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## Experimental study of the VOC emitted from crude oil tankers

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### ABSTRACT

Light hydrocarbons vaporize to the space between crude oil interface and roof of the storage tank during loading of crude oil tankers in marine oil terminals. When crude oil is loaded to the tank, these hydrocarbons are vented into the atmosphere which is considered as a main source of emission of volatile organic compounds (VOCs) in oil terminals. VOCs emitted from the crude oil not only create severe air pollution problems but also a considerable amount of valuable hydrocarbons are wasted to the atmosphere. On the other hand, VOCs are flammable which create major safety hazards to the loading process. Therefore, the oil industry has largely focused on control of VOCs. In this research, an experimental study was conducted to characterize VOCs emitted from storage tanks of crude oil in a large-scale oil export terminal. Using the industrial data and simple mathematical tools, effect of different parameters on the composition of emitted gases was investigated. Furthermore, an experimental procedure is proposed to assess the potential of a crude oil absorption process for recovering emitted gases. Experimental results showed that the crude oil absorption process can be adapted to the situation of considered marine terminal for recovering this vent stream of emitted gases. This work can help plant engineers to decide on an appropriate strategy to control VOCs.

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**Keywords:** Volatile organic compounds; Oil terminal; Crude oil; Oil tanker

### 1. Introduction

Volatile organic compounds (VOCs) are a wide group of organic compounds which evaporate and release into the atmosphere easily because of their high vapor pressure. Light hydrocarbons, such as methane, ethane and propane, are considered as part of this group of organic compounds. From an environmental point of view, methane is a greenhouse gas which contributes to climate changes and global warming. Non-methane VOCs (NMVOCs) such as ethane, propane, butane, pentane and hexane react with NO<sub>x</sub> to form the ground level ozone which has harmful effects on human health and adverse impacts on plants.

In the recent years, VOC emission has become one of the greatest concerns of oil and process industries where VOC emissions are tightly regulated in different countries

around the world. In the air quality standards developed by US Environmental Protection Agency, the maximum 3-h concentration of hydrocarbon content is  $1.6 \times 10^{-4}$  kg/m<sup>3</sup> (0.24 ppm), not to be exceeded for more than a year (Khan and Ghoshal, 2000). The recently passed European Community stage emissions limit is 35 g total organic compounds (TOC) per cubic meter gasoline loaded (Khan and Ghoshal, 2000). The 1999 Gothenburg Protocol to abate acidification, eutrophication and ground-level ozone was adopted to set emission levels for four pollutants including sulfur, NO<sub>x</sub>, VOCs and ammonia. Once the protocol is fully implemented, European VOC emissions should be reduced by 40% compared to 1990 (Derwent et al., 2010).

Production, storage and transport of crude oil and gasoline produce emissions of VOCs (De Luchi, 1993). Among these operations, two are encountered as the main sources of VOC

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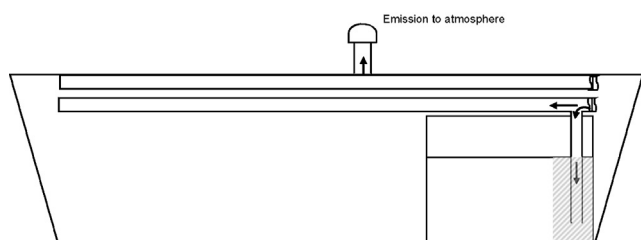
<http://dx.doi.org/10.1016/j.psep.2013.10.005>

### Nomenclature

$C_i$	concentration of component $i$ , ( $\text{mol}/\text{m}^3$ )
$T$	time, (s)
$u$	velocity in the direction of tank height, (m/s)
$D_{im}$	diffusion coefficient of component $i$ in gas mixture
$C_{i0}$	concentration of component $i$ at liquid–gas interface, ( $\text{mol}/\text{m}^3$ )
$C_{oi}$	concentration of component $i$ at time $t=0$ , ( $\text{mol}/\text{m}^3$ )
$h$	height of gas layer in the tank, (m)

emissions in oil terminals. The first source is emissions from storage tanks and the second one is emissions from the transport of crude oil during loading/unloading operations into the oil tankers. Emissions from storage tanks are discussed widely in literature (Paulauskienea et al., 2009; Rota et al., 2001; Karbassi et al., 2009; Pasley and Clark, 2000). Paulauskienea et al. (2009) conducted a study on VOC concentrations in oil terminal storage tank parks and evaluated the effect of oil product type, the level of an oil product in the storage tank, storage tank construction (capacity, type of insulation) and the meteorological conditions. There are few published works in open literature on emissions from crude oil tankers (Lee et al., 2013; Huang et al., 2011; Martens et al., 2001; Rudd and Hill, 2001). Martens et al. (2001) developed a simulation program for computation of the evaporation rate and emission from various crude oil types and procedures of cargo handling. They calculated NMVOC emission reduction and energy consumption for liquefaction and absorption processes as possible process plants for VOC recovery installed on shuttle tankers and proposed measures to reduce emissions on tankers.

There are different processes for reducing VOC emissions, such as adsorption, cryogenic condensation, absorption, thermal oxidation, catalytic oxidation and membrane separation which are extensively discussed in literature. An overview of the published research concerning VOC abatement techniques is given in Table 1. As seen in this table, VOC emissions originate from different sources in process industries and operations in oil terminals (storage, loading and unloading) is considered as one of the main sources of VOCs emissions to the environment. During loading, light hydrocarbons of crude oil vaporize and occupy the spacing between the crude oil and roof of the storage tank. As shown in Fig. 1, when the crude oil is loaded into a marine tanker, this vapor is displaced into a vent facility on the tanker deck and released into atmosphere. The vent stream is considered as a major source of VOC emission in oil terminals. In many countries, emissions



**Fig. 1 – Schematic of crude oil loading into marine tankers and VOC emission source during loading operation (Benkert, 1987).**

from tank vessels are not subject to control. However, VOCs emitted from the crude oil not only create severe air pollution problems but also a considerable amount of valuable hydrocarbons are wasted to atmosphere. On the other hand, these gases are flammable, introducing safety hazards to the loading process.

