



# **Volatile Organic Compound Emissions from Cargo Systems on Oil Tankers**

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**Oil Companies International Marine Forum**

29 Queen Anne's Gate

London SW1H 9BU

United Kingdom

Telephone: +44 (0)20 7654 1200

Email: [enquiries@ocimf.org](mailto:enquiries@ocimf.org)

[www.ocimf.org](http://www.ocimf.org)

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## Glossary

**Absorption** A physical or chemical phenomenon or a process in which atoms, molecules or ions enter some bulk phase – gas, liquid or solid material.

**Adsorption** The adhesion of atoms, molecules or ions from a gas, liquid or dissolved solid to a surface.

**Carcinogenic** Any substance that is an agent directly involved in causing cancer.

**Catalytic oxidisers** Oxidation systems that control Volatile Organic Compound (VOC) and volatile emissions.

**Energy recovery** Method in which a part or all the waste material produced in a process is burned to generate heat or electricity.

**Evaporation** Vaporisation of a liquid that occurs from the surface of a liquid into a gaseous phase that is not saturated with the evaporating substance.

**Flashing** When crude is exposed to temperature increases or pressure decreases during transfer and VOCs are released.

**Fractionate** A separation process in which a certain quantity of a mixture (gas, liquid, solid, enzymes, suspension or isotope) is divided during a phase transition into a number of smaller quantities (fractions) in which the composition varies according to a gradient.

**Inert gas** A gas that does not undergo chemical reactions under a set of given conditions.

**Light end products** More volatile products that are the result of the refining process, pure components that are separated out from crude oil.

**Recommendations** OCIMF supports and endorses a particular method of working or procedure.

**Teratogenic** Any agent that can disturb the development of an embryo or foetus.

**Toxic** A substance that is poisonous to a living organism.

**Vaporisation** A phase transition from the liquid phase to vapour.

**Vapour balancing** The transfer of vapour displaced by incoming cargo from the receiving tank of a vessel to the tank of a facility/offshore unit delivering the cargo.

**Vapour Emission Control System (VECS)** An arrangement of piping and equipment used to control vapour emissions collected in a tank. Includes the vapour collection system and vapour processing unit.

**Vapour pressure** The pressure produced by a vapour in contact with its liquid or solid form at a given temperature in a closed container.

**Vapour saturation** Vapour at the temperature of the boiling point corresponding to its pressure and so incapable of being compressed or cooled without condensing.

**VOCON procedure** A procedure that requires the monitoring and the recording of the pressure drop during a release of gas from the cargo tank vapour system.

**VOCON research project** A project sponsored by private enterprises and government agencies to advance the competence in the petroleum transportation industry for the development of a cost-effective solution for reduction in VOC emissions from crude storage and tanker transport.

**VOCON valve** A vapour pressure release control valve used to monitor pressure drops during vapour releases limiting VOC emissions.

**Volatile Organic Compound (VOC)** Any organic compound having an initial boiling point less than or equal to 250°C (482°F) measured at a standard atmospheric pressure of 101.3 kPa.

**Volatility** A condition of a substance that is capable of being evaporated or changed to a vapour at a relatively low temperature.

## Abbreviations

<b>CO<sub>2</sub></b>	Carbon Dioxide
<b>IAPP</b>	International Air Pollution Prevention
<b>IMO</b>	International Maritime Organization
<b>IPCC</b>	Intergovernmental Panel on Climate Change
<b>MARPOL</b>	The International Convention for the Prevention of Pollution from Ships
<b>MEPC</b>	Marine Environment Protection Committee
<b>NMVO</b>	Non-Methane Volatile Organic Compound
<b>NO<sub>x</sub></b>	Nitrogen Oxides
<b>P/V</b>	Pressure/Vacuum
<b>Sm<sup>3</sup></b>	Standard Cubic Metre
<b>SO<sub>x</sub></b>	Sulphur Oxides
<b>STTA</b>	Sequential Transfer of Tank Atmosphere
<b>VECS</b>	Vapour Emission Control System
<b>VOC</b>	Volatile Organic Compound
<b>VOCON</b>	Volatile Organic Compound Control

## **Bibliography**

*CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O Emissions from Transportation-Water-Borne Navigation. In Background papers: IPCC Expert Meetings on Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (Intergovernmental Panel on Climate Change (IPCC))*

*MEPC.185(59) Guidelines for the Development of a Volatile Organic Compound (VOC) Management Plan for Tankers Carrying Crude Oil (IMO)*

