

## AIR POLLUTION PREVENTION FROM VOLATILE ORGANIC COMPOUND ON SHUTTLE TANKERS

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### ABSTRACT

*Ecology and preservation of human environment have become a newly one of the most important parts of scientific advancement research. Since they are primarily resolve issues of pollution from the land, today more and more demanding paying attention to pollution from the ships. Air pollution is a serious problem for both human health and the overall ecosystem. Emissions from ships include air pollutants, greenhouse gases and substances that destroy the ozone layer with the consequence of endangering human health and the environment. Emissions of sulfur (SO<sub>x</sub>) and nitrogen oxides (NO<sub>x</sub>) cause acidification. Emissions of volatile organic compounds (VOCs) from tankers, combined with nitrous oxide, participate in the formation of ground-level ozone, which adversely affects the health and the environment. The reason for intense need for a solution to this problem is the growing increase in air pollution emissions and this boat because the emissions of stationary plants significantly reduced the adoption of various environmental laws. This problem has become so primary, so join the international and national regulations on emission limits from ships in some countries, especially those which are exposed to more emissions from ships, which are closer to the sea waterway.*

**Key words:** tanker, emission, volatile organic compounds (VOCs), IMO, MARPOL, MEPC

### 1. INTRODUCTION

When talking about air pollution from ships, primarily though emissions such as nitrogen oxides, sulfur oxides and solid particles that are the product of combustion of fossil fuels in marine diesel engines and which are released into the atmosphere through engine exhaust system. However, except mentioned pollutants particular attention should be paid to the another atmospheric pollutant that is released during commercial operations with liquid cargo tankers, particularly those for the transport of crude oil. In fact, it's about the emission of Volatile Organic Compounds (VOCs) from crude oil tankers. During the loading, navigation and unloading, crude oil is not always in a state of equilibrium in the tank atmosphere, which is a consequence of the release VOCs in the tank atmosphere. Most released gases was emitted in the atmosphere during the loading and unloading of cargo and during the voyage. Light component of VOCs (mainly methane) participate in the greenhouse effect while other components of VOCs (mainly butane and propane), under the common name Non Metan Volatile Organic Compounds (NMVOC), chemically react with NO<sub>x</sub> and participate in the formation of ground-level ozone. According [1] about 114 million tons of crude oil loading operations are made in EU, of which 101,3 million tons is made in the UK (81% from land and 19% from offshore). Further 129 million tonnes (43% from land and 57% from offshore) of crude oil loading operations are made in Norway. It is estimated that these loading operations release 114,000 tons of VOCs, which represents approximately 0.8% of all emissions of VOCs in the EU. Air pollution is mainly regulated by international and regional agreements that control the emission of

VOCs into the atmosphere. The aim of this paper is to present emissions of VOCs from crude oil tankers from the aspect of international and national legal regulations for the prevention of air pollution from ships, as well as technical solutions to reduce emissions of the same.

## **2. VOLATILE ORGANIC COMPOUNDS (VOCs)**

VOCs are a mixture of hydrocarbons, mainly methane, propane, butane and several other gases that are formed by evaporation of crude oil and its products. VOCs are usually divided into non-methane and methane (CH<sub>4</sub>). During the loading or unloading of crude oil tankers from terminals the VOCs can be collected and liquefied with different methods and reused. In the process of crude oil loading cargo tanks are under inert gas, however, it is inevitable that except inert gas an atmosphere of storage tanks contain VOCs which remain from previous cargo. During the crude oil loading mixture of VOCs and inert gas is discharged from the cargo tank and the new emission of VOCs is generated on the surface by evaporation of oil. VOCs emissions from ships compared to total global emissions of VOCs is very small and is moving in the EU around 0.07% of total emissions of VOCs [2]. After crude oil load completion, the level of the crude oil is usually about 300 mms under the tank top. During the voyage that space is protected with mixture of VOCs and inert gas. During the unloading of crude oil level decreasing and the space above is filled with inert gas. During a loading phase cargo level rises again and force out a mixture of VOCs vapour and inert gas from the tank causing atmosphere pollution. After unloading cargo concentration of volatilize cargo inside the tank is not uniform but decreases with increasing height from the surface to the maximum load level in the tank. VOCs emission rate depends on many factors and the most significant are: previous cargo characteristics, characteristics of the loading cargo, temperature, loading rate, turbulence in the atmosphere of storage tank, sea condition, the elapsed time of unloading the previous cargo and vessel condition.

