

# SIMULATION OF VOC EMISSION DURING LOADING OPERATIONS IN A CRUDE OIL TANKER

(DOI No: 10.3940/rina.ijme.2021.a1.603)

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KEY DATES: Submitted: 22/10/19; Final acceptance: 09/11/20; Published: 25/03/2021

## SUMMARY

“Volatile Organic Compounds” (VOCs) are known to contribute significantly to environmental pollution. Crude oil loading operations in a marine oil tanker produces a significant quantity of hydrocarbon (HC) vapours in the surrounding atmosphere. A large percentage of these HC vapour emission consists of ‘Volatile Organic Compounds’ (VOCs). This VOC emission has not been previously analysed in detail to understand health and environmental impact. The scope of the study reported in this paper demonstrates the use of chemical processing simulation software (Aspen HYSYS®) to model and identify significant VOCs in this HC vapour emission during crude oil loading operations. The objective is to determine the detailed variation in the volume and the composition of the HC vapour emission and hence, VOCs, as the level in a ship's tank rises while being filled and the influence of crude oil temperature and pressure in the filled tank has on the extent of VOC emission. Total VOC emission per tonne of crude oil is calculated and compared with other similar field measurements. The analysis identifies the concentration of toxic VOCs in the hydrocarbon emission, as well as the liquid fraction lost in the loading operation. The simulation data is analysed for crude oil temperature between 10°C to 45°C and tank level from empty to 90% full. The resulting information is useful to assess the environmental and health impact and efficiency of the current crude oil loading operations. Potential to recover the monetary loss by increasing tank pressure and installation of the 'VOC Recovery Unit' is analysed.

## NOMENCLATURE

dwt	Deadweight
GT	Gross Tonnage
HC	Hydrocarbon
IMO	International Maritime Organisation
PEL	Permissible Exposure Limit
VOC	Volatile Organic Compound

impact on climate, both due to their properties as greenhouse gases and due to their ability to form aerosol particles (Koppmann, 2008).

The assessment of oil vapour emissions on the global and regional scale is of interest due to their impact on human health, climate, and ecosystem (Viana et al., 2014). The vapour emission from the storage tanks at oil refineries or near oil terminals has been analysed in the available literature (Ras et al., 2009, Paulauskiene et al., 2009, Wei et al., 2014, DeLuchi, 1993, Milazzo et al., 2017).

## 1. INTRODUCTION

The crude oil transfer operation from shore-based tanks to marine crude oil tankers is known as Loading Operation. The flow process towards a ship's tank results in the hydrocarbon vapour generation. The generated vapours, known as 'Hydrocarbon Vapours,' are vented to the atmosphere as per tank design rules and operational practices. The HC vapour contains a significant percentage of 'Volatile Organic Compounds' (VOCs). VOCs present in the surrounding air reacts with oxides of nitrogen (NO<sub>x</sub>) to form ozone when exposed to sunlight. In some cases, the strong poison Hydrogen Sulphide (H<sub>2</sub>S) is present in the oil vapours as well (Martens et al., 2001). VOCs exist in the oil vapour emission in minor concentrations and referred to as trace organic compounds.

Trace organic compounds have profound effects on the atmosphere. To investigate organic trace gases in the atmosphere, accurate concentration measurements and careful modelling studies must be made. In addition to influencing local, regional, and even global photochemistry, several such compounds have a potential

Piped emissions, defined as emission from exhaust pipes or stacks, have been analysed and regulated by various authorities. All emissions that are released as leakage from equipment, e.g. leaking seals, is termed as Fugitive emission. Oil vapour emission due to crude oil transfer operations is termed as evaporative emission. Fugitive emission and evaporative emission, collectively termed as 'Diffuse Emissions,' are a source of concern, as they are not well regulated. Monitoring diffuse emission is more complicated as compared to piped emission sources. Abatement and regulation of diffuse emissions are a relatively new issue in some member states of the European Union (EU). It is, however, not a common practice in all EU member states, this contrary to the USA, where it is a common practice for about 10 to 20 years (IMPEL, 2000). Much less attention has been paid to the pollution that may occur as a result of diffuse emissions during the transportation of liquid commodities, such as loading, unloading, and transit emissions (Mihajlović et al., 2016). Evaporative losses are estimated to be 2.9 kg/t of fuel at service stations (McInnes 1996) (Koppmann, 2008).

The emission of oil vapours, and the resulting Volatile Organic Compounds (VOC) emission, to the atmosphere from crude oil tankers worldwide is not known to have been measured and assessed systematically. The emission poses not only environmental and health risks but also represents a loss of considerable monetary value.