Hydrocarbon vapor emissions may be controlled by any of several available technologies to recover or destroy hydrocarbons (Rudd and Hill, 2001; Benkert, 1987). In selecting a vapor control process for a given situation, determination of two factors is crucial. The first one is the amount of evaporation loss during crude oil loading operations of tankers. This can be achieved using the correlations or equations reported in literature. The latest versions of emission estimation equations developed by American Petroleum Institute (API, 2009) can be used for this purpose. The next factor is determining the nature of the vent stream, changes in the composition and amount of vent stream during the loading operation. In fact, VOCs recovery technique or destruction may differ from one terminal to another depending on the composition of emitted gases and the amount of valuable hydrocarbons shown in the vent stream.

In the present work, experimental studies were carried out on the nature of gases emitted from crude oil tankers. The vapor stream composition was determined based on several sets of experimental data gathered from a large scale terminal. Based on these data, a simple mathematical model was developed. Effect of parameters such as crude oil characteristics and shipment conditions were investigated on minimizing VOC emission in marine terminals. Attention was also given to the absorption process as an appropriate choice of recovery and by performing an absorption test experiment, the potential of two types of crude oils in absorbing waste stream gases was investigated. It is important to mention that most studies reported in literature were focused on recovery methods for low concentration VOC vent streams while this study deals with high concentration crude oil vapor emission vent stream and effect of industrial operation conditions on the vapor emission was also investigated.

## 2. Experiments

Experimental studies were carried out in a large scale marine oil terminal in which crude oil is delivered and loaded into the marine tankers by means of two jetties. Samples were gathered from 10 marine tankers berthed in both jetties in various operating conditions and from different storage tanks in complete loading cycles.

### 2.1. Gas sampling apparatus and procedure

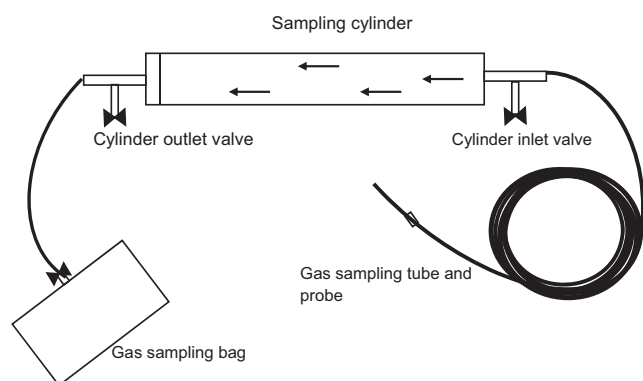
The apparatus shown in Fig. 2 was used to acquire samples from gases in the storage tanks of oil tankers. The sampling device consists of the following accessories: a 200 mL stainless steel gas sampling cylinder, an earth cable to prevent accidents resulting from static electricity, aluminum bags of 1L, 5L and 10L capacity as gas sample containers, 20 m PTFE (Teflon) sampling tube of 5 mm inside diameter and 7 mm outside diameter and valves with a connection size of 1/8" to transfer the gas sample from gas sampling cylinder to the aluminum bag.

Before taking the gas samples, pressure of the storage tank and type of crude oil was recorded. Furthermore, the level of

**Table 1 – Overview of investigations on VOC emission and control measures.**

Reference	Description
Lee et al. (2013)	Optimization studies on a condensation system for VOC recovery during crude oil loading operations
Gupta and Verma (2002) Dwivedi et al. (2004)	Investigation on cryogenic condensation followed by adsorption for removal of VOCs Study on the removal of VOCs by condensation using liquid nitrogen and adsorption by activated carbon fiber
Liu et al. (2006)	Investigation on the separation of gasoline vapor from nitrogen by hollow fiber composite membranes
Everaert and Baeyens (2004)	Experimental studies on a catalyst-coated sintered metal fleece for Catalytic combustion of VOCs
Jodeiri et al. (2010)	Experimental studies on a counter-diffusive reactor for the destruction of natural gas glycol dehydration unit emissions
Ghoshal and Manjare (2002) Papanicolaou et al. (2009)	Study on the selection of appropriate adsorption techniques for recovery of VOCs Investigation on adsorption capacity of activated coals for NO, SO <sub>2</sub> , C <sub>3</sub> H <sub>6</sub> and a mixture of light hydrocarbons
Chuang et al. (2003) Nastaj et al. (2006)	Model development for the adsorption of C <sub>6</sub> H <sub>6</sub> , CCl <sub>4</sub> and CHCl <sub>3</sub> onto activated carbon Theoretical study of combined vacuum/temperature swing adsorption for removing VOC from air streams
Liu et al. (2000)	Simulation of Pressure Swing Adsorption for recovery of butane, benzene and heptane vapors from nitrogen
Park et al. (2008) Bay et al. (2006) Ozturk and Yilmaz (2006)	Development of a jet loop reactor to decrease the concentration of hydrophobic VOCs Investigation on vapor-liquid equilibrium of some VOCs for absorption in biodiesel Experimental studies on absorption of VOCs into vegetable and lubricant oils and water in a bubble column
Roizard et al. (2009)	Investigation on a liquid-vapor membrane separation for regeneration of the solvent after VOCs' absorption
Dubray and Vanderschuren (2004)	Study on a combined absorption/adsorption process to reduce the emission of hydrophilic VOCs
Lalanne et al. (2008)	Development of a bio scrubber to treat a mixture of VOCs by absorption in aqueous solutions of soluble cutting oil
Nikolajsen et al. (2006)	Development of an adsorber with sintered metal fibers for purification of low-content VOCs gas-streams
Yazbek and Delebarre (2004) Shine (1996) Bhatia and Dinwoodie (2004) Huang et al. (2011) De Luchi (1993)	Modeling of VOCs (methanol and acetone) condensation in a fluidized bed A review of methods for estimating VOC emissions from batch processing facilities Study on the crude oil loss rates and loss sources in North Sea shipping operations Study on the evaluation methods for oil vapor emission Estimation of upstream VOC and petroleum refinery emissions

