

SNAP CODES: **040101**
040102

SOURCE ACTIVITY TITLE: **PROCESSES IN PETROLEUM INDUSTRIES**
Petroleum Products Processing
Fluid Catalytic Cracking

NOSE CODE: **105.08.01**
105.08.02

NFR CODE: **1 B 2 a iv**

1 ACTIVITIES INCLUDED

A basic refinery converts crude petroleum into a variety of sub-products. Principal products of a petroleum refinery include:

Table 1.1: Refinery Principal Products

Product Type	Principal Products
Liquid Fuels	Motor Gasoline
	Aviation Gasoline
	Aviation Turbine Fuel
	Illuminating Kerosene
	High-Speed Diesel
	Distillate Heating Fuel
	Medium-Speed Diesel
	Residual Oil
By-Product Fuels and Feedstocks	Naphtha
	Lubricants
	Asphalt
	Liquefied Petroleum Gases
	Coke
	Sulphur (Product of Auxiliary Facility)
	White Oils
Primary Petrochemicals	Ethylene
	Propylene
	Butadiene
	Benzene
	Toluene
	Xylene

The production of the latter group, primary petrochemicals, is, however, not included in this chapter, even if these chemicals are produced at a petroleum refinery. Please refer to the relevant chapters for sub-sector 040500 (chapters B451-B4522).

The petroleum refining industry employs a wide variety of processes. The types of processes operating at any one facility depend on a variety of economic and logistic considerations such as the quality of the crude oil feedstock, the accessibility and cost of crude (and alternative feedstocks), the availability and cost of equipment and utilities, and refined product demand. The four categories of general refinery processes are listed in Table 1.2.

Table 1.2: General Refinery Processes and Products

General Process	Products
Separation Processes	Atmospheric Distillation
	Vacuum Distillation
	Light Ends Recovery (Gas Processing)
Petroleum Conversion Processes	Cracking (Thermal and Catalytic)
	Coking
	Viscosity Breaking
	Catalytic Reforming
	Isomerization
	Alkylation
	Polymerization
Petroleum Treating Processes	Hydrosulfurization
	Hydrotreating
	Chemical Sweetening
	Acid Gas Removal
	Deasphalting
Blending	Motor Gasoline
	Light Fuel Oil
	Heavy Fuel Oil

The major direct process emission sources of NMVOCs are vacuum distillation, catalytic cracking, coking, chemical sweetening and asphalt blowing (U.S.EPA 1985a). Process-unit turnaround (periodical shut-down of units) has also been reported as contributing to VOC emissions (CEC 1991).

Fugitive emissions from equipment leaks are also a significant source of NMVOC emissions from process operations at a refinery. Emissions from storage and handling are also classified as fugitive emissions. To avoid confusion, fugitive emissions from equipment leaks will be referred to as fugitive process emissions in this chapter.

Table 1.3 summarises significant sources of common pollutants from process and fugitive process emissions sources at refineries.

Table 1.3: Significant Process Emissions Sources at Petroleum Refineries (U.S. EPA 1985)

Process	Particulate	NO _x	SO _x	CO	NM VOC
Vacuum Distillation	x	x	x	x	X
Catalytic Cracking	X	x	x	X	X
Thermal Cracking	x	x		x	X
Sweetening					X
Blowdown Systems	x	x	x	x	X

X - Possibly significant sources (depending upon the degree of contract)

x - Minor sources

This section is a summary of the main products possibly produced at a refinery and the major processes that could be present, with an indication of the processes that are potentially significant sources of emissions to the air. All of these processes are currently under SNAP code 040101, with the exception of FCCs with CO boiler. However it is difficult to use this code separately from other processes, particularly for simpler emission estimation methods, which tend to encompass a wide variety of sources. It is therefore proposed that FCCs with CO boiler also be inventoried under 040101.

It is important to note that fugitive process emissions are somewhat difficult to characterise by their area (process vs. storage/handling vs. waste treatment), as they are estimated based on equipment counts and are not usually classified as to type of use or area of the refinery. Therefore fugitive process emissions for the entire refinery are inventoried under SNAP code 040101.

