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air pollutant emission estimation methods for EPER and PRTR reporting by refineries (revised)

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Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Emission Reporting Methodologies (STF-64)

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ABSTRACT

This report provides algorithms to permit emission estimates to be made by refineries to meet the requirements of both the current European Pollutant Emissions Register (EPER) and forthcoming Pollutant Release and Transfer Register (PRTR) on reporting air pollutants.

KEYWORDS

Air pollution, EPER, PRTR, emission factors, refinery distribution, sources, marketing

INTERNET

This report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org).

REVISIONS

This report is a revised version of the withdrawn report 9/05. The main changes are in Table 10 and in the section with the Fuel NO_x formulas on page 40-41.

NOTE

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SUMMARY

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

CONCAWE has reviewed the emission estimation methodologies for pollutants emitted to air available in the public domain. This report provides recommended algorithms and emission factors for uncontrolled releases of those pollutants from oil refineries which may be in excess of the reporting thresholds.

Details are provided for the factors including references to the literature sources used.

1. INTRODUCTION

The European Directive 96/61/EC on integrated pollution prevention and control (IPPC) [1] mandated the publication of a regularly updated pollutant inventory. Details of this European Pollutant Emission Register (EPER) were outlined in the Commission Decision 2000/479/EC [2]. The Register requires the reporting of a number of pollutants, both to air and water, from all facilities listed in Annex 1 of the IPPC Directive. Member States have to report to the Commission on a regular basis. The reporting interval is set initially at three years (reports from Member States to be provided to the EC in June 2003 and 2006 for the reporting years of 2001 and 2004 respectively). Guidance on the implementation of the EPER requirements has been provided by the EU [3].

The EPER requirements will be replaced by those of the UNECE Kiev Protocol on Pollutant Release and Transfer Registers (PRTR) [4] [5] for the reporting year 2007. The PRTR has more extensive reporting requirements (as it also includes the transfer of pollutants) and annual reporting is mandated. The list of air pollutants is also greater: 59 versus 37 in the EPER. The air pollutants, and the threshold values above which emissions must be reported for both EPER and PRTR, are specified in **Appendix 1**.

With regard to the data submissions for both EPER and PRTR, CONCAWE have 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 both comparable sites and 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 EPER threshold values from sources found at the majority of European refineries.

It was noted that currently there are no emission estimation guidelines for all 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 [6] for the major air pollutants, estimation methodologies are not available for all of the EPER or 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 [7] and a number of nationally agreed methods such as that published by the UK Energy Institute [8].

CONCAWE, therefore, has drawn up a compendium of emission factors, with associated references, for the uncontrolled release of air pollutants. The compendium can not be fully comprehensive as emission factors are not available in

the public domain for all sources and/or pollutants. CONCAWE, however, considers this to be the most appropriate set of emissions factors for the refining sector.

This report provides the air pollutant emission estimation algorithms, incorporating those factors, which CONCAWE recommends for EPER and PRTR reporting purposes. The emission factors provided are for uncontrolled releases. Reported emissions must take account of any abatement equipment installed e.g. wet gas scrubbers, electrostatic precipitators, etc.

Where emission factors are available, algorithms are provided for sources found in the majority of European refineries. There are, therefore, 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 EPER or 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 85/54 [9] which was widely used by Industry is now out of date and is no longer available. This current report provides NMVOC estimation algorithms which can be applied at gasoline distribution terminals. Estimation methods for gasoline storage and handling at service stations are also provided for completeness.

2. EMISSION ESTIMATION METHODOLOGIES

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

Class M: emission data are based on measurements using standardised or accepted methods; often additional calculations are needed to convert the results of measurements into annual emission data.

Class C: emission data are based on calculations using nationally or internationally accepted estimation methods and emission factors, which are representative of the industrial sectors.

Class E: emission data are based on non-standardised estimations derived from best assumptions or expert guesses.

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

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

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

- Oil industry associations e.g. CONCAWE, API, UK Energy Institute (formerly IP), etc.
- Oil companies who have published methods in the professional press
- National and international environmental authorities e.g. US EPA, European Environment Agency, etc.
- International organisations e.g. IPCC, etc.

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

To establish which estimation methods should be used for EPER reporting; only those which are currently in the public domain were considered. The hierarchy used to determine which methodologies are the most representative for oil industry sources placed the following in order of preference:

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

3. POLLUTANTS

There are 37 air pollutants which must be reported under the EPER requirements if their respective annual emission threshold values are exceeded at a facility. The PRTR Regulation lists another 22 pollutants. All of these are shown in **Appendix 1** with their threshold values.

The EU Guidance Document on EPER Implementation [3] provides an indicative list 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 installations with ratings in excess of 50MW, which are also listed as an “activity”.

Those pollutants considered within the EU Guidance Document to be “likely” air pollutants from these two activities are listed in **Appendix 1**.

Information was requested from CONCAWE's member companies in 2002 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 EPER thresholds.

Appendix 1 indicates discrepancies between the lists of pollutants that may require reporting under the EPER Regulation.

The oil industry list includes:

- HFCs
- Ammonia
- SF₆

The list in the EU guidance document [3] includes the following, which are not on the industry list:

- Dioxins and furans (PCDD and PCDF)
- Fluorine and inorganic compounds (as HF)

Dioxins and furans are generated in some combustion processes where specific conditions exist. **Appendix 2** provides emission factors for dioxins and furans and includes a review of the worst case refinery emissions. This shows that the emissions are below both the EPER reporting threshold of 0.001 kg/year and the PRTR threshold of 0.0001 kg/year.

Due to the properties of hydrogen fluoride (HF), emissions of this pollutant are strictly controlled. It is considered that the only circumstance where emissions could possibly be in excess of the reporting threshold (5000 kg/year) would be a major accidental release. No emissions factors for this pollutant are therefore provided.

The EPER reporting requirements will be superseded by those of the PRTR Protocol [4] [5]. All of the air pollutants which could be emitted by refineries above the EPER reporting threshold are included in the PRTR list. Of the additional pollutants on the PRTR list, only three - HCFCs, anthracene and naphthalene - were initially considered to have the potential to exceed the PRTR thresholds. Their reporting thresholds are shown in **Appendix 1**.

The sources of these pollutants in the refining sector and their published emission factors were reviewed. It was concluded that due to maintenance of refrigeration

equipment it is possible that emissions of HCFCs could exceed the reporting threshold of 1 kg/year.

However, even at the largest refineries, neither anthracene nor naphthalene emissions would exceed their PRTR threshold values. For completeness, emission factors are provided in **Appendix 2** for these two pollutants along with example emission calculations.

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:

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

Process sources included are:

- Bitumen blowing
- Blowdown systems
- Hydrogen plants
- Fluid Coking units
- Fluidised Catalytic Cracking units
- Catalytic Reforming units

Miscellaneous sources included are:

- Process drains
- Oil-water separators
- Fugitive emissions from pressurised pipe work and components
- Refrigeration systems
- Laboratory and test operations

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 for which emission factors are available [10] is coke calcining.

4.2. GASOLINE MARKETING FACILITIES

Some sources at distribution terminals are the same as at refineries. These are primarily storage and loading, although some terminals have small steam raising boilers to heat heavy oil storage tanks. The emission estimation methods listed in this report for refineries can be used for distribution facilities.

Service stations have very different sources of emissions. Unlike refineries, storage at service stations is in underground horizontal tanks. Emissions occur from these during filling and also due to "breathing" as the stored gasoline evaporates. Emissions also occur due to the filling of automobile fuel tanks and from minor drips

and spills during those operations. Estimation methods for these sources are provided in **Appendix 3**.

5. EMISSION ESTIMATION ALGORITHMS

5.1. INTRODUCTION

Algorithms are provided for the air pollutants on the EPER and PRTR lists which may exceed the 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 to 29**, in the order of the pollutant list in **Appendix 1, Table A1.1**, but with the addition of HCFCs i.e. as in Annex II of the Kiev Protocol [4].

Algorithms are also provided in **Appendix 2** for three additional pollutants (anthracene, dioxins and furans, and naphthalene). The emissions of these are shown not to exceed their reporting thresholds for either EPER or PRTR.

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.

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

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 the average of data points both 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, the weighted value (as calculated below) has been used in this report.

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

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 references [10], [11] and [12], both the mean and median values of pollutant emission data sets are provided. The mean values have been used in this report, unless the mean to median ratio is >10.

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

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 permits 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 4**.

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 can be determined from HHV using:

For liquid fuels

$$NCV = 0.95 \times HHV$$

For gaseous fuels

$$NCV = 0.9 \times HHV$$

Reference: [13], Section 3.6.3

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 no 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 × 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 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 CATALYTIC CRACKING UNITS

The algorithms for particulate (PM₁₀) and metals emissions from these units assume that there is a primary cyclone installed. If secondary or tertiary cyclones are fitted, then the effect of these additional controls to reduce PM₁₀ 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 reference [12]. 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 [12] 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 (CH₄)

Estimation methods are provided for emissions due to:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Venting to atmosphere of blowdown systems

7.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 1**.