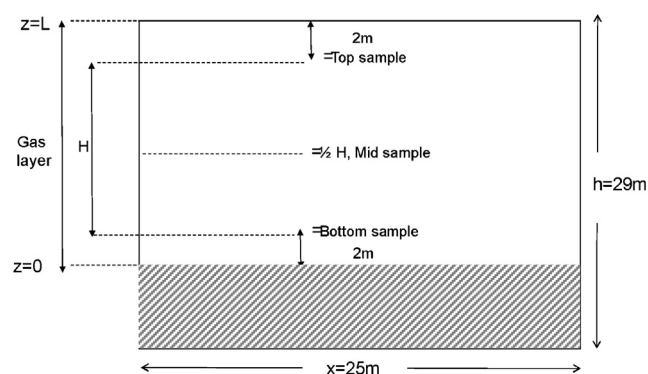
crude oil in the tank and temperatures of liquid and vapor were measured by means of a tank measuring instrument (MMC portable tank gauging device model D-2401-2). Total hydrocarbon content and oxygen content of gases were also measured by means of a portable explosion-proof gas detector. Sampling locations were determined to be at top, middle and bottom of the gas layer in the tank as shown in Fig. 3. The sampling tube was lowered to the specified depth from the tank hatch on the tanker deck and the gas was sucked into the sampling cylinder. The collected gas was stored in sample collection bags and analysis of the gas composition was carried out in less than an hour after sampling to minimize the possible changes in the composition of the collected sample

**Fig. 2 – Gas sampling apparatus.**

gas over the time (as a result of changes in temperature and VOCs diffusing off the sample bag).

## 2.2. Absorption test equipment and procedure

An absorption test was carried out to assess whether or not the crude oils available in the terminal are suitable for absorption of light hydrocarbons presented in the emitted gases. This experiment also helped to compare the absorption ability of different types of crude oils. Absorption ability was determined by measuring the difference between the amount of hydrocarbon concentration in the inlet and outlet of the test set up. Absorption experiments were carried out in a

**Fig. 3 – Sampling locations in the tank.**

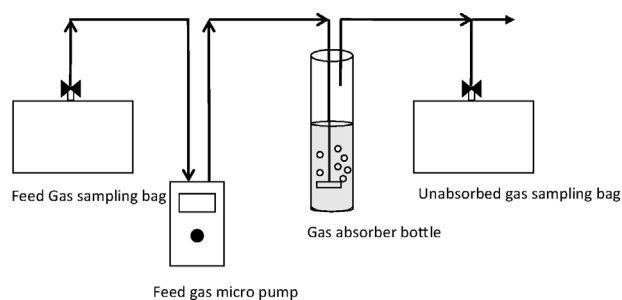


Fig. 4 – Schematic of the absorption test equipment.

laboratory scale set-up schematically shown in Fig. 4. This equipment consisted of a gas washing bottle (as absorption column), a feed gas container, a gas container for unabsorbed gas exiting in the absorption column and a feed gas pump. The absorption experiments were performed at room temperature.

To choose a suitable absorbent, different criteria, such as viscosity, solubility of gases in the absorbent and the costs of the absorbent, should be considered. Martens et al. (2001) studied reabsorption of VOCs in crude oil and their simulation studies showed 75–80 wt.% NMVOC emission reduction. Besides availability of crude oil in oil terminals, using crude oil as the absorbent eliminates the need for solvent stripping and related costs. In this case, the saturated oil from the absorber can be returned back to the cargo storage tanks in the oil terminal which are equipped with floating roofs with negligible emission. Therefore, in this study, crude oil was considered as the absorbent.

Two types of crude oils available in the storage tanks of the target terminal were used as the absorbent in two separate experiments. Characteristics of each type of crude oil, including specific gravity, API gravity, viscosity, vapor pressure and pour point are reported in Table 2. The vapor collected from the storage tanks of marine vessels was used as the feed gas in the absorption test experiment.

The gas washing bottle with a total volume of 100 mL was filled with crude oil as the absorbent. The feed gas was contained in a sample bag with a total volume of 10 L and was introduced through the absorption chamber (gas washing bottle) by means of a micro pump. The gas flow rate was adjusted to 1 L/h to allow a continuous and slow flow of the feed gas to the absorption chamber. The feed gas entered near the bottom of the bottle, contacting the crude oil as flowed up to the gas outlet at the top of the bottle. A sample from unabsorbed gas was taken in every 1 h and analyzed by a gas chromatograph. The test experiment was continued for 6 h, thus, 6 samples were taken for each crude oil type. By comparing the hydrocarbon content of gases in the inlet and outlet of the absorption bottle, the absorption ability of crude oils was determined.

### 2.3. Gas analysis

Gas chromatography was used for analyzing the gases collected from storage tanks of marine tankers and also for analyzing the gases collected from the outlet of absorption test equipment. Gas chromatograph (Varian model 3800) with flame ionization detector (FID) was used for analysis of hydrocarbon gases including  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ , and  $\text{C}_6\text{H}_{14}$ . Analysis of other inorganic gases including  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{S}$  was performed using Orsat analyzer (Apex model VSC-33).

### 3. Mathematical approach

Due to the marine custody transfer regulations and some limitations on the loading operation of marine tankers, it was not possible to investigate the effect of changes in some parameters such as temperature and pressure of the storage tanks experimentally. However, a mathematical model was used to predict such effects. In order to properly design a vapor recovery unit, the first step is to define the composition of vapors which should be introduced to the recovery unit during crude oil loading operation. If a model is available for a specific oil terminal, there is no need to conduct several experiments. The model can indeed be improved in different aspects; however, if it predicts the composition, it would be satisfactory for most industrial applications.