The sufficient details to ascertain the qualitative and quantitative impact of oil vapours during crude oil loading operations in the available literature seems to be lacking. The current literature on VOC emission from ships has focussed only on the impact of the exhaust emission from the main engines of the crude oil tankers (Winebrake et al., 2007, Agrawal et al., 2008, Rahman et al., 2015). There is a need to do a detailed analysis of VOC emission from cargo tanks during crude oil transfer operations due to large quantities being transshipped from one continent to another.

The objective of the present research is to provide a methodology to use a process simulation software to model the crude oil flow from shore storage tanks to crude oil tankers. The simulated model will provide the volumetric and qualitative information of the resulting vapour emission. The aim is to know the VOC emission in kg per tonne of crude oil being loaded to understand the environmental impact of this point source of emission. Finally, the data will quantify the evaporative loss and identify the toxic potential of identified VOCs. The influence of the crude oil temperature and pressure in the ship tank is analysed to understand the mechanism of minimising VOC emission. The resulting data is compared with field measurements done in other similar studies. Significant components of identified VOCs can assist in formulating workplace procedures to protect marine personnel and the surrounding environment.

Oil-producing countries ship enormous quantities of crude oil to various consumer countries across different continents. Small oil shipments to nearby regions can be done using pipelines, railway wagons, and road transport. Crude oil tankers, as can be seen from Figure 1 and Figure 2, are the most economical means to transfer crude oil in bulk across continents due to economy of scale.

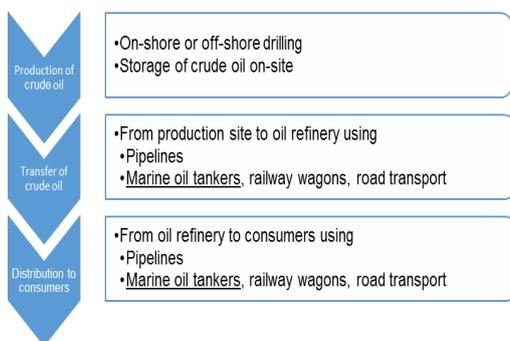


Figure 1: Supply chain diagram for crude oil production, transfer, and distribution

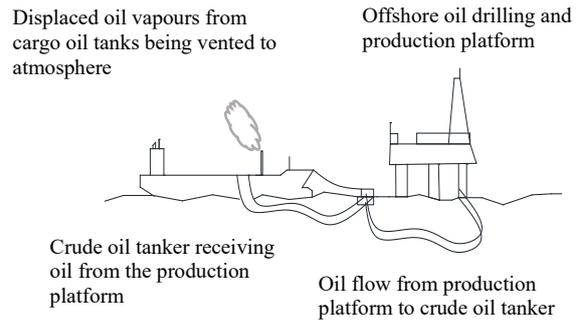


Figure 2: Crude oil loading at an offshore oil production platform

The total world oil demand, as well as refinery output, has been increasing steadily since 2000. Global oil production per day increased by 21.5 million barrels per day in the last 18 years, from 76.7 million barrels per day in 2000 to 98.2 million barrels per day in Feb 2018. Total world refinery throughput is reported to be 80.6 million barrels per day in 2017 (OPEC, 2001, OPEC, 2018). Fossil fuels are projected to dominate future energy usage. Their share is projected to be around 78% share by 2040. For the next 20 years, the oil will remain the fuel with the most significant share of global energy use (OPEC, 2015). Petroleum and other liquid fuels remain the most significant source of energy, but its share of world marketed energy declines from 33% in 2015 to 31% in 2040 (EIA, 2017). Oil production and refining have been rising steadily for the last two decades. This increase directly corresponds to the rise in the quantum of oil vapours released in the surrounding environment.

The current practice of oil transfer in the offshore regions (e.g., from the oil well to FPSO / FSO / shuttle tanker) and in the coastal areas (from storage tanks/refinery to tankers) uses free venting of petroleum vapours to the atmosphere. This practice of free venting of petroleum vapours in the atmosphere presents the following challenges:

- Exposure risk (health) to marine personnel working on tankers as well as nearby areas of oil terminals and storage tanks or refineries
- Air pollution of the surrounding environment
- Loss of valuable hydrocarbon content resulting in monetary loss

Oil vapours are mostly released into the atmosphere during the various stages of oil extraction and transportation before it reaches the consumer. The enormous amount of oil involved in the crude loading operations has equally vast potential to pollute the surrounding air. There are many legislative controls for various stages of extraction to limit the release of vapours in the surrounding environment. The rules to limit vapour emission varies across multiple regions around the world.