Table 1 CH₄ 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)	1.80E+00	[13] Section 4, Table 4.4a
	Refinery Fuel Oil	4.84E+00	[13] Section 4, Table 4.4a
	LPG ¹	9.63E-01	[13] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[13] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	2.64E-01	[13] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content > 65% v/v	1.94E-01	[13] Section 4, Table 4.4a
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	1.68E-01	[13] Section 4, Table 4.4a
	Refinery Fuel Oil	3.02E+00	[13] Section 4, Table 4.4a
	LPG ¹	9.63E-01	[13] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[13] Section 4, Table 4.4a

SOURCE	FUEL	EF _{NCV} g/GJ	REF
Boilers and Furnaces 10 MW to 100 MW	Refinery Fuel Gas - hydrogen gas content < 65% v/v	2.64E-01	[13] Section 4, Table 4.4a
Boilers and Furnaces 10 MW to 100 MW	Refinery Fuel Gas - hydrogen gas content > 65% v/v	1.94E-01	[13] Section 4, Table 4.4a
Boilers and Furnaces > 100 MW	Distillate (gas oil)	9.05E-01	[13] Section 4, Table 4.4a
	Refinery Fuel Oil	8.45E-01	[13] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[13] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	2.64E-01	[13] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content > 65% v/v	1.94E-01	[13] Section 4, Table 4.4a
Gas Turbine ²	Natural Gas	4.08E+00	[13] Section 4, Table 4.5
Gas Engine ³ 4-stroke, Lean Burn	Natural Gas	5.97E+02	[13] Section 4, Table 4.5
Diesel Engine ⁴ Large, Stationary	Diesel Fuel	3.90E+00	[13] Section 4, Table 4.5
Incinerator Support Fuel or Flare Pilot Fuel	LPG ¹	9.63E-01	[13] Section 4, Table 4.4a
	Natural Gas	1.08E+00	[13] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content < 65% v/v	2.64E-01	[13] Section 4, Table 4.4a
	Refinery Fuel Gas - hydrogen gas content > 65% v/v	1.94E-01	[13] Section 4, Table 4.4a

Notes:

1. Assumes NCV of 3.75 MBtu/bbl (Reference [13], Section 3, Table 3.5),
2. Factor derived from units without emission controls operating at > 80% load.
3. Factor derived from subtracting ethane & VOC from TOC emission factor.
Factor is based on 4-stroke lean-burn engines operating at < 90% load.
4. Factor is based on TOC with 9% CH₄ by weight in the exhaust gas.

7.1.1. Other Fuels

For other gaseous fuels (e.g. low joule gas) assume EF_{NCV} of natural gas.

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:

$$\text{Mass emitted (kg)} = 5.00\text{E-}03 \times M \times \text{MF}_{\text{CH}_4}$$

where:

M = total mass of gas flared (in kg)

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: [13], Section 4.4, Figure 4-2.

7.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used:

$$\text{Mass emitted (kg)} = 2.28\text{E-}05 \times \text{Refinery Feed (in m}^3\text{)}$$

Reference: [13], Section 4.4, Table 4-7.

7.2.2. Incinerators

The following algorithm is for emissions from the combustion of the incinerator gas streams. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 7.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 1.08\text{E-}03 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled furnace.

7.3. UNCONTROLLED BLOWDOWN SYSTEMS

The gaseous emissions from refinery blowdown systems are normally recovered and/or flared. Where these controls are not operational and the emissions are emitted to atmosphere:

Mass emitted (kg) = 1.66E-02 × Refinery Feed (in m³)

This uses the conservative assumption that methane makes up 1% of the total organic compounds by mass in the blowdown system vapour.

Reference: [7], Table 5.1-1 for Total Hydrocarbons and note b.

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 fluidised catalytic cracking units (FCCUs)
- Regeneration of catalytic reforming units

8.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 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)	1.62E+01	[14] Section 1.3, Table 1.3-1
	Refinery Fuel Oil	1.51E+01	[14] Section 1.3, Table 1.3-1
	LPG ¹	9.40E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[14] Section 1.4, Table 1.4-1
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	1.62E+01	[14] Section 1.3, Table 1.3-1
	Refinery Fuel Oil	1.51E+01	[14] Section 1.3, Table 1.3-1
	LPG ¹	1.58E+01	[14] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[14] Section 1.4, Table 1.4-1
Boilers and Furnaces > 100 MW	Distillate (gas oil)	1.62E+01	[14] Section 1.3, Table 1.3-1
	Refinery Fuel Oil	1.51E+01	[14] Section 1.3, Table 1.3-1
	Natural Gas	3.93E+01	[14] Section 1.4, Table 1.4-1

SOURCE	FUEL	EF _{NCV} g/GJ	REF
Gas Turbine ²	Distillate (gas oil) ³	1.49E+00	[15] Section 3.1, Table 3.1-1
	Natural Gas	3.17E+01	[15] Section 3.1, Table 3.1-1
Gas Engine ⁴ 4-stroke, Lean Burn	Natural Gas	2.16E+02	[15] Section 3.2, Table 3.2-2
Diesel Engine Large, Stationary	Diesel Fuel	3.85E+02	[15] Section 3.4, Table 3.4-1
Incinerator Support Fuel or Flare Pilot Fuel	LPG ¹	9.40E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	3.93E+01	[14] Section 1.4, Table 1.4-1

Notes:

1. NCV calculated from HHV of 91.5 MBtu/10³ US gal (Reference [14], Section 1.5.1.3)
2. Uncontrolled, no water-steam injection. Factor derived from units operating at > 80% load.
3. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-1).
4. Factor is based on 4-stroke lean-burn engines operating at < 90% load.

8.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

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:

$$\text{Mass emitted (kg)} = 1.77\text{E-}01 \times M \times \text{NCV}$$

where:

M = mass of flare gas combusted (in tonnes)

NCV = net calorific value of the flare gas combusted (in MJ/kg)

Reference: [16], Section 4.2.1, Table 8

8.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used:

$$\text{Mass emitted (kg)} = 1.20\text{E-}02 \times \text{Refinery Feed (in m}^3\text{)}$$

Reference: [6], Activity 090203, Section 8, Table 2.

8.2.2. Incinerators

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 8.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 3.93\text{E-}02 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

8.3. 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.

8.3.1. Full Burn Regeneration

CO emissions are deemed to be negligible

8.3.2. Partial Burn with CO Boiler

CO emissions are deemed to be negligible

Reference: [7], Table 5.1-1

8.3.3. Partial Burn without CO Boiler

If there is no CO boiler in operation:

$$\text{Mass emitted (kg)} = 3.92\text{E+}01 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [7], Table 5.1-1

8.4. CATALYTIC REFORMING UNITS

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

Reference: [12], Table 1. This reference uses data from a number of units with varying degrees of abatement equipment installed – see **Section 6.3**.

9. CARBON DIOXIDE (CO₂)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators
- Other catalyst regeneration e.g. in catalytic reforming units
- Fluid and Flexi-cokers
- Hydrogen plants

9.1. COMBUSTION

For all fuel combustion, the following algorithm applies:

$$\text{Mass emitted (kg)} = M \times \text{MF}_{\text{CARBON}} \times \text{CFC}_{\text{MW}} \times \text{OXF}$$

where:

M = mass of fuel burnt (in kg)

MF_{CARBON} = mass fraction of carbon in fuel

CFC_{MW} = Molecular weight conversion from C to CO₂ = 44 / 12

OXF = Oxidation factor

= 0.995 for gaseous and liquid fuels, or

= 0.99 for solids

Thus for refinery oil and gaseous fuels:

$$\text{Mass emitted (kg)} = 3.65\text{E}+00 \times M \times \text{MF}_{\text{CARBON}}$$

Reference: Oxidation factors provided in [17].

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 algorithms 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

MF_{CARBON} = mass fraction of carbon in flare gas

9.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used:

$$\text{Mass emitted (kg)} = 3.14\text{E}+00 \times \text{Refinery Feed (in tonne)}$$

Reference: [18], Section 3, Table 5.

9.2.2. Incinerators

Use algorithm in **Section 9.1**, where:

M = mass of gas incinerated

MF_{CARBON} = mass fraction of carbon in gas incinerated

9.3. CATALYTIC CRACKING UNIT REGENERATORS

Although reference [17] requires the algorithm in **Section 9.1** to be used, where the fuel is the coke burned, CONCAWE [19] recommends the following algorithm which is more pragmatic and used in practice in most refineries.

$$\text{Mass emitted (kg)} = (\text{AR} + \text{SR}) \times (\text{VF}_{\text{CO}_2} + \text{VF}_{\text{CO}}) \times \text{CON}_{\text{VOL}} \times \text{TIME}$$

where:

AR = Air blower capacity (in m³/minute)

SR = Supplemental oxygen addition rate (in m³/minute)

VF_{CO₂} = Volume fraction of CO₂ in flue gas

VF_{CO} = Volume fraction of CO in flue gas

CON_{VOL} = Volume conversion factor at 15 C = 44 / MCF

MCF = Molar conversion factor at 15 C = (22.4 × 288 / 273) = 23.631 m³/kgmole

TIME = time blower operated (in minutes)

Thus:

$$\text{Mass emitted (kg)} = 1.86\text{E}+00 \times (\text{AR} + \text{SR}) \times (\text{VF}_{\text{CO}_2} + \text{VF}_{\text{CO}}) \times \text{TIME}$$

Reference: [13], Section 5.2.1, equation 5-4.