To develop such a model, the following assumptions were made:

- (1) No reaction takes place in the storage tank.
- (2) System temperature is constant. According to the gathered data given in Table 3, the difference between the temperature of crude oil stored and the ambient temperature is negligible (with a standard deviation of  $0.05^\circ\text{C}$ ) and since there is no source of heat generation or heat consumption in the tank, temperature variation in the tank is neglected.
- (3) Fluid density is constant.
- (4) Transfer of components in only axial direction was considered and transport of components in other directions is negligible.
- (5) Molecular diffusion coefficients are constant.
- (6) Diffusion occurs from liquid phase to gas phase and diffusion in the opposite direction is negligible.
- (7) System boundaries are considered constant as shown in Fig. 1. It is important to note that there is a moving boundary during loading. However, with the rate of loading of  $4770\text{--}8585\text{ m}^3/\text{h}$  (which is the case for the experiments of this work) and the tank dimension of  $25\text{ m} \times 25\text{ m} \times 29\text{ m}$ , a rather slow velocity was observed. Thus, it is a reasonable simplification to consider the boundaries at  $z=0$  and  $z=L$  instead of a moving boundary. For example, samples S9–S11 were from the same tanker and the total crude oil loaded to this tanker was  $174,886\text{ m}^3$  with the rate of  $8585\text{ m}^3/\text{h}$  which lasted around 21 h to fill the tanks.

Considering these assumptions, the following diffusion-convection equation can be derived from mass conservation equation:

$$\frac{\partial C_i}{\partial t} + u \frac{\partial C_i}{\partial z} = D_{im} \frac{\partial^2 C_i}{\partial z^2}$$

$$C_i(z, 0) = C_{0i}$$

$$C_i(0, t) = C_{i0}, \quad \frac{\partial C_i(h, t)}{\partial z} = 0$$
(1)

This equation was solved by the finite difference implicit method and the results were used to determine the concentration profile of components along the tank height. For solving this equation, the equilibrium concentration of components in the vapor-liquid interface was calculated considering the constant boundaries conditions using Peng–Robinson equation of state (Peng and Robinson, 1976).



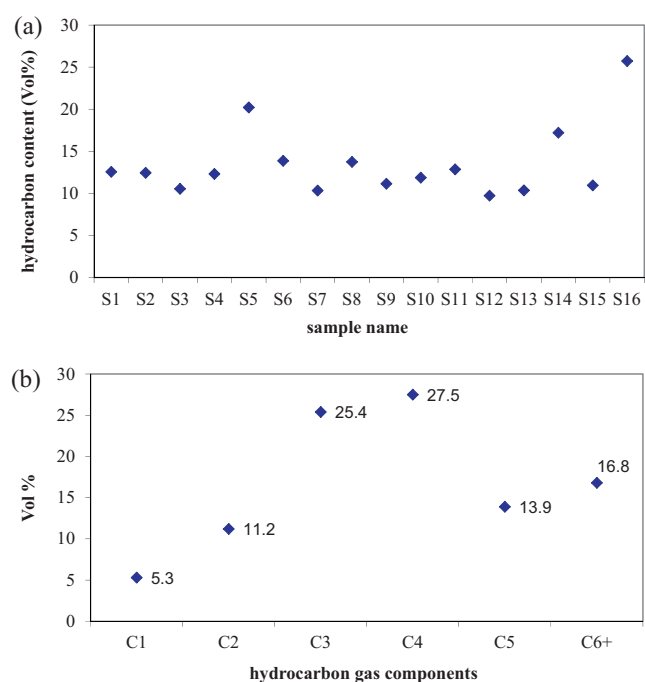
**Table 2 – Properties of crude oils.**

Specification	Test method	Crude oil No. 1	Crude oil No. 2
Specific gravity at 15.5 °C	ASTM D 1298	0.8583	0.8792
API	ASTM D 1298	33.36	29.44
Kinematic viscosity at 10 °C (cSt)	ASTM D 445	21.49	38.71
Reid vapor pressure (kPa)	ASTM D 323	54.39	48.53
Pour point (°C)	ASTM D 97	-15	-24

#### 4. Results and discussion

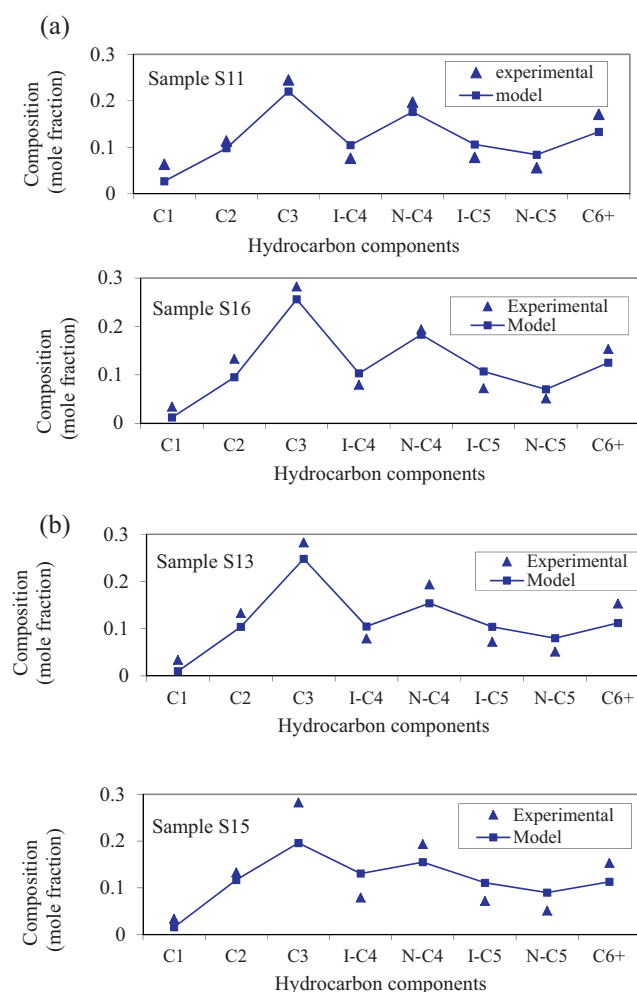
Several sets of experimental data were gathered from different tanks at various operating conditions given in Table 3. Composition of emitted gases was determined by the method described in the experimental section and reported in Table 4. Fig. 5 demonstrates the hydrocarbon content of different gas samples and average concentration of hydrocarbons (C<sub>1</sub>–C<sub>6+</sub>) obtained by gas chromatography. When recovery methods are considered as a measure for controlling VOC emission, the concentration of hydrocarbon gases in the waste stream becomes very important. As shown in Table 4, almost 13% of emitted gases are hydrocarbons and based on the results reported in Fig. 5, propane and butane constitute the major components of hydrocarbon gases in the waste stream which is in agreement with studies conducted by Martens et al. (2001).