2 CONTRIBUTION TO TOTAL EMISSIONS

Table 2.1 summarises emissions from petroleum refining processes in the CORINAIR90 inventory. In a Canadian study (CPPI and Environment Canada 1991), the process/fugitive process sources contributed 51.5% (process 4.7% (Only FCCU estimated) and fugitive process 46.8%) of total VOC emissions for 29 refineries surveyed. Blending losses were not estimated separately. The process/fugitive process sources would represent approximately 2.6% of total anthropogenic emissions.

Table 2.1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO ₂	NO _x	NM VOC	CH ₄	CO	CO ₂	N ₂ O	NH ₃
Petroleum Products Process.	040101	0.5	0.1	0.7	0	0	0.2	0.1	-
Fluid Catalytic Cracking	040102	0.4	0.1	0	-	0	0.1	-	-

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

3 GENERAL

3.1 Description

3.1.1 Direct Process Sources

There are four main categories of processes in a petroleum refinery:

Separation Processes

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

Conversion Processes

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

Treating Processes

Petroleum treating processes stabilise and upgrade petroleum products. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstocks prior to refining. Undesirable elements such as sulphur, nitrogen and oxygen are removed from product intermediates by hydrodesulphurization, hydrotreating, chemical sweetening and acid gas removal. Deasphalting is used to separate asphalt from other products. Asphalt may then be polymerised and stabilised by blowing (see SNAP code 060310).

Blending

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

3.1.2 Fugitive Process Sources

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

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

3.2 Definitions

3.3 Techniques

See section 3.1 (above).

3.4 Emissions/Controls

3.4.1 Direct Process Emissions

Vacuum distillation, catalytic cracking, thermal cracking, sweetening, blowdown systems, sulphur recovery, asphalt blowing and flaring processes have been identified as being potentially significant sources of SO₂ and NMVOC from those sources included under SNAP code 040101, with a relatively smaller contribution of particulate, NO_x and CO. (U.S.EPA 1985a).

Vacuum Distillation

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

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

Methods of controlling these emissions include venting into blowdown systems or fuel gas systems, and incineration in furnaces (SNAP code 090201) or waste heat boilers (SNAP code 030100). These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions.

Note that the emissions from blowdown and vapour recovery systems have been included under this SNAP code rather than under SNAP code 090100 (see below).

Catalytic Cracking

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

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

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

Aside from combustion products from heaters, emissions from catalytic cracking processes are from the catalyst regenerator. These emissions include NMVOC, NO_x, SO_x, CO, particulates, ammonia, aldehydes, and cyanides.

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

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

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

Thermal Cracking

Thermal cracking units break heavy oil molecules by exposing them to higher temperatures. In viscosity breaking (visbreaking), topped crude or vacuum residuals are heated and thermally topped in a furnace and then put into a fractionator. In coking, vacuum residuals and thermal tars are cracked at high temperature and low pressure. Historically, delayed coking is the most common process used, although fluid coking is becoming the more preferred process.

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

Sweetening

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

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

Asphalt Blowing

Please refer to SNAP code 060310 for inventory methods for asphalt blowing.

Sulphur Recovery

Please refer to SNAP code 040103 for inventory methods for sulphur recovery plants.

Flaring

Please refer to SNAP code 090203 for inventory methods for flaring in a refinery.

Blowdown Systems

Many of the refining process units subject to hydrocarbon discharges are manifolded into a collection unit (i.e., blowdown system), comprising a series of drums and condensers, whereby liquids are separated for recycling and vapours are recycled or flared with steam injection. Uncontrolled blowdown emissions consist primarily of hydrocarbons, while vapour recovery and flaring systems (see SNAP code 090203) release lesser NMVOC and greater combustion products including SO₂, NO_x and CO.

3.4.2 Fugitive Process Emissions

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

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

Of these sources of NMVOC, valves are the major source type. This is due to their number and relatively high leak rate.

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

Applicable control technologies are summarised in Table 3.1.