9.3.1. FCCU With CO Boiler

$$\text{Mass emitted (kg)} = 1.86\text{E}+00 \times (\text{AR} + \text{SR}) \times (\text{VF}_{\text{CO}_2} + \text{VF}_{\text{CO}}) \times \text{TIME}$$

9.3.2. FCCU Without CO Boiler

$$\text{Mass emitted (kg)} = 1.86\text{E}+00 \times (\text{AR} + \text{SR}) \times \text{VF}_{\text{CO}_2} \times \text{TIME}$$

9.4. OTHER CATALYST REGENERATION

CO₂ is produced during the catalyst regeneration in reforming and hydro-processing units.

$$\text{Mass emitted (in kg)} = 3.67\text{E}+00 \times \text{CR} \times \text{MF}_{\text{CARB}} \times \text{Feed}$$

where:

CR = Mass ratio of coke produced per feed

MF_{CARB} = Mass fraction of carbon in coke

Feed = Feed to unit (in kg)

Reference: [13], Section 5.2.4

9.5. FLUID AND FLEXI-COKERS

CO₂ is produced from the coke burner.

$$\text{Mass emitted (in kg)} = 3.67\text{E}+00 \times \text{CR} \times \text{MF}_{\text{CARB}} \times \text{Feed}$$

where:

CR = Mass ratio of coke produced per feed

MF_{CARB} = Mass fraction of carbon in coke

Feed = Feed to unit (in kg)

Reference: [13], 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 9.1.

9.6. HYDROGEN PLANTS

CO₂ is produced during the hydrogen production process.

$$\text{Mass emitted (kg)} = 4.74\text{E}-0.1 \times \text{Volume of Hydrogen produced (in m}^3\text{)}$$

Reference: [13], Section 5.2.2.

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 (N₂O)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators

11.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 N₂O 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	[13] Section 4, Table 4.4a
	Refinery Fuel Oil	1.60E+00	[13] Section 4, Table 4.4a
	LPG ¹	4.22E-01	[13] Section 4, Table 4.4a
	Natural Gas	1.03E+00	[13] Section 4, Table 4.4a
	Natural Gas (where low NO _x burners fitted)	3.00E-01	[13] Section 4, Table 4.4a
Gas Turbine ²	Natural Gas	1.43E+00	[13] Section 4, Table 4.5
Gas Engine 4-stroke, Lean Burn	Natural Gas	Not Detected ³	[13] Section 4, Table 4.5
Diesel Engine Large, Stationary	Diesel Fuel ⁴	2.21E+00	[13] Section 4, Table 4.5
Incinerator Support Fuel or Flare Pilot Fuel	LPG	4.22E-01	[13] Section 4, Table 4.4a
	Natural Gas	1.03E+00	[13] Section 4, Table 4.4a

Notes:

1. Assumes NCV of 3.75 MBtu/bbl (Reference [13], Section 3, Table 3.5)
2. Factor derived from units operating at > 80% load only. Based on limited source tests on a single turbine with water-steam injection.

3. Compound was not detected. The emission factor stated in reference [13] represents the detection limit. For the purposes of this report the emission factor is considered to be zero as source not proven (See **Section 5.2** of this report).
4. Assumes NCV of diesel fuel of 36.2 GJ/m³ (Reference [13], Section 3, Table 3.5)

11.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

11.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 11.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of mass).

$$\text{Mass emitted (kg)} = 1.03E-03 \times M \times NCV$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

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
- Catalytic Cracking Unit Regenerators

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:

$$\text{Mass emitted (kg)} = 3.50\text{E-}01 \times V_{\text{OIL}}$$

or

$$\text{Mass emitted (kg)} = 2.88\text{E+}02 \times V_{\text{GAS}}$$

where:

V_{OIL} = Volume of oil combusted in device connected to SNCR (in m³)

V_{GAS} = Volume of gas combusted in device connected to SNCR (in million m³)

Reference: [20], Section 5.4, Table 5.5

12.1.2. SCR

The emission algorithms are:

$$\text{Mass emitted (kg)} = 1.70\text{E-}01 \times V_{\text{OIL}}$$

or

$$\text{Mass emitted (kg)} = 1.46\text{E+}02 \times V_{\text{GAS}}$$

where:

V_{OIL} = Volume of oil combusted in device connected to SCR (in m³)

V_{GAS} = Volume of gas combusted in device connected to SCR (in million m³)

Reference: [20], 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.

$$\text{Mass emitted (kg)} = \text{Mass used to top-up refrigerant systems (in kg)}$$

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

12.3. CATALYTIC CRACKING UNIT REGENERATORS

NH₃ 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

12.3.2. Partial Burn with CO Boiler

Emissions are deemed to be negligible

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 m³)

Reference: [20], 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
- Catalytic cracking unit regenerators
- Fluid cokers
- Venting to atmosphere of blowdown systems
- Uncontrolled bitumen blowing
- 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

13.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (EF_{\text{NCV}} \times M \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	3.41E+00	[14] Section 1.3, Table 1.3-3
	LPG ¹	2.47E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	2.58E+00	[14] Section 1.4, Table 1.4-2
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	6.47E-01	[14] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	8.45E-01	[14] Section 1.3, Table 1.3-3
	LPG ¹	2.47E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	2.58E+00	[14] Section 1.4, Table 1.4-2

SOURCE	FUEL	EF _{NCV} g/GJ	REF
Boilers and Furnaces > 100 MW	Distillate (gas oil)	2.46E+00	[14] Section 1.3, Table 1.3-3
	Refinery Fuel Oil	2.29E+00	[14] Section 1.3, Table 1.3-3
	Natural Gas	2.58E+00	[14] Section 1.4, Table 1.4-2
Gas Turbine ²	Distillate (gas oil) ³	1.86E-01	[15] Section 3.1, Table 3.1-2a
	Natural Gas	1.00E-00	[15] Section 3.1, Table 3.1-2a
Gas Engine ⁴ 4-stroke, Lean Burn	Natural Gas	5.64E+01	[15] Section 3.2, Table 3.2-2
Diesel Engine ⁵ Large, Stationary	Diesel Fuel	3.71E+01	[15] Section 3.4, Table 3.4-1
Incinerator Support Fuel or Flare Pilot Fuel	LPG ⁷	2.47E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	2.58E+00	[14] Section 1.4, Table 1.4-2

Notes:

- Factor is for TOC and therefore includes methane. It assumes an NCV of 3.75 MBtu/bbl (Reference [13], Section 3, Table 3.5)
- Factor derived from units operating at > 80% load. Factor represents the sum of all organic emissions.
- NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-1).
- Factor based on the sum of the emission factors for all speciated organic compounds except methane & ethane.
- Based on data from 1 engine with TOC composition by weight of 9% methane and 91% non-methane.

13.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

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 algorithms in **Section 13.1**.

13.2.1.1. Flare Stream Details Known

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

$$\text{Mass emitted (kg)} = 5.00\text{E-}03 \times M \times \text{MF}_{\text{NMVOC}}$$

where:

M = total mass of gas flared (in kg)

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: [13], Section 4.4

13.2.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used:

$$\text{Mass emitted (kg)} = 2.00\text{E-}03 \times \text{Refinery Feed (in m}^3\text{)}$$

Reference: [6], Activity 090203, Section 8, Table 2.

13.2.2. Incinerators

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 13.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 2.58\text{E-}03 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled furnace.

13.3. 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: [7], 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 m³)

Reference: [7], 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 (in kg) = 4.60E-02 × Feed to unit (in m³)

Reference: [16], Section 4.2.1, Table 8

13.5. UNCONTROLLED BLOWDOWN SYSTEMS

The gaseous emissions from refinery blowdown systems are normally recovered and/or flared. Where these controls are not operational and the emissions are emitted to atmosphere:

Mass emitted (kg) = 1.65E+00 × Refinery Feed (in m³)

This assumes that methane makes up 1% of the total organic compounds in the blowdown gas.

Reference: [7], Table 5.1-1

13.6. UNCONTROLLED BITUMEN BLOWING

The gaseous emissions from bitumen blowing are normally passed through a scrubber and then fed to an incinerator. Where these controls are not operational and the emissions are emitted to atmosphere:

Mass emitted (kg) = 2.72E+01 × Mass of blown bitumen (in tonne)

This assumes that there is no methane content in the off-gas from the blowing process.

Reference: [6], Activities 040101 & 040102, Section 8.2.1, Table 8.2.

13.7. 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:

- Undertaking monitoring of a selected sample (or all) of components
- 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 and product storage tanks. Emission estimation methodologies for these sources are provided separately – see **Sections 13.8, 13.9 and 13.12**.

13.7.1. Measurement - Leak Monitoring Surveys

NMVOC emissions from pressurised components can be determined using leak monitoring surveys on a sample of equipment and then extrapolating using emission factors.

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

There are three tiers of measurement methodology:

- Applying average emission factors based on a leak/no leak criteria. This requires the use of VOC monitoring equipment to measure threshold VOC concentrations at each fitting.
- Applying emission correlations based on actual VOC concentration values determined at each fitting.
- Applying unit specific factors to individual fittings. This requires extensive bagging studies.

This report does not provide details of these measurement methods. Full details on the calculation of emissions are provided by the US EPA [21] and in the European CEN Standard [22].

13.7.2. Calculated Emissions - Component Count Data Available

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

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

where:

F_{COMP} = Average emission factor for the particular equipment type as in **Table 5**.

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).