Experimental data are compared with the model predictions in Fig. 6. This figure demonstrates that there is a close agreement between experimental data and model predictions (mean error for S11 = 0.02, S16 = 0.02, S13 = 0.03 and S15 = 0.04). The results for the rest of the samples are not provided because they were mostly similar with the error in the range of 0.02–0.05. It can be noted that experimental values fall below the model predictions for i-C<sub>4</sub>, i-C<sub>5</sub> and n-C<sub>5</sub> concentrations. This deviation can be explained by the fact that there is a possibility of liquefying heavier components in the sample bags before performing gas chromatography.



**Fig. 5 – (a) Hydrocarbon content of gas samples and (b) average concentration of hydrocarbon gas components.**

As marine tankers carry different grades of crude oils in the same cargo tanks, there is a specific amount of vapor in the tank from previous cargo. Also, washing the tanks affects the emission during the loading operation. The tanks can be cleaned by water, but slop tanks on the tanker are needed to store the oily water mixture. There is another method for tank washing, known as crude oil washing (COW). In this method, the crude oil is injected on the tank walls, dissolving the sediments sticking to the tank and converting them into useful cargo which can be stored same as typical crude oil with no need for a slop tank. To investigate the effect of tank initial condition on the concentration of emitted gases, samples were collected from different tanks in various conditions and results are compared in Fig. 7. S3 sample was collected from a tank washed by water while S8 sample was from a tank washed by crude oil and S16 sample was gathered from a tank without washing during the last three loading operations. As can be seen in Fig. 7, the hydrocarbon content of samples from



**Fig. 6 – Hydrocarbon gas composition of samples collected from (a) tanks filled with crude oil No. 2 and (b) tanks filled with crude oil No. 1.**

**Table 3 – Operating conditions during experimental data gathering.**

Sample name	Crude oil type	Crude oil temperature (°C)	Gas temperature (°C)	Ambient temperature (°C)	Tank pressure (kPa)	oil loading rate (m <sup>3</sup> /h)	Loading (%)	Sampling location	Total hydrocarbon content (Vol %)
S1	No. 2	32.3	33.4	35	106.23	8585	10	Middle	12.56
S2	No. 2	32.2	33.3	35	106.23	8585	0	Middle	12.45
S3	No. 2	31.5	32.4	34	105.84	4770	50	Top	10.54
S4	No. 2	32.2	33.3	35	106.23	8585	10	Top	12.32
S5	No. 1	32.4	33.1	36	103.32	8585	30	Bottom	20.21
S6	No. 2	31.2	32.5	34	106.23	8585	30	Middle	13.84
S7	No. 1	32.3	32.8	36	103.32	4770	10	Middle	10.34
S8	No. 2	31.2	32.5	34	106.23	8585	0	Bottom	13.74
S9	No. 2	32	33.2	34	106.23	8585	10	Middle	11.15
S10	No. 2	31.1	31.3	34	106.23	8585	10	Bottom	11.87
S11	No. 2	32.1	32.8	34	106.23	8585	30	Middle	12.86
S12	No. 2	31.3	32.8	34	106.23	8585	60	Middle	9.73
S13	No. 1	32.3	32.8	36	103.32	4770	30	Middle	10.36
S14	No. 1	32.3	33.1	36	103.32	8585	10	Middle	17.21
S15	No. 1	30.1	30.3	28	105.32	8585	30	Middle	10.95
S16	No. 2	29.5	29.6	27	105.34	8585	30	Middle	25.72

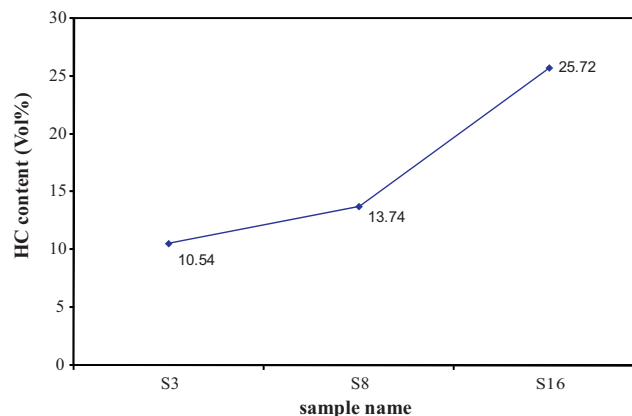
**Table 4 – Average composition of emitted gases from storage tanks of marine vessels.**

Volume (%)	Components
13	HC
70	N <sub>2</sub>
10	CO <sub>2</sub>
5	O <sub>2</sub>
2	Other components such as H <sub>2</sub> S