Table 3.1: Control Technologies for Fugitive Sources (U.S. EPA 1985a)

Fugitive Source	Control Technology
Pipeline Valves	monitoring and maintenance programs
Open-Ended Valves	Instillation of cap or plug on open end of valve /line
Flanges	monitoring and maintenance
Pump Seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Compressor Seals	mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlling degassing vents
Process Drains	Traps and covers
Pressure/Relief Valves	Rupture disks upstream of relief and/or venting to a flare

4 SIMPLER METHODOLOGY

The simplest inventory methodology is to combine the crude oil throughput of each refinery with either a single emission factor, or two emission factors (one for process and one for fugitive process emissions) for each refinery. The first approach would be the easiest to use if very limited information is available. However, the second approach would allow the user to in some way reflect the type of processes and related controls at the refinery as well as accounting for the sophistication of the fugitive emissions inspection and maintenance programs typical of the region and/or that particular refinery.

It is strongly recommended that the detailed methodology be used for petroleum refineries.

5 DETAILED METHODOLOGY

The detailed methodology requires each refinery to estimate its process emissions for each process, using detailed throughput information and emission factors. Site specific emission factors or data would be preferable, wherever possible. Remote sensing, using Fourier transform techniques, is making it possible to measure total refinery emissions, although it may be difficult to identify the individual source strengths.

The state-of-the-art technology for estimating fugitive process emissions is to use an emission testing program to classify equipment into groupings and then estimate emissions using emission factors or algorithms (see section 16, Verification Procedures). However, this is a very expensive and time-consuming proposition and is considered beyond the resources of most inventory personnel. The methodology proposed below is a compromise between a testing program vs. estimates of the number of each type of equipment that might be in a refinery based on either its throughput or production data.

Fugitive process emissions, which are considered to be the major source of NMVOCs at a petroleum refinery, are inventoried using emission factors for each type of equipment and stream, based on a count of the number of sources, a characterisation of the NMVOC content of the stream in question and whether the refinery conducts an inspection and maintenance program.

The U.S. EPA has published a detailed protocol for equipment leak emissions estimates (U.S.EPA 1993). In the average emission factor method, the following unit-specific data is required:

1. the number of each type of component in a unit (valve, connector etc.);
2. the service each component is in (gas, light liquid, or heavy liquid);
3. the NMVOC concentration in the stream (weight fraction) and;
4. the number of hours per year the component was in service.

The equipment is then grouped into streams, where all of the equipment within the stream has approximately the same NMVOC weight percent. Annual emissions are then calculated for each stream using equation 1 as follows:

$$\text{NMVOCs} = \text{AEF} * \text{WFnmvoc} * \text{N} \quad (1)$$

where:

NMVOCs	= NMVOC emission rate from all equipment in the stream of a given equipment type (kg/hr)
AEF	= applicable average emission factor for the equipment type (kg/hr/source)
WFnmvoc	= average weight fraction of NMVOC in the stream and
N	= the number of pieces of equipment of the applicable equipment type in the stream.

If there are several streams at the refinery, as is usually the case, the total NMVOC emission rate for an equipment type is the sum of emissions from each of the streams. The total emission rates for all of the equipment types are summed to generate the process unit total NMVOC emission rate from fugitive process sources.

6 RELEVANT ACTIVITY STATISTICS

For the simpler methodology, the crude oil throughput of each refinery is required.

For the detailed methodology, specific data will be required on the throughput for each process area. For fugitive process emissions estimates, each emission source must be counted by type and process stream, and the NMVOC content for each stream must then be characterised. The number of annual hours of operation for each stream is also required. Finally it must be determined if an inspection and maintenance program is conducted at the refinery.

7 POINT SOURCE CRITERIA

All refineries are to be inventoried as point sources.

8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

8.1 Simpler Methodology

Total hydrocarbon emission factors based on an inventory of Canadian refineries in 1988 (CPPI and Environment Canada 1991) were 0.05 kg/m³ feedstock for process emissions and 0.53 kg/m³ for fugitive process emissions. Of the latter, valves accounted for 0.35 kg/m³ feedstock. Data was not available for NMVOC only. This inventory was based on a survey of individual refineries, in which some reported their own emission estimates and some reported base quantity data for which emissions were estimated using a variety of techniques.