As per a report by the UN (United Nations) agency on maritime transport (UNCTAD, 2017, UNCTAD, 2020),

- Crude oil share in world seaborne trade has been increasing steadily on an annual basis (e.g. from 1838 million tonnes in 2016 to 1886 million tonnes in 2018, a yearly increase of 24 million tonnes).
- Similarly, the total deadweight of oil tankers is also steadily increasing on an annual basis ( e.g. from 534,855,000 dwt in 2017 to 567,533,000 dwt in 2019, approximately a yearly increase of 16,339,000 dwt).

Based on the above data, an increase in crude oil trade and tanker tonnage directly corresponds to an increase in HC emission on an annual basis. The volume of VOCs being released into the environment due to tanker loading operations will continue to rise for many years into the future if no intervention measures are taken. A report produced for European commission has indicated an emission factor of 1 kg of VOC per tonne of crude oil loaded, for marine oil transfer.

Using the data quoted, the crude oil shipment of 1886 million tonnes in 2018 corresponds to 1886 thousand tonnes of VOC being emitted in the earth's environment. This amount of emission does not include the emission due to the shipment of clean petroleum products and venting during the transit. Thus, it is critical to understand the detailed mechanism of VOC emission during crude oil tanker loading operations. The analysis will assist in devising the strategy to reduce the health and environmental impact and improve the sustainability of crude oil loading operations.

Crude oil is mined from the seabed or the ground from the different geographic regions. Each crude oil contains a different composition of paraffin, naphthene, and aromatic components. Crude oil produced from various geographical areas was studied, and three samples were formulated to model the crude oil flow in the process simulation software.

The quantitative data obtained from the simulation are analysed to highlight the importance of stopping or minimising the vapour emission, to improve the efficiency of crude oil transfer operations. This is achieved by analysing data such as the effect of temperature of the crude oil being transferred and pressure in the tank onboard crude oil tanker on vapour emission, as well as the variation of vapour emission with the tank filling levels.

The qualitative data obtained from the simulation will be analysed to compare the results with other similar studies for validation of this simulation methodology. The analysis will be used to identify recoverable hydrocarbons in vapour emission to support the decision making of the installation of VOC recovery equipment. Significant VOCs identified in the emission will be compared with safe exposure limit so that safe work

practices can be established for the personnel working near crude oil transfer operations such as onboard tankers and tanker terminals.

First, the current oil tanker design and their operational practice are described. This is followed by the explanation of the classification of crude oil in three samples. Lastly, the methodology for modelling used in the Process Simulation Software is described, and the results are analysed.

## 1.1 BASIC DESIGN OF A CRUDE OIL TANKER

A crude oil tanker uses its inner hull as a container to carry oil in bulk quantities. The side view, elevation, and midship section of a typical crude oil tanker are shown in Figure 3. The hull of the ship is used as a containment for transporting oil. The hull is subdivided into different compartments such as segregated water ballast tanks, cargo oil tanks, fuel oil tanks, fresh water tanks. The wing tanks, which are ballast water tanks, act as a protective barrier in case of collision or grounding of the ship. The transverse and longitudinal compartments, within the interior hull, are known as cargo oil tanks.

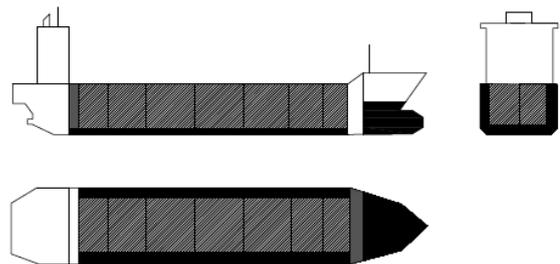


Figure 3: The layout of a marine oil tanker

Crude oil or clean petroleum products are carried in these cargo oil tanks. These compartments are oil-tight and gas-tight to prevent any leakages of oil and vapours. The cargo tanks are interconnected to other cargo tanks by a network of steel pipelines. These cargo pipelines, which are situated at the bottom level of each tank, are used to load and unload petroleum oil and products in the tanks.

When the ship has no cargo on board, cargo tanks are empty and typically contain Inert Gas or hydrocarbon vapours. The seawater is filled in ballast tanks, to ensure adequate propeller immersion for maximum propulsion efficiency. Petroleum oil is filled in a marine oil tanker via steel pipelines. This pipeline, located on the main deck in the amidships area, are known as ship's Manifold. The manifold is connected to the tank inlet (Bellmouth) via Dropline and Bottom Line, as shown in Figure 4. Crude oil is received on board at ship's Manifolds and flows down to cargo tank via Drop Lines and Bottom Lines.