Table 5 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: [22]

Definitions of “Service”

Reference [22] 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. Examples: gasolines (automotive, aviation), crude. Exclusions: kerosene and heavier products

Component counts

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

If actual counts are not available, reference [23], 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	-	1
Pump seals per pump	-	1.35
Compressor seals per compressor	2	-

Alternatively, an extrapolation can be made from published information. Reference [24] cites an example of a US refinery of 52 500 m³/day capacity having 11 500 valves, 46 500 flanges, 350 pump seals, 70 compressor seals and 100 relief valves.

13.7.3. Calculated Emissions - No Component Data Available

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

$$\text{Mass emitted (kg)} = 3.00\text{E-}01 \times \text{Refinery feed (in tonnes)}$$

Reference: [8], Section 1.5.

13.8. PROCESS DRAINS

The following algorithm provides an estimate for emissions from the entire refinery process drain system. Process drain openings (sumps, etc.) are normally fitted with an emission control device such as a water seal or sealed cover. An assessment needs to be made to establish how many of the drain covers are unsealed and vent directly to atmosphere.

$$\text{Mass emitted (kg)} = 3.20\text{E-}02 \times N \times \text{TIME}$$

where:

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

TIME = period of emission estimate in hours e.g. for EPER and PRTR annual reports = 365 × 24.

Reference: [23], Section 7.4, Table 7-1.

If the total number of drains is unknown, the above reference (Section 7.4.1) quotes a drain count of 2.6 drains per pump in process areas.

13.9. OIL-WATER SEPARATORS

Emissions are dependent on the type of separator installed.

$$\text{Mass emitted (kg)} = \text{EF}_{\text{SEP}} \times \text{VOL}_{\text{WATER}}$$

where:

EF_{SEP} = Emission factor for the type of separator given in **Table 6**.

VOL_{WATER} = Volume of waste water treated by the separator (in m³).

Reference: [23], Section 7.4, Table 7-1.

Emissions from basins and ponds that handle clean water or storm water are considered negligible - reference: [23], Section 7.4, table 7-1.

For ponds temporarily storing oily-water use the emission factor for an uncovered, gravity type separator in **Table 6**.

Table 6 Emission Factors for Oil-Water Separators

SEPARATOR TYPE	EMISSION FACTOR (EF _{SEP}) kg/m ³ waste water treated
Gravity type - uncovered	1.11E-01
Gravity type - covered	3.30E-03
Gravity type – covered and connected to flare	0
DAF or IAF (Note 1) - uncovered	4.00E-03
DAF or IAF - covered	1.20E-04
DAF or IAF - covered and connected to flare	0

Note 1:

DAF = Dissolved air floatation type

IAF = Induced air floatation type

13.10. 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.

Reference: [23], Section 7.4, Table 7-1.

13.11. 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.

13.11.1. Uncontrolled Emissions

$$\text{Mass emitted (kg)} = \text{EF}_{\text{LOAD}} \times \text{VOL}_{\text{LOAD}} \times \text{TVP}$$

where:

EF_{LOAD} = Emission Factor from **Table 7**, depending on loading mode.

VOL_{LOAD} = Volume of product loaded (in m³).

TVP = True Vapour Pressure of product at loading temperature (in kPa).

Reference: [8], Section 3.

For gasolines, TVP can be calculated from:

$$TVP = RVP \times (10E(((7.047E-06 \times RVP) + 1.32E-02) \times TEMP + ((2.311E-04 \times RVP) - 5.236E-01)))$$

where:

RVP = Reid Vapour Pressure (in kPa)

TEMP = product loading temperature (in degrees Centigrade)

Reference: [8], Appendix 1.

Table 7 NMVOC Emission Factors for Loading of Mobile Containers

LOADING MODE	EMISSION FACTOR EF _{LOAD}
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	1.08E-02
Marine tanker - typical cargo tank condition ¹	6.10E-03
Barge - typical cargo tank condition ¹	1.17E-02

Notes

1. 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 reference [8].

13.11.2. 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.

13.11.2.1. VRU Fitted with a CEM

$$\text{Mass emitted (kg)} = 1.00E-03 \times \text{MEAS}_{\text{CONC}} \times \text{VOL}_{\text{LOAD}} \times (1 - \text{TVP} / 100)$$

where:

MEAS_{CONC} = Measured VRU vent concentration (in g/m³)

VOL_{LOAD} = Volume of product loaded (in m³)

TVP = True Vapour Pressure of product at loading temperature (in kPa)

Reference: [8], Section 3.2.

13.11.2.2. VRU Efficiency Known

Emissions should be calculated using the algorithm in **Section 6**.

13.12. 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.

13.12.1. Floating Roof Tanks

Floating roof tanks can be of the following types:

- External floating roof (EFR)
- EFR fitted with domed cover
- Internal floating roof

For all of these tank types, use the latest edition of reference [25].

13.12.2. Vertical Fixed Roof Tanks (VFRT)

For these tanks in normal service, use the latest edition of reference [26].

13.12.2.1. 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, the 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 in the worst case to equal only the “working losses”.

13.12.3. Aboveground Horizontal Tanks

For these tanks, use the latest edition of reference [27], Section 7.1.3.1.

Note that reference [27] normally contains the latest version of references [25] and [26]. The emission calculation software is available from the US EPA via their website, <http://www.epa.gov>, or on a CD-ROM [28]. This CD also contains the EPA publication AP-42 *Compilation of Air Pollutant Emission Factors* and references [20] and [21].

13.12.4. Underground Tanks

Use the algorithms for service station storage tanks provided in **Appendix 3**.

14. NITROGEN OXIDES (NO_x)

Estimation methods are provided for emissions of NO_x from:

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

14.1. COMBUSTION IN BOILERS AND FURNACES

NO_x emissions from combustion comprises two components:

- Thermal NO_x; 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 NO_x; 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 reference [29].

Total NO_x Emissions = Thermal NO_x + Fuel NO_x

Thermal NO_x

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

where:

TNF = Thermal NO_x 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

$$\text{HHV} = 1.05 \times \text{NCV}$$

For gaseous fuels

$$\text{HHV} = 1.11 \times \text{NCV}$$

Where NCV = Net calorific value (in MJ/kg)

TNF = F_{BASE} × F_{H2} × F_{CONTROL} × F_{PREHEAT} × F_{H2O} × 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 8**.

Table 8 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_{H_2} is the adjustment factor for the amount of hydrogen gas in the fuel.

For all liquid fuels, methane, natural gas and LPG: $F_{H_2} = 1.0$

For other refinery gaseous fuels, values for F_{H_2} are given for some hydrogen concentrations in **Table 9**. These can be used to extrapolate for other compositions.

Table 9 Values for F_{H_2}

FUEL	H ₂ CONCENTRATION % vol	F _{H₂}
Refinery Fuel Gas	0 - 23	1.00
	33	1.04
	43	1.09
	53	1.25
	63	1.46
Low Joule Gas	0 - 14.7	1.00
	24.7	1.04
	34.7	1.09
	44.7	1.25
	54.7	1.46

$F_{CONTROL}$ is the adjustment factor for at-the-source control technologies, including burner type. Values are given in **Table 10**.

Table 10 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 11**.

Table 11 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_{H2O} is the adjustment factor for the moisture content of the combustion air. Values are given in **Table 12**.

Table 12 Values of F_{H2O}

MOISTURE CONTENT kg H ₂ O / kg dry air	F_{H2O}
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. Values are given in **Table 13**.

Table 13 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 $> 700 \text{ kW/m}^3$
- Low intensity is $< 30 \text{ kW/m}^3$

Values for F_{BURN} are given in **Table 14**.

Table 14 Values for F_{BURN}

BURNER INTENSITY	F_{BURN}
High	1.8
Low	1.0

Fuel NO_x

$$\text{Fuel NO}_x \text{ Mass emitted (kg)} = 1.00\text{E-}03 \times \text{FNF} \times \text{M} \times \text{HHV}$$

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)

$$\text{FNF} = (1.00\text{E+}04 \times \text{MP}_{\text{NITROGEN}} \times \text{CFN}_{\text{MW}} \times \text{F}_{\text{N}_2\text{CONTENT}}) / \text{HHV}$$

where:

$\text{MP}_{\text{NITROGEN}}$ = Mass Percentage of Nitrogen in the fuel combusted

CFN_{MW} = Molecular weight conversion from N to NO₂ = $46 / 14 = 3.286$

$\text{F}_{\text{N}_2\text{CONTENT}}$ = Adjustment factor for nitrogen content. Values are given in **Table 15**.

Table 15 Values for $\text{F}_{\text{N}_2\text{CONTENT}}$

FUEL NITROGEN % Mass	$\text{F}_{\text{N}_2\text{CONTENT}}$	
	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	0.05

Combining the above equations:

$$\text{Fuel NO}_x \text{ Mass emitted (kg)} = 32.86 \times \text{MP}_{\text{NITROGEN}} \times \text{F}_{\text{N}_2\text{CONTENT}} \times \text{M}$$

where:

$\text{MP}_{\text{NITROGEN}}$ = Mass Percentage of Nitrogen in the fuel combusted (see note below).

$\text{F}_{\text{N}_2\text{CONTENT}}$ = Adjustment factor for nitrogen content. Values are given in **Table 15**.

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).

Reference: [29].