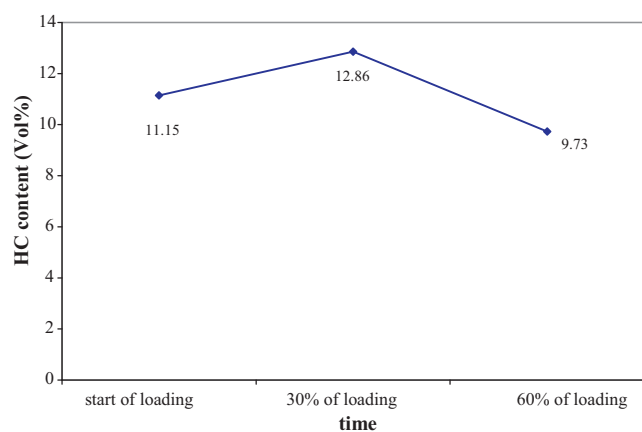
the tank without washing (S16) is 87% more than a sample collected from a tank washed with crude oil (S8) and 144% more than a tank washed with water (S3). Therefore, it can be concluded that washing storage tanks before loading a fresh cargo significantly reduces the hydrocarbon emission in marine terminals.

As described in Section 2.1, samples are taken from different locations in the tank. To examine the effect of sampling position, S1 and S4 (given in Table 3) are collected at the same operating conditions but from different locations in the tank. Results showed that the hydrocarbon content slightly changes from 12.56% in the middle of the tank to 12.32% at the top. This trend can also be seen when comparing S9 and S10 samples with 11.15% HC content in the middle and 11.87% at the bottom. At the beginning of loading, this difference is even more. Comparing S8 and S2 samples shows that there is 12.45% HC content in the middle and 13.74% at the bottom. This should specially be considered in designing the downstream VOC control unit to be aware of lower gas concentration entering the unit at the beginning of operation.

The vapor emitted from the tanks to the atmosphere has two main sources: one is the gases remained in the tank from the previous cargo loading/unloading operation and the other source is the evaporation of crude oil during loading. Therefore, it can be expected that the hydrocarbon content of the emitted gas from the tank is increased as the loading time passes. It is also expected that the increasing trend in the hydrocarbon concentration continues until pressure of the tank reaches the maximum allowable pressure and the tanker releases the gases to the atmosphere to balance the pressure. After this venting operation, the hydrocarbon content of the vent decreases significantly. Samples were gathered and analyzed in order to investigate the changes in the hydrocarbon content of emitted gases over the loading time during crude oil loading operation. The hydrocarbon content of three samples extracted from the same tank at various loading times is shown in Fig. 8. The samples were taken at the start of



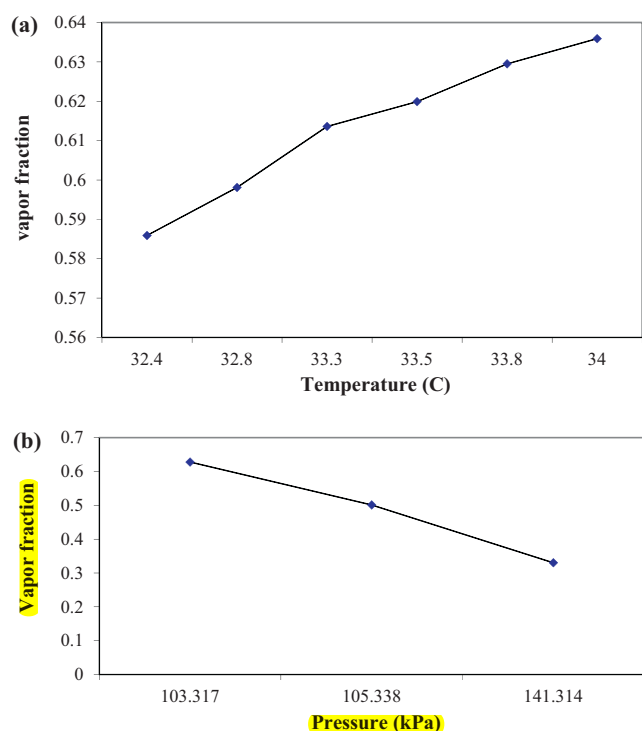
**Fig. 7 – Effect of tank condition on hydrocarbon content of emitted gases.**



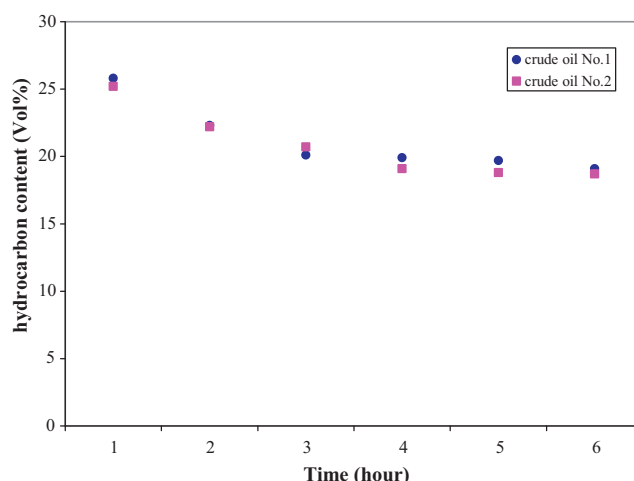
**Fig. 8 – Changes in hydrocarbon content of emitted gases over loading time.**

loading, after loading 30% of the total compartment and after 60% of the loading. As shown in Fig. 8, when 30% of total crude oil is loaded into the tanker, the hydrocarbon content of gas samples increases 15% compared to the start of the loading operation. In contrast, when 60% of the loading is elapsed, this amount is decreased to 9.73%. This trend can be explained by the fact that gases are vented to the atmosphere due to an increase in the tank pressure up to the operational allowable pressure of the tanker vessel. In fact, this venting operation is the source of vapor emission and this problem would be solved if there were a pipeline available to return the gases through a vapor recovery or the destruction unit.