*MEPC.1/Circ.680 Technical Information on Systems and Operation to Assist Development of VOC Management Plans (IMO)*

## 1 Introduction

Volatile Organic Compounds (VOCs) are any organic compounds that have an initial boiling point less than or equal to 250°C (482°F) when measured at a standard atmospheric pressure of 101.3 kPa. VOCs are a mixture of light end hydrocarbons (such as methane, ethane, propane or butane) that evaporate within the range of normal atmospheric conditions. VOCs are generated when cargo flashes in the piping system from the source to the cargo tanks, and from evaporation from the oil surface inside the cargo oil tanks during and after loading. During loading of crude oil tankers and the subsequent vessel transit, VOCs may be released to the atmosphere together with the inert gas.

The cargo tank atmosphere initially contains nitrogen, Carbon Dioxide (CO<sub>2</sub>), other non-methane compounds, and traces of VOCs from previous cargo. During loading, hydrocarbon gases (methane–pentane and heavier components) are also released from the cargo. The release of these compounds, combined with the rising cargo level, results in a pressure increase of the cargo tank that is eventually vented to the atmosphere. The reasons for reducing VOC emissions are twofold: environmental protection and to minimise light end product losses.

This information paper presents the technologies and methods that are currently available for controlling or treating VOC emissions from oil tanker loading and during vessel transit.

## 2 Regulations

The International Maritime Organization has published technical information on system and operation guidelines to assist in the development of VOC Management Plans in MEPC.1/Circ.680 (27 July 2009), which is a supplement to resolution MEPC.185(59) that came into effect on 1 July 2010. The IMO requires all member states to develop a VOC Management Plan that follows Marine Environment Protection Committee (MEPC) guidelines. The circular states: “The purpose of the VOC management plan is to ensure that the operation of a tanker, to which regulation 15 of MARPOL Annex VI applies, prevents or minimises VOC emissions to the extent possible.”

Vapour Emission Control System (VECS) MSC/Circ.585 (16 April 1992) – MARPOL Annex VI/15 are the standards that have been developed for the design, construction and operation of vapour collection systems on tankers. In addition to these requirements, each tanker that has a vapour processing unit onboard should meet the vapour collection and processing design requirements for a shoreside terminal, to the satisfaction of the country/Flag State of the ship’s registry. While there is a requirement for a VOC Management Plan, there is no requirement for a VECS.

Because of heightened local regulations, Norway has produced a number of technologies for controlling the escape of VOCs. On 1 January 2012, the Norwegian Climate and Pollution Directorate imposed an upper limit for emissions of 0.45 kg Non-Methane VOC (NMVOC)/Sm<sup>3</sup> crude oil per loading point as a mean value measured over one calendar year and with a maximum of 135,000 tonnes of emissions per year. This requirement will be met if the mean emissions from all fields on the Norwegian continental shelf do not exceed 0.45 kg NMVOC/Sm<sup>3</sup> crude oil loaded during a calendar year. This requirement was increased to 0.68kg NMVOC/Sm<sup>3</sup> between 2015 and 2019 by the Norwegian authorities.



### 3 Volatile Organic Compound generating mechanisms

VOCs in cargo tanks are caused by a build-up of positive pressure that occurs during loading, the loaded voyage to the discharge port and transit from discharge to the next load port.

During the loading of oil tankers, the inert gas tank atmosphere (which is infused with residual VOC) has to be displaced. It can be displaced to the atmosphere, to an onboard VOC control method or to an onshore VOC processing unit (via a VECS connection) to allow the cargo to fill the tank while keeping the tank's atmosphere below the Pressure/Vacuum (P/V) valve pressure setting. For tankers this venting is normally done using a vent mast riser system.

During the loading process or in the transit stages, the amount of VOCs that have evolved into the inert gas tank atmosphere is linked to the oil's volatility. Volatility is the tendency of a substance to vaporise.

VOC emissions are created through vaporisation, evaporation and boiling. These processes can be manipulated to control VOC production in the tank atmosphere and capture VOCs in any fitted processing equipment before it is vented into the atmosphere.

Vaporisation is the process of phase transformation between solid or liquid to the gaseous phase. The main vaporisation processes that drive the production of VOCs are evaporation and boiling.

Evaporation is a type of vaporisation from a liquid's surface into a gaseous phase that is not saturated with the evaporating substance. Factors that affect evaporation and therefore the VOC content of a tank's vapour space are temperature, pressure, concentration of substance evaporating in the vapour space, concentration of other substances in the vapour space, flow rate of vapour in the vapour space, density and surface area.