Each cargo tank is connected to a common vent pipeline, known as the 'Inert Gas Line' (IG line). This IG line is connected to a common Venting Pipe, known as 'Mast Riser,' as shown in Figure 5. Each cargo tank is also fitted with automatic 'Pressure – Vacuum Valve,' known as 'P-V Valve' or 'High-Velocity Vent.' (HVV). This valve is a simple weight-activated relief valve to govern maximum allowable pressure and a vacuum setting for each cargo tank (SOLAS, 2014).

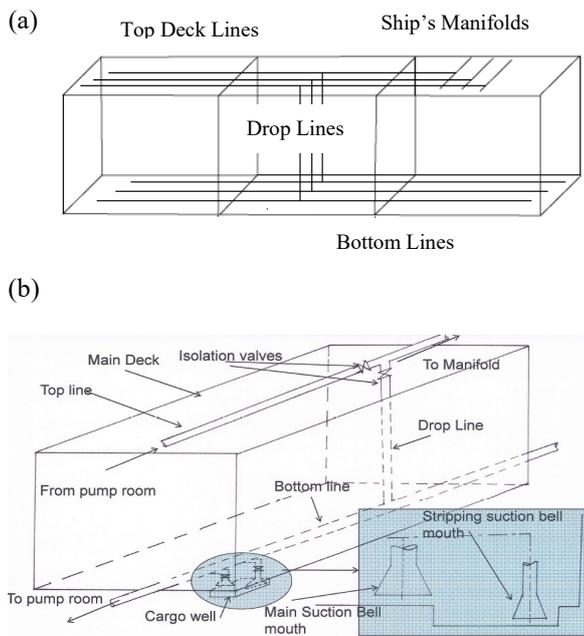


Figure 4: Layout of cargo pipeline in a crude oil tanker showing (a) overall view and (b) detailed view inside one of the cargo tanks

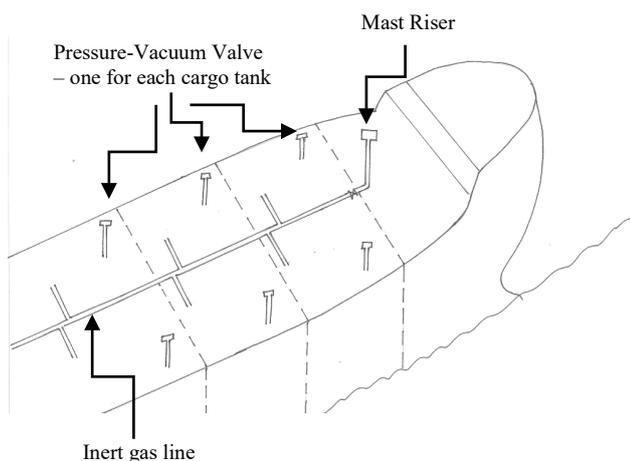


Figure 5: Layout of venting arrangements on the deck of a crude oil tanker

## 1.2 CRUDE OIL VAPOUR EMISSION

Oil vapour emission from a storage tank on a crude oil tanker can occur in two stages.

- First stage: During oil transfer from shore storage tanks to a crude oil tanker, known as loading operations, and
- Second stage: During the voyage

The current study focusses on the first stage only, i.e., oil transfer from shore tanks to ships' tanks.

## 1.3 VAPOUR EMISSION FROM LOADING OPERATIONS

Before commencing loading in a crude oil tanker, the empty cargo oil tanks contain only an inert gas. Inert gas is composed of mainly nitrogen and carbon dioxide with oxygen content 8% or below. This composition is used to make the tank atmosphere incapable of catching fire.

Smaller tankers, usually with 8,000 dwt or below, may have fresh air in the tanks. When crude oil loading operation is carried out, the existing tank atmosphere must be vented to keep the safe pressure within the tank. Usually, an open venting method, using a single Mast Riser, is used to carry out this venting.

## 1.4 CRUDE OIL LOADING

Loading is a process of filling crude oil or clean petroleum products in cargo tanks. During this process, existing inert gas mixed with cargo vapours is vented as follows:

- Release freely to the atmosphere via Mast Riser based on maintaining safe tank pressure as per 'VOC Management Plan'
- Release in a controlled manner via P-V Valve (Figure 5 and Figure 6)
- Flow back to shore tank, using the 'Vapour Emission Control System' (VECS) if such a possibility exists.