The use of CONCAWE derived VOC emission factors, based upon a hypothetical 5 Mt/yr refinery, as follows was recommended as a default method for the Corinair 1990 project (CEC 1991). The emission factor for fugitive process emissions is 0.25 kg/t crude (0.21 kg/m³ crude assuming specific gravity of 0.85 (BP 86)).

Sixty percent of these emissions are reported to be from valves. CONCAWE also indicates that average fugitive emissions in the same refinery with a maintenance and monitoring programme is 0.01% by weight (.085 kg/m³) of refinery throughput (CONCAWE Report 87/52 1987). The CORINAIR90 default emission handbook also reports a U.S.EPA factor of 0.18 kg/Mg crude (U.S.EPA 1985b) for process unit turnaround, and estimates that Western European refineries would emit half of this for turnaround, or 0.09 kg/Mg.

It is apparent that detailed emission inventory data is required for several refineries in differing regions in order to develop meaningful emission factors. Major factors affecting regional differences include crude characteristics, product demand (and hence refinery processes) and regulatory requirements.

Emission factors for non-combustion process sources of other contaminants were not identified, other than as provided in Table 4 of SNAP sector 040100.

8.2 Detailed Methodology

The more detailed methodology involves the use of process-specific emission factors based on the throughput of the unit and fugitive process emission factors based on equipment counts. It is important to note that the factors presented below must be used with caution, as they do not account for regional differences in crude, product demand and regulatory requirements. Wherever possible, site-specific emission estimates based on monitoring should be considered.

8.2.1 Process Emission Factors

Table 8.1 lists emission factors for refinery processes based on tests conducted in the 1970's, noting that overall, less than 1 % of the total hydrocarbons emissions are methane (U.S.EPA 1985a). Note that new emission factors are being developed by the U.S. EPA, with some speciation. These are due for release soon (Zarate 1992).

Table 8.1: Emission Factors for Petroleum Refineries (U.S. EPA 1985a and 1995)

Process	Particulate	Sox (as SO ₂)	CO	THC ^a	NOx (as NO ₂)	Aldehydes	NH ₃	Quality
Fluid catalytic cracking units								
Uncontrolled kg/10 ³ liters fresh feed	0.695 (0.267-0.976) ^b	1.143 (0.286-1.505)	39.2	0.630	0.204 (0.107-0.416)	0.054	0.155	B
ESP and CO boiler kg/10 ³ liters fresh feed	0.128 (0.020-0.428)	1.413 (0.286-1.505)	Neg ^c	Neg	0.204 ^d (0.107-0.416)	Neg	Neg	B
Moving-bed catalytic cracking units								
kg/10 ³ liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
Fluid coking units								
Uncontrolled	1.5	NA ^e	NA	NA	NA	NA	NA	C

Process	Particulate	Sox (as SO ₂)	CO	THC ^a	NO _x (as NO ₂)	Aldehydes	NH ₃	Quality
kg/10 ³ liters fresh feed								
ESP and CO boiler kg/10 ³ liters fresh feed	0.0196	NA	Neg	Neg	NA	Neg	Neg	C
Blowdown systems								
Uncontrolled kg/10 ³ liters refinery feed	Neg	Neg	Neg	1.662	Neg	Neg	Neg	C
Vacuum distillation column condensers								
Uncontrolled kg/10 ³ liters refinery feed	Neg	Neg	Neg	0.052	Neg	Neg	Neg	C
Uncontrolled kg/10 ³ liters vacuum feed	Neg	Neg	Neg	0.144	Neg	Neg	Neg	C
Controlled	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

^a Overall, less than 1 percent by weight of the total hydrocarbon emissions are methane

^b Numbers in parenthesis indicate range of values observed

^c Negligible emission

^d May be higher due to the combustion of ammonia

^e NA, Not Available.

The VOC emission factors listed in Table 8.2 were used to estimate emissions from processes in the United Kingdom (Passant n.d.).

Table 8.2: United Kingdom VOC Emission Factors (Passant n.d.)