Boiling is the rapid vaporisation of a liquid, which occurs when a liquid is heated to its boiling point, i.e. the temperature at which the vapour pressure of the liquid is equal to the pressure exerted on the liquid by the surrounding atmosphere.

## 4 Environmental impact of Volatile Organic Compound emissions

There are two types of VOCs: methane and non-methane (NMVOC). The lightest components (mainly methane) contribute to the greenhouse effect (see the Intergovernmental Panel on Climate Change (IPCC) paper *CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O Emissions from Transportation-Water-Borne Navigation*). The heavier components (NMVOC) contribute to low-level petrochemical oxidants, such as ozone, which may be detrimental to human health, food production and the environment. In addition, some VOC emissions from light end products are classified as toxic, carcinogenic and teratogenic.

During tanker loading operations, there is a higher flow of inert gas/VOC emissions exiting the cargo tanks through the mast riser into the atmosphere. The high flow rate can result in higher than normal VOC generation and can trap oil in the inert gas/VOC flow, which can then spill on the vessel deck.

## **5 Light end product losses: minimising Volatile Organic Compound emissions**

Light end product losses resulting from VOC emissions also mean a loss of cargo if the light end products are not captured, processed and incorporated back into the cargo tanks. Dictated by local, regional or international requirements, vessel owners/operators have been testing and finding economic and efficient means to recover VOC emissions. The proper use of vapour emission control systems and the associated technologies helps to reduce these cargo losses.

## 6 Volatile Organic Compound emission control methods, systems and procedures

There are two generic approaches to VOC recovery, known as active and passive VOC recovery technology. Active VOC emission systems typically include a compression step followed by condensation, absorption and/or adsorption. Passive VOC systems use vapour-balanced loading/unloading with VOC as blanket gas.

This section lists the VOC emission control methods, systems, procedures and associated technologies that are available for treating or limiting VOC emissions from oil tankers while loading and during vessel transit.

### 6.1 Reduced volatility

Cargo volatility can be reduced by removing the volatile components of the crude oil from the tank of the facility or offshore platform before it is loaded onto the vessel. However, in most cases this is not feasible due to the use of equipment that is found in the petroleum refining process and associated safety considerations, and therefore it is not considered a viable option.

### 6.2 Vapour balancing

Vapour is displaced by incoming cargo from an oil tanker's receiving tank back to the offloading tank at the terminal or on the offshore facility delivering the crude oil. This vapour balancing method is not practical because the difference in temperature between the offloading and receiving tank can lead to a mismatch in volumes of vapour, vapour contaminants may be incompatible and the methods for collecting vapour in the tanks may be different.

### 6.3 Thermal oxidation

Thermal oxidation (via thermal combustion) is the most common method of controlling VOC emissions during offshore loading. VOC-laden air is combusted using enclosed flares to catalytic oxidisers with heat recovery. Risks to consider include safety and combustion emissions (CO<sub>2</sub>, Nitrogen Oxides (NO<sub>x</sub>), Sulphur Oxides (SO<sub>x</sub>), etc.). These risks can be mitigated by using flame/detonation arrestors, inerting, enrichment or dilution, and by following management procedures.

### 6.4 Absorption

Absorption by chilled or cryogenic liquid is a common method and is the most popular. The chilled liquid absorbent is fed concurrent to the flow of the hydrocarbon vapours through a packed column. The hydrocarbon vapours dissolve in the absorbent and are removed from the air/vapour mixture.

### 6.5 Adsorption

Adsorption is the process where an air/vapour/gas mixture passes through a bed of activated carbon. Organic molecules are adsorbed on to the carbon and permanent gases such as air or CO<sub>2</sub> pass through the carbon bed and are vented to the atmosphere. If the activated carbon becomes saturated (the breakthrough point), no more molecules can adsorb and vapours will pass through. In order to maintain uninterrupted operation, two activated carbon beds with automatic switching between the two is recommended. The standby activated carbon bed is then regenerated while the active carbon bed is in use. Regeneration of the adsorbent is usually accomplished by stream stripping or by vacuum. Depending on the carbon bed sizes, the nature of the adsorbent material used and the degree of regeneration, this method can reach up to 99% efficiency.

## 6.6 Membrane separation

The membrane separation technique uses a liquid compressor and a semi-permeable membrane to separate organic molecules from air/vapour mixtures, with the membrane more permeable to organic compounds than to inorganic gases. The air/vapour mixture passes over one side of the membrane. Organic molecules selectively migrate through the membrane, are removed by a vacuum pump and are returned to the inlet side of the compressor.