## 1.5 VAPOUR EMISSION CONTROL SYSTEMS (VECS)

The crude oil tankers are generally fitted with Vapour Emission Control Systems (VECS), which complies with the standards for VECS as per IMO MSC Circ.585 (MSC/Circ.585, 1992). This system assists in collecting oil vapours when such a system is available in the terminal where loading operation is being carried out. As per information available from IMO, only South Korea and The Netherlands have some oil terminals where this system is currently being used, though some other oil terminals in the USA and Europe are also known to be using VECS at their oil terminals.

## 1.6 INERT GAS

The empty storage tank in the crude oil tanker initially contains Inert Gas. Inert gas onboard crude oil tankers are usually obtained from the exhaust gas from the combustion chamber of a marine boiler. The conventional fuel used in the boiler is heavy fuel oil. The combustion in the boiler is to be adjusted to obtain an exhaust gas with a maximum oxygen content of 5% (SOLAS, 2014). This exhaust gas with an oxygen content of 5% or below is known as Inert gas. The inert gas is cooled with seawater in a scrubber and checked for the oxygen content before directing to various cargo tanks. The ambient air in the cargo tanks is replaced with inert gas until all the tanks have an inert gas with 8% oxygen or below.

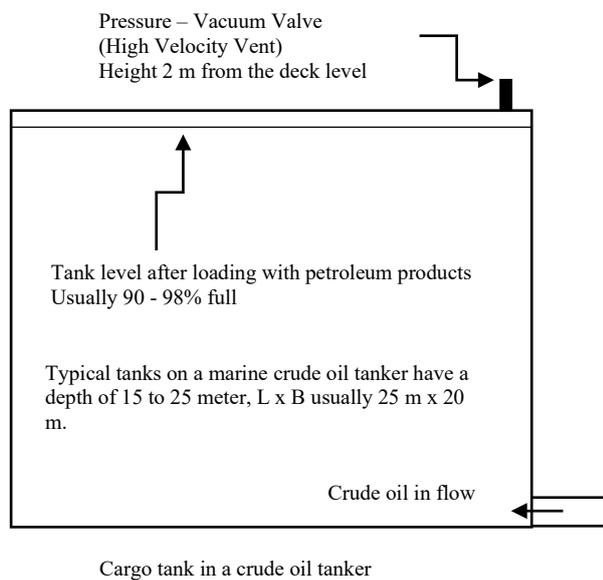


Figure 6: Filling a tank onboard a crude oil tanker with petroleum cargo

## 2. APPROACH USED

The upstream and downstream oil and gas industry use chemical process simulation software HYSYS (Aspentech®), for optimising various processes and safety analysis (Aspentech, 2016). This software was used to model the vapour-liquid equilibrium of the crude oil and vapours resulting from the three different model sample categories. The resulting data from the simulation allows us to identify the various individual components in crude oil vapour emission, thereby identifying relevant VOCs as per the objective of this research work.

'Peng Robinson' Equation of State (EOS) thermodynamic model package is selected for this simulation study, which is used widely with reliable accuracy for hydrocarbon mixtures at atmospheric conditions. (Fahim et al., 2010)

## 2.1 CRUDE OIL ANALYSIS

Crude oil is extracted from the seabed and under the ground at different geographical locations around the globe. Some crude oil has higher proportions of the lower-boiling-point components, and others (heavy oil and bitumen) have higher ratios of higher-boiling components (asphaltic). This diversity in materials from different sources leading to different boundary limits makes it difficult to map in a precise manner. Hydrogen to carbon ratio affects the physical properties of crude oil. The specific gravity and boiling point of the hydrocarbon compounds increases as hydrogen to carbon ratio decreases (Fahim et al., 2010).

The primary component of petroleum are hydrocarbons (compounds containing hydrogen and carbon). The significant hydrocarbons groups are the simplest chain shaped molecules of hydrocarbons, known as 'Paraffins'; saturated hydrocarbons containing a ring, known as 'Naphthenes'; and a single or condensed aromatic ring, known as 'Aromatics' (Speight, 2016).

Sutton (2006) mentioned that:

"No crude oil has ever been completely separated into its components, although many components can be identified." Therefore, a representative model for different origin samples was used in this study.

For example, an analysis of crude oil from Oklahoma showed paraffinic components as all normal paraffin to C<sub>10</sub>H<sub>22</sub>, Isobutane, 2-Methylbutane, 2,3-Dimethylbutane, 2-Methylpentane, 3-Methylpentane, 2-Methylhexane, 3-Methylhexane, 2-Methylpentane, 2,6-Dimethylheptane, 2-Methyloctane, naphthenic components as Cyclopentane, Cyclohexane, Methyl Cyclopentane, 1,1-Dimethylcyclopentane, Methylcyclohexane, 1,3-Dimethylcyclohexane, 1,2,3-Trimethylcyclohexane and aromatic components as Benzene, Toluene, Ethylbenzene, Xylene, and 1,2,4-Trimethylbenzene (Sutton et al., 2006).