Temperature of the crude oil loaded into the storage tank is another parameter which affects the amount of crude oil vaporization. Fig. 9(a) illustrates the effect of crude oil temperature on the fraction of liquid that turns into vapor in the tank at 106.18 kPa. As shown in this figure, an increase in the temperature of crude oil leads to an increase in the



**Fig. 9 – Vaporization of crude oil in (a) tank operating temperatures and (b) operating pressures.**



**Fig. 10 – Changes in hydrocarbon content of gases during absorption experiment.**

evaporation of crude oil and consequently hydrocarbon gas emission increases from the tank. Since the temperature has a significant effect on emission, it is important to maintain the temperature of crude oil as low as possible. In the geographic regions with warm weather condition, this can be done by insulating the pipelines, applying insulating colors on the storage tanks walls or performing the loading operation during the minimum average temperature in the day.

Another parameter affecting vapor emission is pressure of the storage tank. In order to reduce the vapor emission, pressure of the storage tank should be maintained at slightly higher than the atmospheric pressure (as recorded in Table 3) by injecting an inert gas into the empty space of the storage tank. Fig. 9(b) illustrates the effect of tank pressure on the fraction of liquid that turns into vapor in the tank at 30°C. As shown in this figure, an increase in the pressure of the tank leads to a decrease in the evaporation of crude oil and consequently less gas is emitted from the tank. This figure shows the importance of keeping a positive pressure on crude oil surface as high as possible by considering the safety guidelines of marine vessels.

In the absorption experiment, VOCs were absorbed by two different absorbents, namely crude oils Nos. 1 and 2. Absorption abilities of these two crude oils were measured and are presented in Fig. 10. The feed gas was a vapor sample from a tanker with hydrocarbon concentration of 27 vol%. The absorption test was performed for 6 h and samples were taken every hour from the gas exiting the absorption test setup. Changes in the composition of the absorbed gas were confirmed using gas chromatography. As illustrated in Fig. 10, hydrocarbon content of the gas is reduced to 19% for crude oil No. 1 and 18% for crude oil No. 2. Furthermore, in designing the absorption facilities, other characteristics such as viscosity and pour point of the absorbent are also important. Pour point is one of the key factors in determining the operating temperature and according to typical operating temperatures of absorption units (5–15 °C) both crude oils are in an acceptable range. Viscosity of the absorbent is another parameter that affects pump selection. Also as showed by Ozturk and Yilmaz (2006) lower viscosity causes higher diffusivity of VOCs in oils. Therefore, lower viscosity of crude oil No. 1 should be taken into account. However, by comparing the absorption ability, crude oil No. 2 shows a higher absorption.

It can also be seen from Fig. 10 that the removal of VOCs from the inlet gas decreases by time due to saturation of the absorbent. As the absorption continues, concentration of light hydrocarbons in the crude oil increases, so decreases the absorption efficiency. It must be mentioned that the absorbent volume in the column was maintained constant and no fresh crude oil was supplied into the absorption chamber during the experiment. Therefore, a limited amount of light hydrocarbons can be absorbed in the given time interval. However, to recover a substantial part of the emitted VOC by absorbing it in crude oil, absorption has to take place at an elevated pressure and low temperature while in these experiments the focus was on the comparison between the absorption ability of two available crude oils. Otherwise, cooling and pressurizing should be taken into account.

## 5. Conclusion

In the present work, experimental investigations were performed on gases emitted from storage tanks of crude oil marine tankers and effect of different parameters on gas emission was determined by experiment and mathematical analysis. It was found that the emitted vapor is comprised of volatile organic compounds including methane, ethane, propane, butane, pentane, hexane and a small amount of heavier components. It was also observed that propane and butane constitute the major components of hydrocarbon gases in the vent stream. According to the emitted gas analysis, it was concluded that in average, gas is composed of 13% hydrocarbons, 70% nitrogen, 10% carbon dioxide, 5% oxygen and 2% other compounds such as hydrogen sulfide. **Furthermore, effect of temperature and pressure was investigated and it was confirmed that crude oil gas emission increases with increasing the oil temperature and decreasing the tank pressure.** Effect of shipment conditions was also determined and it was observed that crude oil loading into the storage tanks, which are not washed and cleaned from previous shipments, considerably increases the hydrocarbon content of emitted gases. Experimental data also showed that hydrocarbon content of emitted gases increases over the loading time. In addition, an absorption experiment was carried out on two types of crude oils and absorption ability of crude oils was compared with each other where crude oil No. 2 showed higher absorption ability. The results of this study may be applied to good loading practice (GLP) in large-scale oil export terminals.