## 6.7 Cryogenic condensation

Cryogenic condensation involves passing the vented gas/vapour through a liquid nitrogen-cooled condenser. This lowers the temperature of the gas/vapour, resulting in lowering of VOC concentrations that exit the nitrogen-cooled condenser, then drains into a collection tank, from which it can be recycled, reclaimed or recovered for reuse. To achieve these low temperatures, a nitrogen generator is needed. This method can reach over 99% efficiency.

## 6.8 Cargo Pipeline Partial Pressure Control

Cargo Pipeline Partial Pressure Control technology is designed to prevent changes in properties by pressure-balancing the crude oil transfer and preventing VOC emissions from being generated. This technology does not use any power and there is no production of harmful combustion emissions, such as CO<sub>2</sub> and NO<sub>x</sub>. Using a large diameter drop pipe with increased pressure inside reduces the evaporation of the VOCs generated through pressure differentials created within the drop lines when loading cargo. This arrangement helps minimise pressure build-up, and therefore VOC generation in the cargo.

## 6.9 Sequential Transfer of Tank Atmosphere

The Sequential Transfer of Tank Atmosphere (STTA) is a procedure that moves cargo tank atmosphere (VOC and inert gas) sequentially between the cargo tanks before venting to the atmosphere. The movement of cargo tank atmosphere is caused by displacement of the gases during the loading of cargo. This procedure requires installation of a special gas piping arrangement from cargo tank to cargo tank. The tanks also need to be separated into several groups so that the cargo tank atmosphere follows a complex route through a series of tanks before it is emitted from the hull into the atmosphere. The piping arrangement should be designed so that it can be opened and closed at different points to account for different loading programmes. This process is used to avoid the excessive venting of VOC gases to the atmosphere by venting clean inert gases from empty cargo tanks several tanks away from the loading tanks for a large proportion of the loading cycle.

## 6.10 VOCON procedure

The VOCON procedure was developed for safety and to reduce cargo loss. It is a method of limiting manual release to a tank pressure that is close to the true vapour pressure of the cargo, instead of a much lower pressure. The VOCON procedure requires both constant pressure valves and an automated release valve. This procedure allows tank pressures of the cargo tanks to be maintained at a higher mean level with smaller, more accurate automated tank venting releases.

## 7 Operational procedures and Volatile Organic Compound Management Plan

The purpose of the VOC Management Plan is to ensure that tanker operations, to which regulation 15 of MARPOL Annex VI Reg.15.6 applies, prevent or minimise VOC emissions as much as possible. VOC emissions generated during loading and transit should be evaluated and operational procedures developed to ensure the best management practices for preventing/minimising their emission. This includes design changes, devices/equipment and operational procedures to manage VOC emissions, such as cargo tank operating procedures, crude oil washing, tank venting, tank operating pressures and adding of inert gas, all with the intent of preventing the release of gas emissions.

The VOC Management Plan, as required by MARPOL Annex VI Reg.15.6, must be approved by the vessel's Flag State or recognised organisation before obtaining an International Air Pollution Prevention (IAPP) Certificate. Model plans are provided by Flag States and recognised organisations that may be used by the ship operators as guidance when developing a fleet's plan.

The plan should be oil tanker-specific and include data related to:

- The VECS manual.
- The vapour recovery system manual.
- Any other VOC control system manuals.
- The inert gas system manual.
- The crude oil washing manual.
- Operation of P/V valves.

As well as the system manuals, the following drawings should also be included in the plan:

- General arrangement.
- Capacity plan.
- Cargo tank venting system piping diagram.
- Inert gas system piping diagram.
- VECS piping diagram.
- Vapour recovery system or other VOC control system drawings.

The plan should state the designated person responsible for implementing the VOC Management Plan and its associated procedures onboard the vessel. It should also allow the delegation of specific tasks and duties to other personnel. Duties and responsibilities of the designated person should be clearly defined within the plan and that designated person should conform to the VOC Management Plan requirements.

## 8 Ship to facility interface

The interface between ship and shore, ship and production (floating and fixed) or ship and storage (floating and fixed) facilities is based on the configuration of the overall system layouts and specific shore and production field situation.

If an oil tanker is loaded from a fixed production and storage platform or floating facility through a loading buoy or submerged turret, the VOC emission control methods and associated systems are installed on the oil tanker, if applicable.