Major global exporters of crude oil are shown in Table 1 (Datamarket, 2018, OPEC, 2017). The range of temperature for crude oil refers to the temperature in the shore tanks.

Crude oil from different geographic regions has other predominant characteristics, which affect their refining and the resulting products. As an example, crude oil produced in Nigeria is high in cyclic paraffin content and a relatively low specific gravity. In contrast, crude oil drilled in Venezuela has high specific gravity and low content of material boiling below 350°C.

The characteristics of crude oils from major worldwide oil-producing locations were analysed, and the data is presented in Table 2.

The classification of crude oil in three samples based on different geographical locations is used in this current article to analyse the detailed vapour emission for qualitative and quantitative analysis.

Table 1: Crude oil-exporting countries

Region	Countries	The range of temperatures for crude oil
Middle East	Saudi Arabia, Iran, Iraq, Kuwait, UAE, Bahrain, Oman, Qatar etc.	25 <sup>0</sup> – 45 <sup>0</sup> C
Africa	Algeria, Nigeria, Angola, Libya etc.	25 <sup>0</sup> – 45 <sup>0</sup> C
North America and Latin America	U.S.A., Canada, Mexico, Brazil, Venezuela, Colombia etc.	15 <sup>0</sup> – 40 <sup>0</sup> C
Europe and Eurasia	Russia, Kazakhstan, Azerbaijan, Norway, UK etc.	5 <sup>0</sup> – 20 <sup>0</sup> C
Asia and Pacific	Malaysia, Indonesia, Australia, Brunei, Vietnam etc.	20 <sup>0</sup> – 30 <sup>0</sup> C

Table 2: Composition of different crude oil samples

Component	Crude Oil Sample 1	Crude Oil Sample 2	Crude Oil Sample 3
	Arabian, Kuwait, Iraq	Iran, Libya, Algeria, North Sea UK	Nigeria, South America
Paraffin	70%	55%	27%
Naphthene	20%	30%	58%
Aromatic	10%	15%	15%

## 2.2 SIMULATION METHODOLOGY AND DESCRIPTION OF VAPOUR-LIQUID EQUILIBRIUM

Assumptions for the composition of three samples of crude oil used to model the crude oil flow from the shore storage tanks to the crude oil tankers for the current simulation study are shown in Table 3.

Table 3: Composition of crude oil samples used in the simulation study

Crude Oil	Sample 1 (S1)	Sample 2 (S2)	Sample 3 (S3)
Component	Mole fraction	Mole Fraction	Mole fraction
<b>Paraffinic components</b>			
Methane	0	0.0005	0.0004
Ethane	0	0.0003	0.0026
Propane	0	0.0004	0.0039
i-Butane	0	0.0004	0.0016
n-Butane	0	0.0004	0.0168
i-Pentane	0	0.0000	0.0241
n-Pentane	0.17	0.0122	0.0244
n-Hexane	0	0.0099	0.0254
n-Heptane	0.15	0.0088	0.0077
n-Octane	0.12	0.1674	0.0345
n-Nonane	0.07	0.1166	0.0345
n-Decane	0.03	0.0770	0.0329
2,3-Methyl butane	0.05	0.0004	0.0005
2-Methyl hexane	0.02	0.0004	0.0004
2-Methyl heptane	0.02	0.0003	0.0003
<b>Naphthenic components</b>			
Cyclo pentane	0.14	0.1654	0.2387
Cyclo hexane	0.06	0.1199	0.1973
Methyl cyclo pentane	0.06	0.1153	0.1898
<b>Aromatic components</b>			
Benzene	0.04	0.1166	0.0884
Toluene	0.03	0.0244	0.0422
E-Benzene	0.03	0.0317	0.0183
m-Xylene	0.03	0.0316	0.0183

A section of the process flow sheet of the vapour-liquid equilibrium of the tank space is shown in Figure 7. Crude oil is filled in an empty tank (V-100), which initially

contains only an inert gas. It was modelled in the HYSYS v9 environment. The filling of the tank is modelled in nine stages, to determine the Vapour-Liquid Equilibrium (VLE) of the hydrocarbon content in the tank at each stage.