14.2. 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.

$$\text{Mass emitted (kg)} = 6.22\text{E-}02 \times \text{M} \times \text{NCV}$$

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 in an uncontrolled furnace – see **Section 14.1**.

Reference: [29].

14.3. DESTRUCTION OF GASEOUS STREAMS

14.3.1. 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 14.2**.

14.3.1.1. Flare Stream Details Known

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

$$\text{Mass emitted (kg)} = 3.22\text{E-}02 \times M \times \text{NCV}$$

where:

M = mass of flare gas burnt (in tonnes)

NCV = net calorific value of the flare gas burnt (in MJ/kg)

Reference: [16], Section 4.2.1, Table 8

14.3.1.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used:

$$\text{Mass emitted (kg)} = 5.40\text{E-}02 \times \text{Refinery Feed (in m}^3\text{)}$$

Reference: [6], Activity 090203, Section 8, Table 2.

14.3.2. Incinerators

For all incinerator gas streams:

$$\text{Mass emitted (kg)} = 3.33\text{E-}02 \times M \times \text{NCV}$$

where:

M = mass of incinerator gas stream burnt (in tonnes)

NCV = net calorific value of the incinerator gas stream burnt (in MJ/kg)

This assumes emissions are equivalent to burning low-joule gas in an uncontrolled furnace – see **Section 14.1**.

Reference: [29].

For emissions from the combustion of the auxiliary gas fuel used to support incinerator combustion, use the algorithms in **Section 14.2**.

14.4. CATALYTIC CRACKING UNIT REGENERATORS

For CCU regenerators, both with and without CO boilers:

$$\text{Mass emitted (kg)} = 2.04\text{E-}01 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [7], Section 5.1, Table 5.1-1

15. SULPHUR HEXAFLUORIDE (SF₆)

Emissions of sulphur hexafluoride (SF₆) 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.

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

16. OXIDES OF SULPHUR (SO_x)

EPER and PRTR require estimates of the total oxides of sulphur (SO₂ and SO₃) reported as SO₂.

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators and flares
- Catalytic cracking unit regenerators
- Catalytic reforming units

16.1. COMBUSTION

For all fuel combustion, the following algorithm applies:

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

where:

M = mass of fuel burnt (in kg)

MF_S = mass fraction of sulphur in fuel

SF_{MW} = Molecular weight conversion from S to SO₂ = 64/32

This assumes all the sulphur in the fuel is converted to SO₂.

For refinery oil and gaseous fuels:

$$\text{Mass emitted (kg)} = 2.00E+00 \times M \times MF_S$$

Reference: [16], 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 algorithms 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

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:

$$\text{Mass emitted (kg)} = 7.70\text{E-}02 \times \text{Refinery Feed (in m}^3\text{)}$$

Reference: [6], Activity 090203, Section 8, Table 2.

16.2.2. Incinerators

16.2.2.1. All Incinerators

For all incinerator 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 algorithms in **Section 16.1**.

16.2.2.2. 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.

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

where:

ERC_{EFF} = recovery efficiency (in %)

PROD = sulphur production (in tonnes)

SF_{MW} = Molecular weight conversion from S₂ to SO₂ = 64.07 / 32.07

Reference: [30], Section 8.13, Table 8.13-1.

16.3. CATALYTIC CRACKING UNIT REGENERATORS

For CCU regenerators, both with and without CO boilers:

$$\text{Mass emitted (kg)} = 1.41\text{E+}00 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [7], Section 5.1, Table 5.1-1

16.4. CATALYTIC REFORMING UNITS

$$\text{Mass emitted (kg)} = 3.63\text{E-}03 \times \text{Volume of feed to unit (in m}^3\text{)}$$

Reference: [12], 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 incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

18.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 16**.

Table 16 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	4.27E-03	[14] Section 1.3, Table 1.3-11
	Natural Gas	3.43E-04	[10], [31] ¹
Gas Turbine	Distillate (gas oil)	Not detected ²	[15] Section 3.1, Table 3.1-5
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	3.43E-04	[10], [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Compound was not detected. The emission factor stated in reference [15] is based on one half of the detection limit. For the purposes of this report the emission factor is considered to be zero as source not proven (See **Section 5.2** of this report).

18.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

18.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 18.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 3.43\text{E-}07 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

18.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 1.39\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

18.4. FLUID COKERS

$$\text{Mass emitted (kg)} = 2.16\text{E-}03 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], 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 incinerators
- Catalytic cracking unit regenerators

19.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 17**.

Table 17 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1.20E-03	[14] Section 1.3, Table 1.3-11
	Natural Gas	7.12E-04	[10], [31] ¹
Gas Turbine	Distillate (gas oil) ²	2.17E-03	[15] Section 3.1, Table 3.1-5
	Natural Gas ³	2.52E-03	[10], [31] ¹
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	7.12E-04	[10], [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Factor derived from units without emission controls, operating at > 80% load. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-5).
3. Factor for gas turbine without duct burner. Reference [10] concludes factors for heaters & boilers fired by natural gas and refinery fuel gas are similar.

19.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

19.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 19.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 7.12\text{E-}07 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

19.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 6.25\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

20. CHROMIUM (Cr)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators

20.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1.48E-02	[10], [31] ¹
	Natural Gas	2.74E-03	[10], [31] ¹
Gas Turbine	Distillate (gas oil) ²	4.98E-03	[15] Section 3.1, Table 3.1-5
	Natural Gas ³	6.26E-03	[10], [31] ¹
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	2.74E-03	[10], [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Factor derived from units without emission controls operating at > 80% load. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-5).
3. Factor for gas turbine without duct burner.

20.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

20.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 20.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 2.74\text{E-}06 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

21. COPPER (Cu)

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

21.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times M \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1.19E-02	[10], [31] ¹
	Natural Gas	2.22E-03	[10], [31] ¹
Gas Turbine	Natural Gas ²	1.97E-02	[10], [31] ¹
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	2.22E-03	[10], [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Factor for gas turbine without duct burner

21.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

21.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 21.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 2.22\text{E-}06 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

21.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 1.39\text{E-}04 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

21.4. FLUID COKERS

$$\text{Mass emitted (kg)} = 1.50\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], 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 incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

22.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	Not Detected ¹	[10], [31] ²
	Natural Gas	8.60E-05	[10], [31] ²
Gas Turbine	Distillate (gas oil) ³	5.43E-04	[15] Section 3.1, Table 3.1-5
	Natural Gas ⁴	7.31E-03	[10], [31] ²
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	8.60E-05	[10], [31] ²

Notes:

1. Compound was not detected. Emission Factor stated in reference [10] 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 [10] is base document, but reference [31] provides the same emission factors to more significant figures.
3. Factor derived from units without emission controls operating at > 80% load. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-5).
4. Data for gas turbine without duct burner

22.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

22.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 22.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 8.60\text{E-}08 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

22.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 6.95\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

22.4. FLUID COKERS

$$\text{Mass emitted (kg)} = 3.00\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], 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 incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

23.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	1,03E+00	[10] [31] ¹
	Natural Gas	3.60E-03	[10] [31] ¹
Gas Turbine	Distillate (gas oil)	Not detected ²	[15] Section 3.1, Table 3.1-5
	Natural Gas ³	7.93E-02	[10] [31] ¹
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	3.60E-03	[10] [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Compound was not detected. The emission factor stated in reference [15] is based on one half of 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).
3. Factor for gas turbine without duct burner.

23.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

23.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 23.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 3.60\text{E-}06 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

23.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 6.12\text{E-}04 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

23.4. FLUID COKERS

$$\text{Mass emitted (kg)} = 5.70\text{E-}04 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], 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 incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

24.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	4.56E-03	[14] Section 1.3, Table 1.3-11
	Natural Gas	1.79E-03	[10], [31] ¹
Gas Turbine	Distillate (gas oil) ¹	6.34E-03	[15] Section 3.1, Table 3.1-5
	Natural Gas ²	1.36E-02	[10], [31] ¹
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	1.79E-03	[10], [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Factor derived from units without emission controls operating at > 80% load. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-5).
3. Factor for gas turbine without duct burner.

24.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

24.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 24.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 1.79\text{E-}06 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

24.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 3.20\text{E-}04 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

24.4. FLUID COKERS

$$\text{Mass emitted (kg)} = 4.50\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], 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 incinerators
- Catalytic cracking unit regenerators
- Fluid cokers

25.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 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	[14] Section 1.3, Table 1.3-10
	Refinery Fuel Oil	4.93E-02	[10], [31] ¹
	Natural Gas	2.55E-02 ²	[10]
Gas Turbine	Natural Gas ³	2.38E+00	[10], [31] ¹
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	2.55E-02 ²	[10]

Notes:

1. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
2. Factor represents median value as this more closely correlates with value provided in reference [14] (US EPA AP-42). Mean value from data set in Reference [10] is 48 times greater than value provided in AP-42 [14] and no qualifying explanation is given.
3. Factor for gas turbine without duct burner.

25.1.1. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

25.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 25.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 2.55\text{E-}05 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

25.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (kg)} = 1.18\text{E-}04 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

25.4. FLUID COKERS

$$\text{Mass emitted (kg)} = 4.50\text{E-}05 \times \text{Volume of fresh feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.3, Tables 10 and 11.

26. BENZENE (C₆H₆)

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

Combustion emissions are typically negligible compared to fugitive emissions.