## **3. LEGAL REGULATIONS OF THE CONTROL OF VOCs EMISSION IN MARITIME TRANSPORT OF CRUDE OIL**

At the meeting in London on 26<sup>th</sup> September 1997 IMO Marine Environment Protection Committee (MEPC) adopted regulations in the form of Protocol 1997 which amended the MARPOL 1973/78 in a way that Annex VI of the Convention was accepted, which regulates harmful gases discharges from ships into the atmosphere such as NO<sub>x</sub>, SO<sub>x</sub>, and various halogen gases (CFCs) that destroy the ozone layer. In the third chapter of Annex VI of MARPOL 73/78 Convention brought the rule 15 which defines supervision and control of emissions of VOCs from tankers. Demands of the rule 15 are primarily related to the regulation of emissions in ports and terminals. The Convention adopted a recommendation by the Government of the States Parties to the Protocol 1997 leaves the decision whether and which terminals under their jurisdiction to declare the terminals where the VOCs emission controls. If the Parties of the Protocol 1997 decide to declare port and terminal under their jurisdiction where the supervised discharge of VOCs, concerned government must do the:

1. Must inform the International Maritime Organization (IMO) of the declaration of ports and terminals under their jurisdiction where the supervised discharge of VOCs. Notice must include information of the tanker size that must be monitored, the loads that require emissions control systems, as well as the date of oversight. Such notification must be sent to the IMO at least six months prior to supervision.

2. Must ensure that emissions control systems, which was approved by the government, keeping in mind the safety standards prescribed by the IMO, put in some ports and terminals, and that handling them on safety way and in a way that eliminates the unnecessary retention of the ship.

All tankers are subject to control VOCs emissions in accordance with the provisions rule 15 of Annex VI of MARPOL 73/78 Convention, must have system to collect emission approved by the Registry under whose control the ship is, and carried out in accordance with the standards to control VOCs emissions from tankers prescribed in the circular MSC/Circ.585 [3], taking into account the safety standards prescribed by the IMO and must use such a system during loading of such cargo. Terminals with built-in systems for monitoring VOCs emissions may make the acceptance of tankers which have no such systems during the period of three years after the date specified in the notices to the IMO of declaring the terminal which is supervised by releasing VOCs. Ships compatible with the demands of Annex VI is issued an International Air Pollution Prevention Certificate (IAPP). On the 58<sup>th</sup> session of the MEPC, held on 30<sup>th</sup> June 2008, the guidelines to create a plan for managing VOCs emissions from

crude oil tankers are presented. The purpose of the plan is to prevent or minimize the VOCs emission from tankers. The plan would include written procedures for the optimization of all relevant procedures of the cargo operations on board tankers, which aimed to control and minimize the VOCs emission. It also would include procedures with instructions how to apply inert gas in to cargo tanks and how to proceed with crude oil washing to reduce VOCs emissions. The plan should also include a written program of crew training for the efficient application of prescribed procedures for safe handling with equipment and installations. Furthermore, the plan would appoint the responsible person who would be responsible for the implementation of the Plan on board ship [4].

#### **4. VOCs EMISSION REDUCTION METHODS**

##### **4.1 System for the return of a mixture of VOCs and inert gas on tankers**

The most common way to reduce VOCs emissions during the loading is installing piping for the VOCs and inert gas mixture return to the terminal for further treatment. Capacity of the return pipeline should be approximately equal of loading capacity of the tank. Marking of the return pipeline is prescribed by the rules of classification under whose control the ship is.

##### **4.2 Methods of reducing evaporation rates**

Crude oil decrease of evaporation rates can be achieved by removing volatile components prior to loading for example, heating oil in heaters and separation of produced vapours. Thus, separated vapours can be stored in special containers as LPG [1]. This technology is still in research stage.

##### **4.3 Thermal oxidation**

In the process of thermal oxidation different systems are used for burning a mixture of VOCs and inert gas. Systems are ranked from highly sophisticated catalytic oxidation systems with internal heat recuperations to the simple closed-torches which are now mostly in use. But in terms of atmosphere protection pollution efficiency of this method is questionable since the combustion products as CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> appear. The method of thermal oxidation of mixtures of VOCs and inert gas prevents the emission of VOCs into the atmosphere, but needs to be kept in mind that so irreversibly destroys part of vaporised cargo. According to [5] the rate of evaporation during loading operations moves between from 10% to 60% of the loaded crude oil volume, which means that from 1 m<sup>3</sup> of loaded crude oil develop from 1.1 to 1.6 m<sup>3</sup> of vapour which needs to be hand over to the atmosphere or burn in torches. That means that about 9 million tons of VOCs is emitted per year on a global level, or showing the monetary value of 3 up 3.5 billion USD losses in cargo value [5].