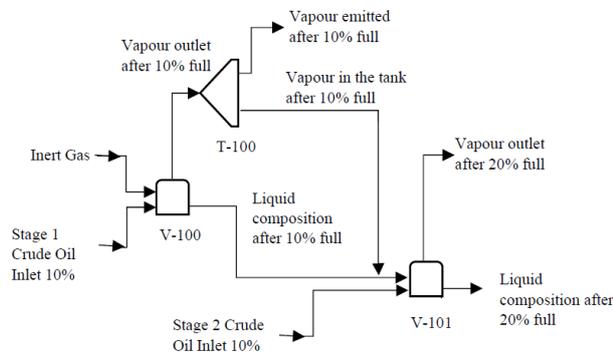


Figure 7: Partial flow diagram of tank filling process in Aspen HYSYS Simulation Environment

The flowsheet is made up of a series of steady-state processes divided into nine stages. In Stage 1, an empty tank (V-100) in the crude oil tanker is filled with crude oil up to 10% level, and the resulting vapour is vented via a tee (T-100). To model the emission of vapour emission from the tank, the vapour in 'T-100', equal to 10% volume of the tank is vented to atmosphere, and the remaining 90% vapour becomes inlet to the second stage. One of the vapour outlets from 'T-100' represents the vapour emission from the tank vent, while the second outlet represents the vapour still present in the tank. The steps are repeated for every 10% incremental tank level until the tank is 90% full. The data is reported and analysed for tank level up to 90% to show the uniform interval of every 10% difference in the filling level. The final volume to which cargo tanks are loaded usually falls between 95% to 98% of tank volume at the observed temperature of the crude oil.

Crude oil tankers, as classified based on their crude oil carriage capacity, are termed as Aframax tankers (80,000 to 120,000 dwt), Suezmax tankers (125,000 to 180,000 dwt), 'Very Large Crude Carrier (VLCC) (up to 320,000 dwt) and 'Ultra Large Crude Carrier' (ULCC) (exceeding 320,000 dwt) (EIA, 2014, Port Economics, 2020). An Aframax crude oil tanker was selected for the purpose of this study so that comparison of the result could be done with other similar studies with field observations of the similar size tanker. For a crude oil tanker of 80,000 dwt, the usual rate of oil transfer varies from 3000 m<sup>3</sup>/h to 6000 m<sup>3</sup>/h. The number of tanks for simultaneous oil transfer is generally 6 to 8. Based on this data, the rate of flow is assumed as 4500 m<sup>3</sup>/h for eight tanks, which translates to a flow rate of approximately 550 m<sup>3</sup>/h for one tank. The assumed flow rate chosen as 535 m<sup>3</sup>/h, is applicable for a loading operation of an Aframax Tanker. The simulation is conducted in a steady-state mode with a tank pressure of 101.3 kPa. The temperature of crude oil in the model

was varied in steps of 5<sup>o</sup>C, starting from 10<sup>o</sup> C in cold countries to 45<sup>o</sup>C for hot Middle East regions. The specific gravity of crude oil generally varies from 0.70 for light crude oil and condensate to 0.95 for heavy crude oil. The value selected for the current study was taken as 0.72, 0.74 and 0.76 for 'Sample 1' (S1), 'Sample 2' (S2) and 'Sample 3' (S3), respectively, which are typical values for a light crude oil. The simulation output provides the information on the composition as well as the amount of vapour emitted during the filling process from an empty tank to a 90% full tank. The data is analysed to identify the significant components of the hydrocarbon emission, as well as evaporative loss during the transfer process. The tank pressure is kept constant when the vapour generation for various temperature is modelled. The crude oil temperature is kept steady when the vapour generation for different tank pressure is modelled.

The resulting oil vapours in the receiving tank are assumed to be vented freely to the atmosphere via Mast Riser onboard crude oil tanker. (Some ships might follow restrictive venting as per VOC Management Plan, Regulation 15 of MARPOL Annex VI, though this is a most individual or local initiative currently) (MARPOL, 2016).

(Note: A cargo tank with an oxygen content of 8% or below is known as 'Cargo tank in inert condition.' This level of oxygen is incapable of supporting fire in the cargo tank.)

The following assumptions were made for the simulation.

- Only two phases, i.e., liquid and vapour exist in the tank.
- No reaction takes place in the storage tank.
- The temperature of Inert Gas and crude oil inflow is the same.
- Individual components in Paraffin, Naphthenes, and Aromatics may vary in different crude oils. It is estimated in the simulation by considering three categories of crude oil samples.
- The temperature of crude oil entering the tank is taken between the ranges of 10<sup>o</sup>C to 45<sup>o</sup>C, based on the geographic location of export terminals in various countries.
- Vapours are vented to the atmosphere to maintain the tank pressure slightly above the atmospheric pressure; the amount of vapour vented is equal to the volume of liquid entering the tank. The tank pressure is taken as 101.3 kPa.
- There is negligible heat transfer between the tank and the surrounding atmosphere.
- The software output is at steady-state conditions at each time step.
- The mole fraction of principal components in the Inert gas present in the tank before the oil transfer, being oxygen 0.05, sulfur dioxide 0.01, carbon dioxide 0.14, and nitrogen 0.8.