Fugitive emissions are diffuse in a large facility like a refinery and hence 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. For completeness, algorithms are provided for the minor sources.

26.1. 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. Details of a methodology are given in reference [32].

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

$$\text{Mass emitted (kg)} = \text{SUMCALC}_{\text{NMVOC}} \times \text{MF}_{\text{BENZENE}}$$

where:

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

$\text{MF}_{\text{BENZENE}}$ = Mass fraction of benzene (from fence line monitoring survey).

26.2. NO SPECIATED FENCELINE NMVOC DATA AVAILABLE

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

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

where:

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

Reference: [23], Section 15.5.3, Table 15-7.

26.3. ESTIMATION BY SOURCE

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

- Combustion of fuels
- Destruction of gaseous streams in flares

- Catalytic cracking unit regenerators
- Fluid cokers
- Uncontrolled blowdown system

If some or all of these 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 26.1 or 26.2

26.3.1. 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 24**.

Table 24 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	[14] Section 1.3, Table 1.3-9
	Natural Gas	2.13E-03 ¹	[10]
Gas Turbine ³	Distillate (Gas Oil) ⁴	2.49E-02	[15] Section 3.1, Table 3.1-4
	Natural Gas	5.73E-03	[15] Section 3.1, Table 3.1-3
Gas Engine 4-stroke, Lean Burn	Natural Gas	6.21E-01	[10], [31] ²
Diesel Engine Large, Stationary	Distillate (Gas Oil)	3.22E-01	[10], [31] ²
Incinerator Support Fuel or Flare Pilot Fuel	Natural Gas	2.13E-03 ¹	[10]

Notes:

1. Factor represents the median value as this more closely correlates with the value provided in reference [14] (US EPA AP-42). The mean value from data set in reference [10] is 30 times greater than value provided in AP-42 [14] and no qualifying explanation is given.
2. Reference [10] is base document, but reference [31] provides the same emission factors to more significant figures.
3. Factor derived from units without emission controls operating at > 80% load.
4. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-4).

26.3.2. Destruction of Flare Streams

26.3.2.1. Flare Stream Details Known

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

$$\text{Mass emitted (kg)} = 5.00\text{E-}03 \times M \times \text{MF}_{\text{BENZ}}$$

where:

M = total mass of gas flared (in kg)

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: [13], Section 4.4

26.3.2.2. Flare Stream Details Unknown

If the mass and composition are not known, a conservative factor based on refinery feed can be used:

$$\text{Mass emitted (kg)} = 1.66\text{E-}06 \times \text{Refinery Feed (in m}^3\text{)}$$

Reference: Derived from [6], Activity 090203, Section 8, Table 2, and [16], Section 4.22, Table 9.

26.3.3. Catalytic Cracking Unit Regenerators

26.3.3.1. Full Burn Regeneration

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

26.3.3.2. Partial Burn with CO Boiler

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

Reference: [7], Table 5.1-1

26.3.3.3. Partial Burn without CO Boiler

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

$$\text{Mass emitted (in kg)} = 1.05\text{E-}03 \times \text{Mass of coke burnt (in tonnes)}$$

Reference: [11], 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 5.3** of this report.

26.3.4. Fluid Cokers

26.3.4.1. Emissions Controlled with CO or Fired Waste Heat Boiler

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

Reference: [7], Table 5.1-1

26.3.4.2. Non-Controlled Emissions

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

$$\text{Mass emitted (in kg)} = 1.75\text{E-}04 \times \text{Feed to unit (in m}^3\text{)}$$

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

Reference: [16], Section 4.2.1, Table 8 and Section 4.2.2, Table 9.

26.3.5. Uncontrolled Blowdown System

The gaseous emissions from refinery blowdown systems are normally recovered and/or flared. Where these controls are not operational and the emissions are emitted to atmosphere:

$$\text{Mass emitted (kg)} = 6.32\text{E-}03 \times \text{Refinery Feed (in m}^3\text{)}$$

This assumes that benzene makes up 0.38% of the VOCs in the blowdown gas.

Reference: [16], Section 4.2.1, Table 8 and Section 4.2.2, Table 9.

27. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

EPER requires the total emissions of the 6 'Borneff' PAHs to be reported These are:

- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Indeno(1,2,3-cd)pyrene
- Benzo(g,h,i)perylene
- Fluoranthene

Note that the PRTR requires the total emissions of only the first four PAHs listed above.

Estimation methods are provided for emissions from:

- Combustion of fuels
- Destruction of gaseous streams in incinerators
- Catalytic cracking unit regenerators

Speciated values are provided for the six individual PAHs in addition to the summations of the emission factors for the 'EPER 6' and 'PRTR 4' PAHs.

Emission factors for total PAH emissions are available for the combustion of distillate fuel in gas turbines (reference [15], Section 3.1, Table 3.1-15) and for flare gas (reference [16], Section 4.2.2, Table 9). These factors are not reproduced in this report as EPER and PRTR require the emissions to be reported of only a limited number of the total PAH compounds.

27.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times M \times \text{NCV}) / 1000$$

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 27.1.1 to 27.1.7**.

27.1.1. Refinery Fuel Oil Combustion In Boilers And Furnaces

Table 25 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
Benzo(g,h,i)perylene	0 ¹
Fluoranthene	2.376E-05
Total EPER 6	2.74E-05
Total PRTR 4	3.67E-06

Notes:

1. Compound was not detected. The emission factor stated in reference [10] represents the detection limit. The emission factor is thus considered to be zero as the source is not proven (See **Section 5.2** of this report).

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

Reference: [10], [31].

27.1.2. Natural Gas Combustion In Boilers And Furnaces

Table 26 PAH Emission Factors for Natural 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
Benzo(g,h,i)perylene	6.067E-07
Fluoranthene	4.161E-06
Total EPER 6	7.83E-06
Total PRTR 4	3.07E-06

Notes:

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: [10], [31].

27.1.3. Natural Gas Combustion In Gas Turbines

Table 27 PAH Emission Factors for Natural 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
Benzo(g,h,i)perylene	9.220E-07
Fluoranthene	5.541E-06
Total EPER 6	9.99E-06
Total PRTR 4	3.53E-06

Notes:

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

Reference: [10], [31].

27.1.4. Natural Gas Combustion In Gas Engines

Table 28 PAH Emission Factors for Distillate Oil 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
Benzo(g,h,i)perylene	4.682E-05
Fluoranthene	1.137E-04
Total EPER 6	6.20E-04
Total PRTR 4	4.60E-04

Notes:

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

Reference: [10], [31].

27.1.5. Distillate Oil Combustion In Diesel Engines

Table 29 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
Benzo(g,h,i)perylene	2.453E-04
Fluoranthene	1.774E-03
Total EPER 6	2.90E-03
Total PRTR 4	8.79E-04

Notes:

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

Reference: [10], [31].

27.1.6. Incinerator Support Fuel and Flare Pilot Fuel

Use values of EF_{NCV} provided in **Section 27.1.2**.

27.1.7. Other Fuels

For other gaseous fuels (e.g. refinery fuel gas, low joule gas) assume EF_{NCV} of natural gas.

27.2. DESTRUCTION OF GASEOUS STREAMS IN INCINERATORS

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 27.1.6**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = \text{EF}_{\text{INC}} \times M \times \text{NCV}$$

where:

EF_{INC} = emission factor from **Table 30**

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

Table 30 PAH Emission Factors for Incinerators

EF_{INC} FOR EPER 6	EF_{INC} FOR PRTR 4
7.83E-09	3.07E-09

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled small furnace.

27.3. CATALYTIC CRACKING UNIT REGENERATORS

Mass emitted (kg) = EF_{FCC} × Mass of coke burned (in tonnes)

where:

EF_{FCC} = emission factor from **Table 31**

Table 31 PAH Emission Factors for FCCU Regenerators

PAH	EF_{FCC}
Benzo(a)pyrene	2.966E-06
Benzo(b)fluoranthene	2.915E-06
Benzo(k)fluoranthene	2.892E-06
Indeno(1,2,3-cd)pyrene	2.883E-06
Benzo(g,h,i)perylene	2.886E-06
Fluoranthene	5.471E-06
Total EPER 6	2.00E-05
Total PRTR 4	1.17E-05

Reference: [11], 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 5.3** of this report.

28. CHLORINE AND INORGANIC CHLORINE COMPOUNDS

EPER and PRTR require estimates of the emissions of chlorine and inorganic chlorine compounds reported as HCl.

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

28.1. 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 in excess of the EPER 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 reference [12], 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.

29. PARTICULATE MATTER WITH DIAMETER <10 µm (PM₁₀)

Estimation methods are provided for emissions due to:

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

29.1. COMBUSTION OF FUELS

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 32**.