Process		Emission Factor	Quality
Catalytic Cracker	Uncontrolled	628 g/m ³ feed	D
	Controlled	negligible	D
Fluid Coking	Uncontrolled	384 g/m ³ feed	D
	Controlled	Negligible	D
Vacuum Distillation	Uncontrolled	51.6 g/m ³ feed	D
	Controlled	negligible	D
Asphalt Blowing	Uncontrolled	27.2 kg/Mg asphalt	D
	Controlled	0.54 kg/Mg asphalt	D

8.2.2 Fugitive Process Emission Factors

Emissions factors for fugitive process emissions of NMVOC are expressed as losses per equipment unit per day. As previously discussed, the methods for estimating mass emissions from process equipment leaks range from the use of emission factors with equipment counts to comprehensive field measurement techniques. These methods have evolved from a number of studies of the organic chemical and petroleum refining industries for the U.S. EPA.

The U.S. EPA (1993) has provided NMVOC emission factors (Table 8.3). These are considered to give a good estimate of fugitive process emissions from a refinery with no inspection and maintenance program.

Table 8.3: Process Fugitive Average NMVOC Emission Factors for Petroleum Refineries (U.S.EPA 1993)

Source		Emission Factor (kg/hr-source)	Quality
Valves	Gas	0.0268	
	Light Liquid	0.0109	
	Heavy Liquid	0.00023	
Open-ended Lines	All Streams	0.0023	
Connectors	All Streams	0.00025	
Pump Seals*	Light Liquid	0.114	
	Heavy Liquid	0.021	
Compressor Seals	Gas	0.636	
Sampling Connections	All Streams	0.0150	
Pressure Vessel Relief Valves	Gas	0.16	

* The light liquid pump seal factor can be used to estimate the leak rate from agitator seals

These emission factors, however, are in most cases considered to overestimate NMVOC emissions from sources in more modern facilities. The U.S. EPA allows a 75% reduction in emissions estimated by using these emission factors if an approved I and M program is conducted at the petroleum refining facility.

Passant (1993) used the VOC emission factors presented in Table 8.4, which were referenced to U.S.EPA 1988.

Table 8.4: Process Fugitive Emission Factors for Petroleum Refineries (Passant 1993)

Source		Emission Factor (kg/hr)	Quality
Valves	gas	0.0056	D
	light	0.0071	D
	heavy	0.0023	D
Pump Seals	light	0.0494	D
	heavy	0.0214	D
Compressor Seals	all streams	0.2280	D
Pressure Relief Seals	all streams	0.104	D
Flanges	all streams	0.00083	D
Open-ended Lines	all streams	0.0017	D
Sample Connections	all streams	0.015	D

Although the derivation of the emission factors in table 8.4 is not given, it would appear that these are actually average synthetic organic chemical manufacturing industry (SOCMI) (1988) uncontrolled emission factors. These sets of factors are thought to be biased on the high side for petroleum refineries due to the inclusion of ethylene plants, which operate at 15,000 to 40,000 psig.

9 SPECIES PROFILES

9.1 Applicability of Generalised VOC Species Profiles

In both North America and Europe, VOC species profiles have been published based on measurements or engineering judgement. There is a need to produce generalised profiles for use by models, the alternative being to obtain refinery specific data. Generalised profiles can be generated at the most detailed process level, however, there are several important influences which should be considered in attempting to specify such generally applicable data. Some of these influences are:

Meteorological and Climatological effects: Ambient temperature and temperature ranges may have important influences on the emitted species profiles. Due to the logarithmic behaviour of vapour pressure, higher temperatures tend to favour the loss of the lower molecular weight compounds from storage vessels and some process streams.

Variability of Raw Materials: The type of crude oil being processed can influence the fraction of more volatile and more easily emitted compounds.

Process Variability: Different refineries will have process differences. Where the species profiles are based on individual operations, process differences can be allowed for. However, overall average refinery profiles will differ between refineries.

Maintenance and Regulation: Equipment maintenance and the enforcement of regulations will have significant effects on the overall emitted species distribution depending on which processes or operations are impacted by maintenance practices or by regulation.

The broad application of generalised profiles should be done with some caution. Where such profiles are necessary, consideration should be given to stratification of the data according to some of the major factors of influence such as climate, country, raw material etc.

