7.5 Mineral oil and gas refineries for VOC emissions

7.5.1 Coverage

This chapter covers activities originating VOC emissions in the oil refineries: fugitive emissions, flare system, storage tanks, and oil separators. Fugitive VOC emission sources (such as leakages from flanges, pumps or any pieces of equipment) and losses from the storage facilities of liquid products may contribute more than 50 % to the total VOC emissions. VOC emissions also occur from processes linked to combustion and from flares but these are lower emitters of VOCs in refineries. The refinery petrol dispatch station is covered by chapter 7.23.

7.5.2 Emission sources

Sources of VOC emissions considered are as follows:

Fugitive emissions:

Fugitive VOC emissions are released from leaking pressurised equipment components on process units, such as valves, flanges and connectors, opened lines and sampling systems containing volatile liquids or gases. Volatile products are defined in CEN 15446 [9] and reference [10] as all products of which at least 20% by weight has a vapour pressure higher than 0,3 kPa at 20C.

The quantity of VOC emissions from sealing elements, depends on:

- Size, type and material of the seal,
- State of maintenance, age of the equipment,
- Pressure, temperature, and physical condition of the product. Emissions are larger at those refineries that are processing light products (fuel producing refineries).
- Valves represent 50-60 % of fugitive emissions [1]. A major portion of fugitive emissions comes from only a small portion of sources (less than 1 % of valves in gas / vapour service may account for more than 70% of the fugitive emissions of a refinery).

The flare systems:

Flares are used for safety and environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situation or upsets [1]. The VOC emissions from flaring itself are a small proportion of the total refinery VOC emissions. Fugitive emissions, however, can result from leaking equipment components in the flare gas collection system.

The oil water separators:

Waste water treatment systems employed in refineries include neutralisers, oil/water separators, settling chambers, clarifiers, dissolved air flotation systems and activated sludge ponds. If contaminated by oil, the waste water from a refinery is passed to a multi-stage water purification via an oil separator or via flocculation.

Emissions from sewage systems and oil separators primarily result from evaporation of NMVOC from liquid surfaces open to the atmosphere. Direct sources include processes that use water for washing (e. g. desalter), sour water stripping and also steam used in jet eductors to produce vacuum. Indirect sources include leaks from heat exchangers, condensers and pumps.

Sources of contamination with hydrocarbons are [4]:

- Desalters: 40 %
- Storage tanks: 20 %
- Slop systems: 15 %
- Other processes: 25 %

Crude oil and volatile product storages:

A significant proportion of the VOC emissions from refineries may arise from storage tanks for crude oil and volatile products in case of no use of BAT. Those products may be stored in different types of storage tanks according to the physical and chemical properties, such as fixed roof tanks, external floating roof tanks or internal floating roof tanks. Fixed roof tanks can only be used for petroleum products with very low vapour pressure.

7.5.3 BAT, associated emission levels (AEL)

BAT for reducing VOC emissions are as follows [1] and [2]:

Fugitive emissions:

- Quantifying VOC emission source in order to identify the main emitters in each specific case,
- Executing leak detection and repair programme (LDAR) campaigns or equivalent. A good LDAR includes the determination of the type of measurement frequency, type of components to be checked, type of compound lines, what leaks should be repaired and how fast action should be taken,
- Using a maintenance drain out system,
- Selecting and using low leakage valves such as graphite packed valves or equivalent for lines containing product with high vapour pressure,
- Using low leak pumps (e.g. seal less designs, double seals, with gas seals or good mechanical seals) on lines containing product with high vapour pressure,
- Blinding, plugging or capping open ended vents and drain vents,
- Routing relief valves with high potential VOC emissions to flare,
- Routing compressor vents with high potential for VOC emissions back to process and when not possible to refinery flare for destruction,
- Using totally closed loop in all routine samplers that potentially may generate VOC emissions,
- Minimizing flaring.

A LDAR programme is established according to the following principles [3]:

1 The definition of what constitutes a leak and fixation of corresponding thresholds,

2 The fixation of the frequency of inspections,

3 The listing and identification of components included,

4 The procedures concerning repair of leaking components depending on the leak category.

Equipment tightening can be made with equipment in operation (except with remote control valves (e.g. tightening bolts to eliminate leaks from valves stems or flanges, installing tightening caps on open ends…).

Maintenance with equipment dismantling or exchange can only be implemented during plant shutdowns with circuit insulation and degassing. This implies that implementing this type of maintenance with the sole objective of reducing fugitive emissions would lead to unacceptable costs.

Maintenance on the equipment can consist in removing some parts or replacing the equipment with a new one of the same technology (named basic maintenance in this document). A complete change of equipment such as valves with valves of the newest not leaking technology can also be operated (not considered in this document).

Water treatment plant [1]:

- Covering separators, basins and inlet bays and by routing off gases in the waste water treatment plant. Implementation of some of these techniques may compromise efficient operation of the waste water treatment plant or cause safety concerns if they are not properly designed and managed. For these reasons, this technique may have some technical problems when retrofitted.