Table 32 PM₁₀ 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	[14] Section 1.3, Table 1.3-7
	Refinery Fuel Oil	Alg. A - see below	[14] Section 1.3, Table 1.3-7
	LPG	1.98E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	3.56E+00	[14] Section 1.4, Table 1.4-2
Boilers and Furnaces 10 MW to 100 MW	Distillate (gas oil)	3.23E+00	[14] Section 1.3, Table 1.3-6
	Refinery Fuel Oil	Alg. B - see below	[14] Section 1.3, Table 1.3-5
	LPG	2.97E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	3.56E+00	[14] Section 1.4, Table 1.4-2
Boilers and Furnaces > 100 MW	Refinery Fuel Oil	Alg. C - see below	[14] Section 1.3, Table 1.3-4
	Natural Gas	3.56E+00	[14] Section 1.4, Table 1.4-2

SOURCE	FUEL	EF _{NCV} g/GJ	REF
Gas Turbine ¹	Distillate (gas oil) ²	5.20E+00	[15] Section 3.1, Table 3.1-2a
	Natural Gas	3.15E+00	[15] Section 3.1, Table 3.1-2a
Gas Engine 4-stroke, Lean Burn	Natural Gas	4.77E+00	[15] Section 3.2, Table 3.2-2
Diesel Engine Large, Stationary	Diesel Fuel	2.59E+01	[15] Section 3.4, Table 3.4-2
Incinerator Support Fuel or Flare Pilot Fuel	LPG	1.98E+00	[14] Section 1.5, Table 1.5-1
	Natural Gas	3.56E+00	[14] Section 1.4 Table 1.4-2

Notes:

- Factor derived from units without emission controls operating at > 80% load.
- NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [14], Section 3.1, Table 3.1-2a).

Algorithms for fuel oil

A. $EF_{NCV} = (17.47 \times \text{MASS\%S}) + 5.772$

B. $EF_{NCV} = (24.229 \times \text{MASS\%S}) + 8.004$

C. $EF_{NCV} = (19.937 \times \text{MASS\%S}) + 6.586$

where:

MASS%S = Percentage mass of sulphur in fuel oil (%)

(i.e. if the fuel contains 1.2% sulphur, then MASS%S = 1.2)

29.1.1. Other Fuels

For other gaseous fuels (e.g. low joule gas) assume EF_{NCV} of natural gas.

29.2. DESTRUCTION OF GASEOUS STREAMS

29.2.1. Flares

For a non-smoking flare, the emissions of PM₁₀ can be assumed to be negligible.

Reference: [16], Section 4.2.1, Table 8.

29.2.2. Incinerators

The following algorithm is for emissions from the combustion of the incinerator gas stream. For emissions from the combustion of the auxiliary fuel used to support incineration, use the algorithms in **Section 29.1**.

As incinerator streams are of very variable composition, it is necessary to know the stream make up to determine the net calorific value (and density if the stream volume combusted is known instead of the mass).

$$\text{Mass emitted (kg)} = 3.56\text{E-}03 \times M \times \text{NCV}$$

where:

M = mass of gas stream incinerated (in tonnes)

NCV = net calorific value of the gas incinerated (in MJ/kg)

This algorithm assumes the EF_{NCV} of the gas stream is equal to that for natural gas in an uncontrolled furnace.

29.3. CATALYTIC CRACKING UNIT REGENERATORS

$$\text{Mass emitted (in kg)} = 5.49\text{E-}01 \times \text{Feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.1, Table 8.

This algorithm is for a unit with a primary cyclone installed – see **Section 6.2**.

29.4. FLUID COKERS

$$\text{Mass emitted (in kg)} = 7.65\text{E-}01 \times \text{Feed to unit (in m}^3\text{)}$$

Reference: [16], Section 4.2.1, Table 8

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APPENDIX 1 EPER AND PRTR POLLUTANTS

A1.1 EPER POLLUTANT REPORTING LIST

Table A1.1 lists the air pollutants that must be reported under EPER requirements if annual emissions exceed the threshold values. It also shows the pollutants emitted by refineries which may be “likely” to exceed the thresholds as shown in the EU Guidance Document [3] and those pollutants which have been calculated by at least one refinery to exceed the reporting threshold.

Table A1.1 List of EPER Air Pollutants

POLLUTANT	REPORTING THRESHOLD kg/year	“LIKELY” POLLUTANT FROM OIL REFINERY ACTIVITIES Ref [3], Table 4	“LIKELY” POLLUTANT FROM COMBUSTION >50 MW Ref [3], Table 4	POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED EPER THRESHOLDS
“ENVIRONMENTAL THEMES”				
CH ₄	100,000	-	X	X
CO	500,000	X	X	X
CO ₂	100,000,000	X	X	X
HFCs	100	-	-	X
N ₂ O	10,000	-	X	X
NH ₃	10,000	-	-	X
NMVOCS	100,000	X	-	X
NO _x	100,000	X	X	X
PFCs	100	-	-	-
SF ₆	50	-	-	X
SO _x	150,000	X	X	X

POLLUTANT	REPORTING THRESHOLD kg/year	“LIKELY” POLLUTANT FROM OIL REFINERY ACTIVITIES Ref [3], Table 4	“LIKELY” POLLUTANT FROM COMBUSTION >50MW Ref [3], Table 4	POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED EPER THRESHOLDS
METALS AND COMPOUNDS				
As + compounds	20	X	X	X
Cd + compounds	10	X	X	X
Cr + compounds	100	X	X	X
Cu + compounds	100	X	-	X
Hg + compounds	10	X	-	X
Ni + compounds	50	X	X	X
Pb + compounds	200	X	X	X
Zn + compounds	200	X	-	X
CHLORINATED ORGANIC SUBSTANCES				
PCDD + PCDF (dioxins and furans) (as TEQ)	0.001	-	X	-
Eleven other chlorinated organic substances	Note 1	-	-	-
OTHER ORGANIC COMPOUNDS				
Benzene	1000	X	-	X
PAHs (Borneff 6)	50	X	-	X

POLLUTANT	REPORTING THRESHOLD Kg/year	“LIKELY” POLLUTANT FROM OIL REFINERY ACTIVITIES Ref [3], Table 4	“LIKELY” POLLUTANT FROM COMBUSTION >50MW Ref [3], Table 4	POLLUTANTS ESTIMATED BY OIL INDUSTRY THAT MAY EXCEED EPER THRESHOLDS
OTHER COMPOUNDS				
Chlorine + inorganic compounds (as HCl)	10,000	X	X	X
Fluorine + inorganic compounds	5000	X	X	-
HCN	200	-	-	-
PM ₁₀	50,000	X	X	X
<i>TOTALS (of 37 on EPER List)</i>		18	14	22

Notes

- List of other chlorinated organic compounds with their reporting thresholds:

Dichlorethane-1,2 (DCE)	1000 kg/year
Dichloromethane (DCM)	1000 kg/year
Hexachlorobenzene (HCB)	10 kg/year
Hexachlorocyclohexane (HCH)	10 kg/year
Pentachlorophenol (PCP)	10 kg/year
Tetrachloroethylene (PER)	2000 kg/year
Tetrachloromethane (TCM)	100 kg/year
Trichlorobenzenes (TCB)	10 kg/year
Trichloroethane-1,1,1 (TCE)	100 kg/year
Trichloroethylene (TRI)	2000 kg/year
Trichloromethane	500 kg/year

A1.2 PRTR POLLUTANT REPORTING LIST

Table A1.2 lists the additional air pollutants that must be reported under PRTR requirements if annual emissions exceed the threshold values

Table A1.2 List Of Air Pollutants On PRTR List Which Are Additional To EPER

POLLUTANT	REPORTING THRESHOLD kg/year
HCFCs	1
CFCs	1
Halons	1
Aldrin	1
Chlordane	1
Chlordecone	1
DDT	1
Dieldrin	1
Endrin	1
Heptachlor	1
Lindane	1
Mirex	1
Pentachlorobenzene	1
PCBs	0.1
1,1,2,2-tetrachloroethane	50
Toxaphene	1
Vinyl chloride	1000
Anthracene	50
Ethylene oxide	1000
Naphthalene	100
Di-(2-ethyl hexyl) phthalate	10
Asbestos	1

Of the additional pollutants in **Table A1.2**, only HCFCs are considered to have the potential to exceed the reporting threshold due to maintenance of refrigeration equipment. The other two halocarbons (CFCs and halons) on the list have been banned under EU Regulations [33] and would not, therefore, be used to top-up existing equipment.

The possible magnitude of emissions of two air pollutants on the PRTR list that are emitted by refineries - anthracene and naphthalene - are reviewed in **Appendix 2**. It is demonstrated that for a very large refinery neither pollutant exceeds the reporting threshold levels.

There are differences between PRTR and EPER concerning the reporting requirements of pollutants that are on both lists:

1. Dioxins and furans - the reporting threshold is an order of magnitude lower at 0.0001 kg/year under the PRTR Regulations.
2. PAHs - the PRTR regulations only specify four of the 'Borneff-6' PAHs - benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene.

APPENDIX 2 POLLUTANTS NOT EXCEEDING EPER AND PRTR THRESHOLDS

A2.1 ANTHRACENE

Estimation methods are provided for emissions due to:

- Combustion of fuels
- Fluidised catalytic cracking units

A2.1.1 Combustion Of Fuels

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 A2.1**.

Reference: [10].

Table A2.1 Anthracene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Furnaces and Boilers	Fuel Oil	9.37E-07	[10] [31] ¹
	Gas	2.26E-06	[10] [31] ¹
Gas Turbine ²	Gas	1.64E-05	[10] [31] ¹
Gas Engine 4-Stroke, Lean-Burn	Gas	1.17E-04	[10] [31] ¹
Diesel Engine Large, Stationary ³	Distillate (Gas Oil)	5.43E-04	[10] [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides emission factors to more significant figures.
2. Factor for gas turbine without duct burner.
3. Factor for stack oxygen concentration <13%

A2.1.2 Catalytic Cracking Unit Regenerator

$$\text{Mass emitted (kg)} = 4.54\text{E-}06 \times \text{Mass of coke burned (in tonnes)}$$

Reference: [11], 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.