9.2 Simplified VOC Speciation

For some applications, where there is no process detail, or where refineries are grouped as a single emission source, there is a need for a single overall species profile to characterise the emissions for modelling or other purposes. Process specific species profiles can be combined into a single overall refinery profile by appropriately weighting the individual profiles according to their relative contribution to the total refinery emissions.

Consideration should be given to stratification of the data according to some of the major factors of influence such as climate, country, raw material (crude) etc.

CONCAWE reports (Report 2/86) that refinery emissions are essentially saturated, with the saturated hydrocarbon content lying between 80 and 90% by weight. The balance of 10 to 20% is unsaturated and/or aromatic hydrocarbons, the actual values depending on the nature of the refinery processes installed. Several overall refinery species profiles are available, such as those reviewed by Veldt (1991) for application to the EMEP and CORINAIR 1990 emissions inventories. On the basis of this review, this chapter proposes an overall species profile for petroleum refining by mass fraction.

Table 9.1: CONCAWE Petroleum Refinery Speciation Profile

Species	CONCAWE (%)	Quality
Methane	0	(Unknown)
Ethane	5	
Propane	20	
n-Butane	15	
i-Butane	5	
Pentanes	20	
Hexanes	10	
Heptanes	5	
>Heptanes	5	
Ethene	1	
Propene	1	
Butene	0.5	
Benzene	2	
Toluene	3	
o-Xylene	0.7	
M,p-Xylene	1.3	
Ethylbenzene	0.5	
TOTAL	100	

The Air Emission Species Manual (AESM) for VOC (U.S. EPA 1994) provides an overall refinery species profile (Profile 9012: Petroleum Industry - Average, Data Quality E - based on engineering judgement) as summarised in Table 9.2.

Table 9.2: US EPA Petroleum Refinery Speciation Profile

Species	CAS Number	Wt (%)	Quality
Methane	74-82-8	13	E
Ethane	74-84-0	6.05	E
Propane	74-98-6	19.7	E
n-Butane	106-97-8	7.99	E
i-Butane	75-28-5	2.89	E
Pentanes	(109-66-0)	21.4	E
Hexanes	(110-54-3)	8.02	E
Heptanes	(142-82-5)	1.87	E
Octanes	(111-65-9)	2.13	E
Nonanes	(111-84-2)	1.01	E
Decanes	(124-18-5)	1.01	E
Cyclo-hexane	110-82-7	0.08	E
Cyclo-heptanes		2.27	E
Cyclo-octanes		0.66	E
Cyclo-nonanes		0.11	E
Propene	115-07-01	1.75	E
Butene	106-98-9	0.15	E
Benzene	71-43-2	0.38	E
Toluene	108-88-3	0.44	E
Xylenes	1330-20-7	0.19	E
Formaldehyde	50-00-0	8.88	E
Total		100.02	

The suggested applications are:

- Blowdown system - vapour recovery./Flare
- Blowdown system - without controls
- Wastewater treatment - excl. Separator
- Vacuum distillation - column condenser
- Sludge converter - general
- Fluid coking - general
- Petroleum coke - calciner
- Bauxite burning
- Lube oil manufacturing

9.3 Detailed Process VOC Speciation

The most detailed speciation of VOC is achievable at the process level using the U.S. EPA AESM (U.S.EPA 1994). Such a detailed method is generally only applicable on an individual refinery basis where estimates of the emission contributions from the various process streams and operations are available. The generalised profiles, which are available for individual processes and operations, as well as fugitive process emissions, are summarised below. These profiles are based on United States data, and in many instances on data from California.

U.S. EPA petroleum refinery species profiles applicable to petroleum refinery process and fugitive process emissions are presented in Tables 9.3 through 9.8.