Storage and handling [1] and [2]:

- Ensure that the liquids and gases stored are in appropriate tanks or vessels based upon the true vapour pressure of the stored materials,

- Use high efficiency seals in floating roof tanks (example provided in reference [1] indicates an incremental reduction potential for changing from a vapour mounted primary seal to a liquid mounted seal was 84%),
- Bund all stored chemicals, with separate bunding for incompatibles,
- Apply emission reduction measures during tank cleaning,
- Apply concept of good house keeping and environmental management,
- Minimise the number of tanks and volume by suitable combination of application of in line blending, integration of processing units, these techniques being much easier to apply on new facilities, e.g. by vapour balance lines that transfer the displaced vapour from the container being filled to the one being emptied. Incompatibility of tank vapours and applicability to external floating roofs tank are some examples of restrictions of application. Applicability needs to reflect economics, the type and size of vessel to be used (e.g. tank, truck, railcar, ship), type of hydrocarbon fraction and frequency of use of the tank. Because this technique is related to the next one, both should be evaluated together when implementing on a specific site.
- Apply vapour recovery (not applicable to non-volatile products) on tanks, vehicles, ships etc. in stationary use and during loading/unloading. Achieved emission levels are very dependent on the application, but recoveries of 95 - >99 % are considered BAT. If VRUs are not considered appropriate for certain streams, vapour destruction units are considered BAT. Properties of streams, such as type of substance, compatibility of substances or quantity need to be considered in the applicability of this BAT. Applicability needs to reflect economics, the type and size of vessel to be used (e.g. tank, truck, railcar, ship), type of hydrocarbon fraction and frequency of use of the tank. Because this technique is related to the above one, both should be evaluated together when implementing on a specific site.
- Reduce the risk of soil contamination by the implementation of an inspection maintenance programme which can include good house keeping measures, double bottom tanks, impervious liners…
- Install self sealing hose connections or implement line draining procedures,
- Some other best practices.

External floating roofs and internal floating roofs can have the following emission reduction efficiency:
The BAT associated emission reduction level associated to an external floating roof for a large tank is at least 97 % (compared to a fixed roof tank without measures), which can be achieved when over at least 95 % of the circumference the gap between the roof and the wall is less than 3.2 mm and the seals are liquid mounted, mechanical shoe seals. By installing liquid mounted primary seals and rim mounted secondary seals, a reduction in air emissions of up to 99.5 % (compared to a fixed roof tank without measures) can be achieved [2].

The achievable emission reduction for a large tank using an internal floating roof is at least 97 % (compared to a fixed roof tank without measures), which can be achieved when over at least 95 % of the circumference of the gap between the roof and wall is less than 3.2 mm and the seals are liquid mounted, mechanical shoe seals. By applying liquid mounted primary seals and rim mounted secondary seals, some further improvement in emission reductions can be achieved. However, the smaller the tank and the smaller the numbers of turnovers are, the less effective the floating roof is.

However, measurements of diffuse sources (e.g. tanks) can only be made over short periods and extrapolation to provide annual estimates of emissions introduces significant errors due to the temporal variations in emissions from these types of sources.

Table 1: Associated Emission Levels with BAT to reduce VOC emissions from storage

Emission sources	**Combination of BAT**	**BAT Associated Emissions Levels for VOCs**
Storage tanks of volatile products	Internal floating roof External floating roof Other tank designs and appropriate colours	97 to 99.5 % compared to a fixed roof tank without measure*

* If the efficiency cannot be reached because of the specific characteristics of a storage tank (such as small throughput, small diameter), best available primary and secondary seals have to used.

Table 2: Associated Emission Levels with BAT to reduce VOC emissions in refinery loading and unloading operations

Emission source	BAT and reduction efficiency	BAT associated emission levels* kg VOC/m³/kPa [1], [6]
Road tanker filling, bottom or top loading and vapour balancing during previous off loading and VRU	VRU with 95 to 99 % efficiency [1]	0.0228 x 0.05 to 0.0228 x 0.01
Rail tanker, top loading and VRU		0.0108 x 0.05 to 0.0108 x 0.01
Marine tanker, typical cargo tank condition		0.004 x 0.05 to 0.004 x 0.01
Barge – typical cargo tank conditions		0.007x 0.05 to 0.007 x 0.01

*Not available in reference [1] but calculated with reference [6].

kPa : True vapour of the volatile product.

7.5.4 Cost data for emission reduction techniques

The EGTEI synopsis sheet [7] on VOC emissions in refineries provides costs of VOC emission reduction techniques.

Cost of a LDAR programme depends on the thresholds defining what constitutes a leak. Reference [1] provides operating costs ranging from 0.04 to 0.08 M€/year for a 10000 ppm programme and 0.8 M€/year for a 100 to 500 ppm.

7.5.5 References used for chapter 7.5

[1] European Commission

Reference document on best available techniques for mineral oil and gas refineries

BREF – february 2003 – European commission – Available at: http://eipccb.jrc.es

[2] European Commission - reference document on BAT on emissions from storage – February 2003 – Available at: http://eipccb.jrc.es

[3] EGTEI background document on the organic chemical industry

[4] VAN DER REST A. and others: Best available techniques to reduce emissions from refineries

CONCAWE report n°BAT/II – air – February 1999

[5] GOODSELL P.: Information mail to CITEPA of September 8, 2003. Provided in reference [3]

[6] CONCAWE - Air pollutant emission estimation methods for E-PRTR reporting by refineries

Report n°1/2009 (Amending report 2007)

[7] EGTEI synopsis sheets on NMVOC from refineries – October 2005

[8] EPA - Emission factor documentation for AP42 section 7.1 - Organic liquid storage tanks

Final report - September 2006

[9] EN15446:2008 Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks

[10] EPA - Protocol for equipment leak - Emission estimates EPA 453-95-017 – 1995

[11] Edda Hoffmann, UBA Germany: comments on the first version of the guidance document