A2.1.3 Emissions From A Very Large Refinery

To establish if anthracene could be emitted in excess of the PRTR reporting threshold, emissions have been calculated for a very large refinery. A survey by CONCAWE identified that the most fuel consumed at a European refinery was $8.4\text{E}+07$ GJ/year, of which $3.6\text{E}+07$ GJ was due to fuel oil use. The same refinery has a FCCU with a capacity of $2.9\text{E}+06$ m³/year, with a resultant coke burn of about 140,000 t/year.

- Fuel oil combusted = $3.6\text{E}+07$ GJ/year
- Fuel gas combusted = $4.8\text{E}+07$ GJ/year
- FCCU coke combusted = $1.4\text{E}+05$ tonnes/year

The emissions from this very large refinery would be:

$$\begin{aligned} &\text{Emissions from oil and gas combustion} \\ &= [(9.37\text{E}-07 \times 3.6\text{E}+07) + (2.26\text{E}-06 \times 4.8\text{E}+07)] \times 1.0\text{E}-03 = 1.42\text{E}-01 \text{ kg} \\ &\text{Emissions from coke burn} = 4.54\text{E}-06 \times 1.4\text{E}+05 = 6.36\text{E}-01 \text{ kg} \end{aligned}$$

Total emissions = 0.78 kg/year

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

A2.2 DIOXINS AND FURANS (PCDD AND PCDF)

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

- Combustion of fuel oil
- Catalytic reforming units

The emission factors for the 17 isomers of PCDD and PCDF must be multiplied by the Toxic Equivalence Factor (TEF) to give the calculated emissions in kg I-TEQ (Toxic Equivalent to the most toxic isomer 2,3,7,8-CDD).

A2.2.1 Combustion Of Fuel Oil

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 A2.2**

Table A2.2 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

ISOMER	I-TEF	Emission Factor lb/MMBtu (HHV)	Emission Factor g I-TEQ/GJ (NCV)
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 [10] 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: [10].

A2.2.2 Catalytic Reforming Unit Regenerator

There are very few data available for the emissions from these units. The US EPA [34] provides emission factors derived from tests on two units with different modes of catalyst regeneration – continuous and semi-regenerative.

Continuous Regeneration Mode

Mass emitted (kg I-TEQ) = 1.91E-11 × Volume of feed to unit (in m³)

Semi-Regenerative Mode

Mass emitted (kg I-TEQ) = 6.35E-15 × Volume of feed to unit (in m³)

Reference: [34], Section 5.4.

A2.2.3 Emissions From A Very Large Refinery

To establish if dioxins and furans could be emitted in excess of the EPER or PRTR reporting thresholds, emissions have been estimated for the very large refinery described in A2.1.3. The same refinery has a continuous regeneration type CRU with a capacity of 2.4E+06 m³/year.

- Fuel oil combusted = 3.6E+07 GJ/year
- Continuous regeneration type CRU feed = 2.4E+06 m³/year

The emissions from this very large refinery would be:

Emissions from combustion = 1.24E-12 × 3.6E+07 = 4.46E-05 I-TEQ kg/year
 Emissions from CRU = 1.91E-11 × 2.4E+06 = 4.58E-05 I-TEQ kg/year

Total emissions = 9.04E-05 I-TEQ kg/year.

This is less than the reporting threshold of 0.001 I-TEQ kg/year for EPER and close to but less than the threshold of 0.0001 I-TEQ kg/year for PRTR.

A review of other refineries in Europe with continuous regeneration type CRUs established that the refinery described above had the greatest emissions of dioxins and furans from the combined sources of fuel oil combustion and CRU regeneration.

There is the potential, however, that dioxins and furans could be emitted from other minor sources at some refineries e.g. sludge incineration, for which emission factors are not provided in this report.

A2.3 NAPHTHALENE

Estimation methods are provided for emissions due to:

- Combustion of fuels
- Fluidised catalytic cracking units

A2.3.1 Combustion Of Fuels

$$\text{Mass emitted (kg)} = (\text{EF}_{\text{NCV}} \times \text{M} \times \text{NCV}) / 1000$$

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 A2.3**.

Reference: [10].

Table A2.3 Naphthalene Emission Factors for Combustion Sources

SOURCE	FUEL	EF_{NCV} g/GJ	REF
Furnaces and Boilers	Fuel Oil	1.83E-04	[10] [31] ¹
	Gas	1.86E-04	[10] [31] ¹
Gas Turbine	Distillate (Gas Oil) ²	1.58E-02	[15], Section 3.1, Table 3.1-4
	Gas ³	3.48E-04	[10] [31] ¹
Gas Engine 4-Stroke, Lean-Burn	Gas	5.54E-02	[10] [31] ¹
Diesel Engine Large, Stationary ⁴	Distillate (Gas Oil)	5.75E-02	[10] [31] ¹

Notes:

1. Reference [10] is base document, but reference [31] provides emission factors to more significant figures.
2. Factor derived from units without emission controls operating at > 80% load. NCV calculated from HHV of 139 MBtu/10³ US gal (Reference [15], Section 3.1, Table 3.1-4).
3. Factor for gas turbine without duct burner.
4. Factor for stack oxygen concentration <13%

A2.3.2 Catalytic Cracking Unit Regenerator

$$\text{Mass emitted (kg)} = 5.64\text{E-}05 \times \text{Mass of coke burned (in tonnes)}$$

Reference: [11], 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.

A2.3.3 Emissions From A Very Large Refinery

To establish if naphthalene could be emitted in excess of the PRTR reporting threshold, emissions have been estimated for the very large refinery described in A2.1.3.

- 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 very large refinery would be:

$$\begin{aligned} &\text{Emissions from combustion} \\ &= [(1.83\text{E-}04 \times 3.6\text{E+}07) + (1.86\text{E-}04 \times 4.8\text{E+}07)] \times 1.0\text{E-}03 = 1.55\text{E+}01 \text{ kg} \\ &\text{Emissions from FCCU coke burn} = 5.64\text{E-}05 \times 1.4\text{E+}05 = 7.90\text{E+}00 \text{ kg} \end{aligned}$$

Total emissions = 16.3 kg/year

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

APPENDIX 3 VOC EMISSIONS FROM SERVICE STATIONS

A3.1 OVERVIEW

VOC emissions from service stations occur due to both gasoline and distillate (diesel) fuel handling. Due to the low volatility of distillate fuels compared to gasolines, the emissions from these fuels are insignificant compared to those from gasolines. As there is no methane in gasoline, CH₄ emissions are zero.

The algorithms provided are for the following sources:

- Storage tanks
- Automobile refuelling

Emissions can be controlled at service stations 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 [8].

Automobile Refuelling: When an automobile is being refuelled, the vapours normally vented to atmosphere from the fuel tank can be fed back to either a carbon canister on-board the car or to the service station storage tank from which the gasoline was dispensed. In Europe, the latter technique has been mandated in a number of countries and is called “Stage 2” vapour balancing.

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

A3.2 EMISSIONS

Mass emitted (kg) = EF × VOL_{DISP} × TVP

where:

EF = Emission Factor from **Table A3.1** depending on source and activity.

VOL_{DISP} = Volume of gasoline dispensed (in m³).

TVP = True Vapour Pressure of gasoline at storage temperature (in kPa).

Reference: [8], Section 4.

Gasoline TVP can be calculated from:

$$TVP = RVP \times (10E(((7.047E-06 \times RVP) + 1.32E-02) \times TEMP + ((2.311E-04 \times RVP) - 5.236E-01)))$$

where:

RVP = Reid Vapour Pressure (in kPa)

TEMP = Gasoline storage temperature (in degrees Centigrade)

Reference: [8], Appendix 1.

Table A3.1 VOC Emission Factors for Service Stations

SOURCE / ACTIVITY		EMISSION FACTOR EF
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	3.70E-03
	Refuelling with on-board carbon canisters	1.80E-03
	Drips and minor spillage	2.20E-03

APPENDIX 4 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 [13], was taken.

$$\text{NCV} = \text{HHV} \times \text{Correction Factor for heat of vaporisation of water in the fuel (f}_{\text{H}_2\text{O}})$$

For Liquid Fuels, Correction Factor (f_{H₂O}) = 0.95

For Gaseous Fuels, Correction Factor (f_{H₂O}) = 0.9

Reference [13], Section 3.6.3, Table 3-5.

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

$$\text{EF g/GJ}_{(\text{NCV})} = (\text{EF lb/MBtu}_{(\text{HHV})} / f_{\text{H}_2\text{O}}) \times (\text{g / lb}) \times (\text{MBtu / GJ})$$

To convert Emission Factor from lb/10³ gal to g/GJ_(NCV)

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

To convert Emission Factor from lb/10⁶ scf to g/GJ_(NCV)

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

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	[35]
Refinery Fuel Oil	150 MBtu / 10 ³ gal	[35]
LPG	3.95 MBtu / bbl	[13] Section 3.6.3, Table 3-5
Natural Gas	1020 MBtu / 10 ⁶ scf	[14] Section 1.4-4