Table 9.3: Profile 0029: Refinery Fluid Catalytic Cracker.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	13.00	C
74-82-8	Methane	36.00	C
50-00-0	Formaldehyde	51.00	C
TOTAL		100.00	

Table 9.4: Profile: 0031 Refinery Fugitive Emissions - Covered Drainage / Separation Pits.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	12.20	C
	C-7 cycloparaffins	16.90	C
	C-8 cycloparaffins	5.20	C
	Isomers of pentane	10.10	C
74-82-8	Methane	2.90	C
74-84-0	Ethane	1.70	C
74-98-6	Propane	5.90	C
106-97-8	N-Butane	14.30	C
75-28-5	Iso-Butane	4.50	C
109-66-0	N-Pentane	12.00	C
110-54-3	Hexane	11.90	C
71-43-2	Benzene	2.40	C
TOTAL		100.00	

Used for: Fugitive hydrocarbon emissions - drains - all streams

Table 9.5: Profile: 0039 Description: Refinery Fugitive Emissions - Compressor Seals - Refinery Gas.

CAS Number	Name	Wt %	Quality
	Isomers of hexane	1.00	D
	Isomers of heptane	0.10	D
	Isomers of pentane	8.60	D
74-82-8	Methane	13.30	D
74-84-0	Ethane	5.60	D
74-98-6	Propane	16.00	D
115-07-01	Propene	8.80	D
106-97-8	N-Butane	23.20	D
106-98-9	Butene	1.20	D
75-28-5	Iso-Butane	10.00	D
109-66-0	N-Pentane	7.60	D
110-54-3	Hexane	4.60	D
TOTAL		100.00	

Used for: Compressor seal - gas streams
 Compressor seal - heavy liquid streams

Table 9.6: Profile: 0047 Description: Refinery Fugitive Emissions - Relief Valves - Liquefied Petroleum Gas

CAS Number	Name	Wt %	Quality
74-84-0	Ethane	4.10	D
74-98-6	Propane	90.40	D
115-07-01	Propene	5.10	D
75-28-5	Iso-Butane	0.40	D
TOTAL		100.00	

Used for: Vessel relief valves
 Pipeline valves - gas streams
 Pipeline valves - lt liq/gas streams
 Pipeline valves - heavy liqd streams
 Pipeline valves - hydrogen streams
 Open-ended valves - all streams
 Flanges - all streams
 Vessel relief valves - all streams

Table 9.7: Profile: 0316 Description: Pipe / Valve Flanges

CAS Number	Name	Wt %	Quality
	C-7 cycloparaffins	0.20	C
	C-9 cycloparaffins	0.10	C
	Isomers of pentane	7.80	C
74-82-8	Methane	28.60	C
74-84-0	Ethane	5.80	C
74-98-6	Propane	11.50	C
115-07-01	Propene	0.10	C
106-97-8	N-Butane	18.30	C
75-28-5	Iso-Butane	7.40	C
109-66-0	N-Pentane	7.70	C
(10-54-3)	Hexanes	5.00	C
(42-82-5)	Heptanes	2.20	C
(11-65-9)	Octanes	2.20	C
(11-84-2)	Nonanes	1.10	C
(24-18-5)	Decanes	1.10	C
110-82-7	Cyclohexane	0.10	C
1330-20-7	Isomers of Xylene	0.20	C
71-43-2	Benzene	0.10	C
108-88-3	Toluene	0.50	C
TOTAL		100.00	

Used for: Pipeline - valves / flanges

Table 9.8: Profile: 0321 Description: Pump Seals – Composite.

CAS Number	Name	Wt %	Quality
	C-7 cycloparaffins	1.10	C
	C-8 cycloparaffins	0.10	C
	C-9 cycloparaffins	0.80	C
74-82-8	Methane	3.30	C
74-84-0	Ethane	1.20	C
74-98-6	Propane	3.70	C
106-97-8	N-Butane	8.10	C
75-28-5	Iso-Butane	0.80	C
109-66-0	Pentanes	17.70	C
(110-54-3)	Hexanes	16.50	C
(142-82-5)	Heptanes	12.60	C
(111-65-9)	Octanes	14.80	C
(111-84-2)	Nonanes	7.00	C
(124-18-5)	Decanes	7.00	C
(110-82-7)	Cyclohexane	0.50	C
1330-20-7	Isomers of Xylene	1.30	C
71-43-2	Benzene	0.50	C
108-88-3	Toluene	3.00	C
TOTAL		100.00	

Used for: Pump seals - with/without controls
 Pump seals - light liq/gas streams
 Pump seals - heavy liqd streams
 Sampling/purging/blind changing

10 UNCERTAINTY ESTIMATES

See next section on: Weakest Aspects/Priority Areas for Improvement in Current Methodology

11 WEAKEST ASPECTS/PRIORITY AREAS FOR IMPROVEMENT IN CURRENT METHODOLOGY

More measurements of emissions from petroleum refineries should be done: based on testing programs in the United Kingdom, currently available emission factors have underestimated emissions typically by 30%.