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## References

2009. *API manual of petroleum measurement standards, chapter 19.5, Atmospheric hydrocarbon emissions from marine vessel transfer operations, first ed.*
- Bay, K., Wanko, H., Ulrich, J., 2006. *Absorption of volatile organic compound in biodiesel. Chemical Engineering Research and Design* 84 (A1), 22–28.
- Benkert, W.M., 1987. *Controlling Hydrocarbon Emissions from Tank Vessel Loading. Committee on Control and Recovery of Hydrocarbon Vapors from Ships and Barges. National Academy Press, Washington, D.C.*
- Bhatia, R., Dinwoodie, J., 2004. *Daily oil losses in shipping crude oil: measuring crude oil loss rates in daily North Sea shipping operations. Energy Policy* 32, 811–822.
- Chuang, C.L., Chiang, P.C., Chang, E.E., 2003. *Modeling VOCs adsorption onto activated carbon. Chemosphere* 53, 17–27.
- De Luchi, M.A., 1993. *Emissions from the production, storage, and transport of crude oil and gasoline. Journal of Air and Waste Management Association* 43, 1486–1495.
- Derwent, R.G., Witham, C.S., Utembe, S.R., Jenkin, M.E., Passant, N.R., 2010. *Ozone in Central England: the impact of 20 years of precursor emission controls in Europe. Environmental Science and Policy* 13, 195–204.
- Dubray, A., Vanderschuren, J., 2004. *Mass transfer phenomena during sorption of hydrophilic volatile organic compounds into aqueous suspensions of activated carbon. Separation and Purification Technology* 38, 215–223.
- Dwivedi, P., Gaur, V., Sharma, A., Verma, N., 2004. *Comparative study of removal of volatile organic compounds by cryogenic condensation and adsorption by activated carbon fiber. Separation and Purification Technology* 39, 23–37.
- Everaert, K., Baeyens, J., 2004. *Catalytic combustion of volatile organic compounds. Journal of Hazardous Materials B109, 113–139.*
- Ghoshal, A.K., Manjare, S.D., 2002. *Selection of appropriate adsorption technique for recovery of VOCs: an analysis. Journal of Loss Prevention in the Process Industries* 15, 413–421.
- Gupta, V.K., Verma, N., 2002. *Removal of volatile organic compounds by cryogenic condensation followed by adsorption. Chemical Engineering Science* 57, 2679–2696.
- Huang, W., Bai, J., Zhao Sh Lv, A., 2011. *Investigation of oil vapor emission and its evaluation methods. Loss Prevention in the Process Industries* 24, 178–186.
- Jodeiri, N., Wu, L., Mmbaga, J., Hayes, R.E., Wanke, S.E., 2010. *Catalytic combustion of VOC in a counter-diffusive reactor. Catalysis Today* 155, 147–153.
- Karbassi, A.R., Nabi Bidhendi, G.R., Moattar, F., Mahin Abdollahzadeh, E., 2009. *Role of oil storage tank structure in the prevention emission of hydrocarbon pollution. Journal of Environmental Studies* 35 (50), 73–82.
- Khan, F.I., Ghoshal, A.K., 2000. *Removal of volatile organic compounds from polluted air. Journal of Loss Prevention in the Process Industries* 13, 527–545.
- Lalanne, F., Malhautier, L., Roux, J.K., Fanlo, J.L., 2008. *Absorption of a mixture of volatile organic compounds (VOCs) in aqueous solutions of soluble cutting oil. Bioresource Technology* 99, 1699–1707.
- Lee, S., Choi, I., Chang, D., 2013. *Multi-objective optimization of VOC recovery and reuse in crude oil loading. Applied Energy* 108, 439–447.
- Liu, Y., Feng, X., Lawless, D., 2006. *Separation of gasoline vapor from nitrogen by hollow fiber composite membranes for VOC emission control. Journal of Membrane Science* 271, 114–124.
- Liu, Y., Ritter, J.A., Kaul, B.K., 2000. *Simulation of gasoline vapor recovery by pressure swing adsorption. Separation and Purification Technology* 20, 111–127.
- Martens, O.M., Oldervik, O., Neeraas, B.O., Strøm, T., 2001. *Control of VOC emissions from crude oil tankers. Marine Technology* 38 (3), 208–217 (10).
- Nastaj, J.F., Ambrozek, B., Rudnicka, J., 2006. *Simulation studies of a vacuum and temperature swing adsorption process for the removal of VOC from waste air streams. International Communications in Heat and Mass Transfer* 33, 80–86.
- Nikolajsen, K., Kiwi-Minsker, L., Renken, A., 2006. *Structured fixed-bed adsorber for low concentration VOC removal. Chemical Engineering Research and Design* 84, 562–568.



- Ozturk, B., Yilmaz, D., 2006. Absorptive removal of volatile organic compounds from flue gas streams. *Process Safety and Environmental Protection* 84, 391–398.
- Papanicolaou, C., Pasadakis, N., Dimou, D., Kalaitzidis, S., Papazisimou, S., Foscolos, A.E., 2009. Adsorption of NO, SO<sub>2</sub> and light hydrocarbons on activated Greek brown coals. *International Journal of Coal Geology* 77, 401–408.
- Park, B., Hwang, G., Haam, S., Lee, C., Ahn, I.S., Lee, K., 2008. Absorption of a volatile organic compound by a jet loop reactor with circulation of a surfactant solution: performance evaluation. *Journal of Hazardous Materials* 153, 735–741.
- Pasley, H., Clark, C., 2000. Computational fluid dynamics study of flow around floating-roof oil storage tanks. *Journal of Wind Engineering and Industrial Aerodynamics* 86, 37–54.
- Paulauskienea, T., Zabukasb, V., Vaitiekūnasc, P., 2009. Investigation of volatile organic compound (VOC) emission in oil terminal storage tank parks. *Journal of Environmental Engineering and Landscape Management* 17 (2).
- Peng, D.Y., Robinson, D.B., 1976. A New two-constant equation of state. *Industrial & Engineering Chemistry Fundamentals* 15, 59–64.
- Rota, R., Frattini, S., Astori, S., Paludetto, R., 2001. Emissions from fixed-roof storage tanks: modeling and experiments. *Industrial & Engineering Chemistry Research* 40, 5847–5857.
- Roizard, D., Lapique, F., Favre, E., Roizard, C., 2009. Potentials of pervaporation to assist VOCs' recovery by liquid absorption. *Chemical Engineering Science* 64, 1927–1935.
- Rudd, H.J., Hill, N.A., 2001. Measures to reduce emissions of VOCs during loading and unloading of ships in the EU. In: AEA Technology Environment report No. EAT/ENV/R/0469.
- Shine, B., 1996. Methods for estimating volatile organic compound emissions from batch processing facilities. *Journal of Cleaner Production* 4, 1–7.
- Yazbek, W., Delebarre, A., 2004. Modeling of volatile organic compounds condensation in fluidized bed. *Chemical Engineering Science* 59, 283–297.