##### **4.4 Absorption**

Absorption of return vapours in cooling organic liquid with low temperature evaporation is a simple method of reliquefaction of returned VOCs from tankers at the terminal during the loading operation. Mixture of VOCs and inert gas are taken to plant at the terminal where they are introduced into the absorber column. In absorber vapour mixture flows to the absorber top and bemoan the chilled liquid absorbent which flows from top to bottom of absorber. Hydrocarbons from a mixture of steam and air melt in absorbent while the air exits into the atmosphere through the line at the top of absorber. Absorbent is separated from hydrocarbons by heating in the column of the separators and hence leads to the cooler, and again in the absorber where the process is repeated. It is necessary to inject methanol to prevent freezing of moist air from the absorber outlet is in the system.

##### **4.5 Adsorption**

Adsorptions imply the accumulation of certain substances in the border area between the two phases (solid/liquid, solid/gas) to a greater concentration than in the interior of adjacent phases. Solid matter is the adsorbent and matter which is adsorbed is adsorptive. Adsorption as a separation process is mainly applied to extract the ingredients from the gas mixture which is in low concentrations. Used as adsorbent are materials that have very large surface area per unit mass or volume of material due to its high porosity (Active carbon, pores > 20 m<sup>-6</sup>, is used as adsorbent for hydrocarbons). Mixture of steam and air introduced into adsorbent and organic molecules accumulate at the boundary surface of adsorbent, and air and CO<sub>2</sub> from the mixture passing through the adsorbent placenta and bleed into the

atmosphere. In the process gradually comes to the saturation of adsorbent, which causes stop of adsorption process. In order to prevent adsorption interruption it regenerates with vacuum pump with the addition of small amounts of air. In order to maintain a constant process two adsorbent placetas are used commonly in a way that one is in the process of adsorption while the other is in the process of regeneration. Liquid hydrocarbons are taken from the separator and thus made VOCs recovery. Effectiveness of this technique varies between 95% and 99% depending on the amount of adsorbent placenta, adsorbent type and degree of regeneration gain.

#### **4.6 Membrane method**

The system is based on the use of semi-permeable membranes for separation of hydrocarbon vapours from the mixture of VOCs and inert gas from cargo tanks. The membrane system has a higher permeability of organic compounds than inorganic. A mixture of VOCs and inert gases is carried out through one side of the membrane while the other side of the membrane supports the vacuum. Organic molecule of vapour selectively migrates through the membrane from where it is removed by vacuum pump. The efficiency of the device is 90% at concentration of 10 g (HC)/m<sup>3</sup> mixture of steam and can grow up to 99.8% at concentrations of 150 mg (HC)/m<sup>3</sup> [6].

The specificity of shuttle tankers led to the need to usage of VOCs emissions as fuel, namely, during the loading from platform tanker need to maintain its position, and for this purpose, it built up with five thrusters for whose drive it is necessary to be provided additionally 5000 kW of power, with the continuous engagement of the main propulsion engine (3000 kW), while for the unloading needed to be provided approximately 6000 kW of power. From this it is evident that fuel consumption is considerable, whether it is a diesel generators or shaft generator. The possibility of using "free" fuel has led to the development of a new generation engine, type MC-GI [7].

### **5. CONCLUSION**

Due this facts at the meeting in London on 26<sup>th</sup> September 1997 IMO Marine Environment Protection Committee (MEPC) adopted regulations in the form of Protocol 1997 which amended the MARPOL 1973/78 in a way that Annex VI of the Convention was accepted, which regulates harmful gases discharges from ships into the atmosphere such as NO<sub>x</sub>, SO<sub>x</sub>, and various halogen gases that destroy the ozone layer. In the third chapter of Annex VI of MARPOL 73/78 Convention brought the rule 15 which defines supervision and control of emissions of VOCs from tankers. Furthermore, Rule 15 governs only systems for VOCs collection from the tanker and does not include other solutions for reducing VOCs emissions. In this paper, are given a brief overview of a few important technical solutions to reduce emissions of VOCs during loading operation at the terminals through a VOCs and inert gas mixture return. Each method carries with it a certain compromise, namely the reduction of VOCs emissions leads to increased emissions of other greenhouse gases especially CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub>. It remains an imperative to explore new ways to reduce VOCs emissions to reduce the pollution of atmosphere.

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