Emission factors must be developed that can account for regional differences in the major sources of NMVOCs in refineries (see above and this part of section 040104). There are also difficulties in determining what the data really represents, as there is a wide variation in the definition of total hydrocarbons, hydrocarbons, non-methane hydrocarbons, VOCs and NMVOCs. There is a need to identify a standard method or definition of speciation of NMVOCs towards which all expert panels could work.

12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

No spatial disaggregation (of national emissions estimates) should be required since refineries are to be inventoried as point sources. However if data is not available on individual refineries, total regional or national crude processing data could be disaggregated based on refining capacity.

13 TEMPORAL DISAGGREGATION CRITERIA

No temporal disaggregation is possible if the simpler methodology is used.

If the detailed methodology is used, then individual refineries can indicate the temporal aspects of shutdowns.

None of the computational methods used to estimate fugitive leaks are based on parameters that show seasonal or diurnal changes. Therefore it is not possible to disaggregate fugitive process emissions at this time.

14 ADDITIONAL COMMENTS

In the European community, CONCAWE (1992) reports that the complexity of refineries has increased with the installation of additional conversion units (e.g. thermal crackers, catalytic crackers and hydrocrackers) as the demand for fuel oil production decreases and the demand for a higher yield of gasoline and other light products. This is shown on the table in which CONCAWE uses a system of refinery classifications that are based on increasing complexity.

Table 14.1: Concawe Petroleum Refinery Classification System

Year	No. of Refineries Reporting	Type I		Type II		Type III		Type IV	
		No.	%	No.	%	No.	%	No.	%
1969	81	34	42	31	38	16	20	-	-
1974	110	49	45	40	36	21	19	-	-
1978	111	50	45	36	32	25	23	-	-
1981	105	38	36	44	42	23	22	-	-
1984	85	18	22	47	54	20	24	-	-
1987	89	12	13	53	60	19	22	5	5
1990	95	9	9	53	56	22	23	11	12

Notes:

- Type I: Simple (non-conversion refinery: composed of crude oil distillation, reforming, treatment of distillate products, including desulphurization and/or other quality improvement processes (i.e. isomerization or specialty manufacturing).
- Type II: Type I plus catalytic cracking and/or thermal cracking and/or hydrocracking.
- Type III: Type II plus steam cracking and/or lubricant production within the refinery fence.
- Type IV: Refineries not in above categories, e.g. those producing only bitumen, lubes, etc. which import their feedstocks from other sources.

This classification system could be adopted for use in developing generic emission factors for application in the simpler inventory method. It could also be useful in developing generic speciation profiles.

15 SUPPLEMENTARY DOCUMENTS

There are no supplementary documents.

16 VERIFICATION PROCEDURES

There are more sophisticated and accurate methods to estimate fugitive process emissions, as developed by the U.S.EPA (1993). All of these methods involve the use of screening data, which are collected by using a portable monitoring instrument to sample air from potential leak interfaces on individual pieces of equipment. A screening value is a measure of the concentration, in ppmv, of leaking compounds in the ambient air near the equipment in question. The EPA has detailed what is involved in an acceptable screening program in the protocol for equipment leak emissions estimation manual (U.S.EPA 1993).

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

1. Screening Ranges Approach
2. EPA Correlation Approach and
3. Unit -Specific Correlation Approach.

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

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

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

All of these methods are described in detail in the protocol document (U.S.EPA 1993). As previously discussed, remote sensing monitoring programs can also provide verification of emissions estimates based on emission factors. However it is often difficult to differentiate between different refinery sources, and so this method would more often be used to verify total refinery emissions (i.e., more than just process and fugitive process emissions).

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