If an oil tanker is loaded from a shore facility, a floating production or a floating storage unit, VOCs are recovered using a fixed piping arrangement (onshore) or a floating hose arrangement (offshore) from the oil tanker to a VOC recovery plant installed at the shore facility, or on the floating production unit if the VOC processing equipment is installed. These arrangements are designed based on the specific requirements and, if installed, can effectively manage VOC emissions.

## 9 Performance expectations

The performance/recovery rates of the different emission control methods and VOC control systems vary, depending on the method and system. Typical recovery rates are approximately:

- STTA: 30%.
- Cargo Pipeline Partial Pressure Control: 60%.
- Absorption and condensation system: 80%.
- Adsorption method: 90%.
- Thermal oxidation (thermal combustion) system: as high as 99%.

Some of the systems noted in this paper are better suited for transit VOC recovery than for loading and their performance and recovery rates will differ accordingly. Two of the systems best suited for vessel transiting are the backpressure control and the VOCON procedure. These emission control systems have VOC recovery rates estimated at 90% during transit (versus approximately 30% during loading). Cargo Pipeline Partial Pressure Control technology is considered a passive technology and has a midrange performance/recovery rate of approximately 50%. It is design dependent on the amount of VOCs in the cargo being loaded onboard the vessel.



## **10 Measurement and verification of Volatile Organic Compound system effectiveness**

MARPOL Annex VI/15 is the requirement for operating a vapour collection system on tankers. A VOC Management Plan, developed by the ship operator, is the means used to measure and verify VOC system effectiveness.

Record keeping is essential for documenting performance. The form of record keeping depends on the method used to minimise VOC emission from the crude oil cargo. Recording the time and pressure before and after a release is required. This information should be compiled by the ship operator to assess and quantify the extent or degree of VOC release.

## 11 Safety concerns

Since there are several types of VOC control methods and systems on the market, and since cargoes are diverse, performing a robust risk assessment with the manufacturer is recommended. The risk assessment should encompass all the conditions that the installed VOC control methods and systems will be certified to operate under, based on all the potential safety hazards. The risk assessment should include the specific cargo operations the vessel may undergo, including fail safe conditions. The risk assessment should also determine personnel training requirements (see section 12).

## 12 Training

Personnel responsible for overseeing the VOC arrangement onboard the vessel must complete a training programme that has been developed for the purpose and included in the VOC Management Plan.

This training programme should cover:

- The purpose of VOC emission control.
- Overview of the regulations.
- Principles of emission control (including VOC generation systems and tanker pressure control/release systems).
- General methods and systems for the control of VOC emissions.
- Vessel-specific methods and systems and their control.
- Methods of monitoring and recording.
- Hazards and safety issues related to VOC emission control.

## 13 Considerations

### 13.1 Design and installation

VOC emission control systems are designed to create an arrangement that will meet the following objectives:

- Best suited for the vessel's trade route, loading terminal and discharge facility.
- Meets the regulatory requirements.
- Operates efficiently.

The design and installation challenges of the VOC emission control systems will depend on whether passive or active systems or a combination of the two are used. Space restriction may be a factor and additional power requirements will be needed to operate more sophisticated active systems. Design and installation is best considered for new building projects as they allow more flexibility in system selection and installation. Retrofitting of existing vessels is limited to the systems that require higher tank pressure or increased power consumption to operate effectively.

### 13.2 Redundancy of systems and equipment

There are no established operating procedures or regulations to ensure system and equipment redundancy and performance standards. However, Classification Societies and Flag State rules and regulations include requirements for specific equipment, redundant safety systems, testing of safety systems and training. The system and equipment redundancy should be risk assessed and based on the equipment being considered, the type of system that is best suited and its overall design and functional requirements.

### 13.3 Electrical loads

The power requirements, as well as the complexity of the process equipment, are somewhat higher for active systems (reliquification, adsorption and absorption) than passive systems. However, passive systems may not maximise VOC emission removal. A combined arrangement of the two technologies can maximise VOC emission removal while minimising the power required and the energy consumed. This should be evaluated on a case-by-case basis.

### 13.4 Materials

Each VOC emission control system is unique. Depending on its arrangement it may require special materials based on the temperature and corrosiveness of VOC emissions. The materials will be subject to the manufacturer's design and the Classification Society's and Flag State's rules and regulations.



A voice for safety

**Oil Companies  
International Marine Forum**  
29 Queen Anne's Gate  
London SW1H 9BU  
United Kingdom

**T** +44 (0)20 7654 1200  
**E** [enquiries@ocimf.org](mailto:enquiries@ocimf.org)  
**ocimf.org**