TERMINALS

The major sources of emissions at terminals are the storage and loading of gasolines. As there is negligible methane in refined transport fuels, it can be assumed that there are no emissions of CH_4.

A 4.1.1   Storage Tanks

Use the methodologies provided in **Section 13.9**.

A 4.1.2   Loading of Mobile Containers

Use the methodologies provided in **Section 13.8**.

A 4.1.3   Fugitive Emissions from Components

Emissions can occur due to leakage past seals, flanges, etc., on components installed in product pipelines and loading systems e.g. pump seals, connectors.

The emissions from fugitives at terminals are very much lower than at refineries because the systems do not operate at such high pressures. The emission factors provided in **Section 13.5**, which were derived from measurements on refinery process plants, should not be used to estimate fugitive emissions at distribution terminals. Equivalent emission factors for terminal equipment are provided in an EPA Protocol [35], Table 2-3. Emissions from this source are typically less than 1 tonne/year for high throughput terminals.

A 4.1.4   Oil-Water Separators

The emission factors provided in **Section 13.6** have been derived from measurements on oil-water separators at refineries and are not appropriate for facilities at distribution terminals due to the differences in inlet conditions.

Emissions can be considered to be negligible if good maintenance and operating procedures are in place.

A 4.2   SERVICE STATIONS

Algorithms are provided for the following sources:
- Storage tanks
- Automobile refuelling

Gasoline vapour emissions at service stations can be controlled using "vapour balancing" techniques:-

Storage tank filling: When the storage tank is filled the vapours normally vented to atmosphere can be fed back into the tanker cargo tank (compartment) from which the gasoline is being off-loaded. This technique is called "Stage 1b" vapour balancing.

Automobile Refuelling: When an automobile is being refuelled, the vapours normally vented to atmosphere from the fuel tank can be fed back to the service station storage tank from which the gasoline was dispensed. This technique has been mandated in the EU and is called "Stage 2" vapour balancing. An alternative, which has been mandated in the USA, is to enlarge the carbon canister fitted on the automobile to control fuel system hot-soak emissions so that refuelling emissions can also be captured.

Other emissions comprise storage tank "breathing" due to evaporation of the gasoline in the tank, and drips and minor spillage during automobile refuelling.

The emissions can be estimated from:

Mass emitted (kg) = EF × VOL$_{DISP}$ × TVP

where:
EF = Emission Factor from **Table A4.3** depending on source and activity.
VOL$_{DISP}$ = Volume of gasoline dispensed (in m^3).
TVP = True Vapour Pressure of gasoline at storage temperature (in kPa).

Reference: [30], Section 3.

Table A4.3   NMVOC Emission Factors for Service Stations

SOURCE / ACTIVITY		EMISSION FACTOR (EF) kg/m^3/kPa
Storage Tank	Filling without Stage 1b	2.44E-02
	Filling with Stage 1b in operation	1.10E-03
	Breathing	3.30E-03
Automobile Refuelling	Refuelling with no emission controls in operation	3.67E-02
	Refuelling with Stage 2 in operation	5.50E-03
	Drips and minor spillage	2.20E-03

Gasoline TVP can be calculated from:

$$TVP = RVP \times 10^{[(7.047E\text{-}06 \times RVP + 1.392E\text{-}02) \times TEMP + (2.311E\text{-}04 \times RVP - 5.236E\text{-}01)]}$$

where:
RVP = Reid Vapour Pressure (in kPa)
TEMP = Gasoline storage temperature (in degrees Centigrade)

If the storage tank temperature is unknown, for the estimation of annual emissions TEMP can be assumed to equal the average annual ambient temperature.

Reference: [30], Annex 1.

APPENDIX 5   CONVERSION FACTORS AND DEFAULT FUEL VALUES

To convert from Higher Heating Value (HHV) to Net Calorific Value (NCV), the following approach, as used in reference [6], was taken.

NCV = HHV x Correction Factor for heat of vaporisation of water in the fuel (CF_{H_2O})

For Liquid Fuels, Correction Factor (CF_{H_2O}) = 0.95
For Gaseous Fuels, Correction Factor (CF_{H_2O}) = 0.9

Reference: [6], Section 4.2.

To convert Emission Factor from $lb/MBtu_{(HHV)}$ to $g/GJ_{(NCV)}$

$$EF\ g/GJ_{(NCV)}\ =\ (EF\ lb/MBtu_{(HHV)}\ /\ CF_{H_2O}) \times (g\ /\ lb) \times (MBtu\ /\ GJ)$$

To convert Emission Factor from $lb/10^3$ gal to $g/GJ_{(NCV)}$

$$EF\ g/GJ_{(NCV)}\ =\ EF\ lb/10^3\ gal \times (10^3\ gal\ /\ MBtu_{(NCV)}) \times (g\ /\ lb) \times (MBtu\ /\ GJ)$$

To convert Emission Factor from $lb/10^6$ scf to $g/GJ_{(NCV)}$

$$EF\ g/GJ_{(NCV)}\ =\ EF\ lb/10^6\ scf \times (10^6\ scf\ /\ MBtu_{(NCV)}) \times (g\ /\ lb) \times (MBtu\ /\ GJ)$$

Unless otherwise stated, emission factors were calculated using the following heating values expressed in their original units.

FUEL	HIGHER HEATING VALUE (HHV)	REFERENCE
Distillate (gas oil)	140 MBtu / 10^3 gal	[33]
Diesel Fuel	137 MBtu / 10^3 gal	[33]
Refinery Fuel Oil	150 MBtu / 10^3 gal	[33]
LPG	94 MBtu / 10^3 gal	[33]
Propane	91.5 MBtu / 10^3 gal	[38] Section 1.5.3.1
Natural Gas	1020 MBtu / 10^6 scf	[38] Section 1.4.1

Some useful conversion factors

Refinery Fuel Oil

1 $lb/10^3$ US gal = 3.017 $g/GJ_{(NCV)}$
1 $lb/10^6 Btu_{(HHV)}$ = 453 $g/GJ_{(NCV)}$

Distillate (Gas Oil)

1 lb/10^3 US gal = 3.233 g/GJ$_{(NCV)}$
1 lb/10^6 Btu$_{(HHV)}$ = 453 g/GJ$_{(NCV)}$

LPG

1 lb/10^3 US gal = 4.815 g/GJ$_{(NCV)}$

Propane

1 lb/10^3 US gal = 4.946 g/GJ$_{(NCV)}$

Natural Gas

1 lb/10^6 scf = 0.468 g/GJ$_{(NCV)}$
1 lb/10^6 Btu$_{(HHV)}$ = 478 g/GJ$_{(NCV)}$