The composition of the three categories of the crude oil samples is shown in Table 3, referred to as 'S1', 'S2', and 'S3' onwards.

### 3. RESULTS AND DISCUSSION

Process Simulation was used to model crude oil transfer operations for crude oil flow from a shore tank to a ship tank. The research was conducted on three different samples of crude oils based on different geographic locations. The modelling was done for one tank for a flow rate of 535 m<sup>3</sup>/h. The vapours are assumed to be vented freely to the atmosphere to keep the tank pressure constant, as per the prevalent tanker practice. The simulation research gathered data for various stages of filling, from an empty tank to 90% full, for crude oil temperature ranging from 10°C to 45°C. The volume and composition of vapour emission are analysed as per the following objective of the report.

- The quantity of vapours emitted based on the crude oil temperature
- The quantity of vapours emitted due to the change in tank pressure
- Effect of temperature on the evaporation of crude oil
- Effect of tank pressure on the evaporation of crude oil
- Detailed analysis of VOC concentration in the vapour emission, for various crude oil temperatures, during the various stages of tank filling level

The concentration of the inert gas was separated to identify the fraction of VOCs in the total vapour emission. The total amount of vapours and the rate of vapour generation were collected to analyse the trend of vapour generation. The trend identifies the period of peak vapour generation during the total loading duration of the tank. The information is useful to guide the surrounding marine personnel for exposure risks.

Additionally, the information is useful for the operation of the vapour recovery system, if installed. The rate of rise of the concentration of various VOCs in the vapour emission was analysed and the trends established to identify significant VOCs for health and environmental impacts. The data can provide information on the evaporating fraction to quantify the economic loss for various temperatures of crude oil. The data is presented in graphical form and discussed further. Most of the information is analysed for a crude oil temperature 25°C, which is mid-way between a low of 10°C and 40°C, based on the geographical location of the crude oil tanker loading terminals in the world.

#### 3.1 QUANTITATIVE DATA

In this study, it was observed that the temperature of crude oil during crude oil transfer operation played a direct relation to the amount of vapours being emitted. The rate of vapour generation is more in the initial stages

of transfer at all temperatures analysed in the report. Figure 8 summarises the amount of vapour emitted for every 10% rise in the tank level for the three samples of crude oil at 25°C. The vapour emission is highest when the tank is empty, decreasing almost uniformly until the tank is 90% full. The same trend was noticed for other crude oil temperatures for all the three samples studied in the simulation.

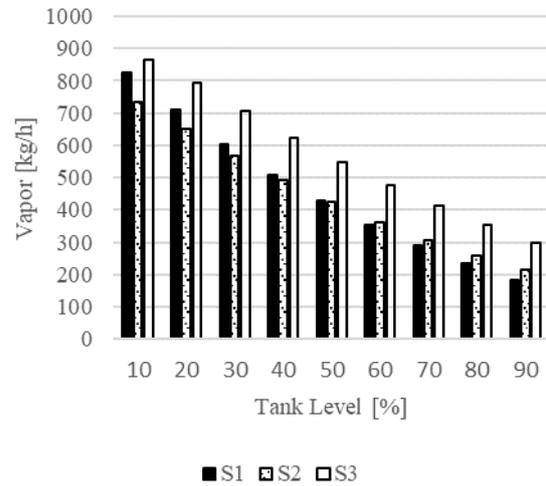


Figure 8: Variation in the rate of vapour emission with tank level, for crude oil at 25°C

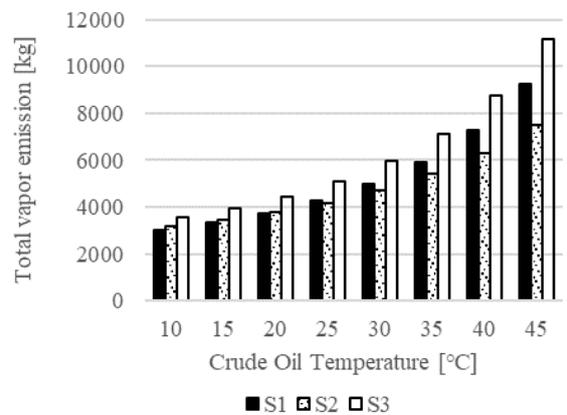


Figure 9: Total vapour emission with different crude oil temperature, for three samples, at a flow rate of 535 m<sup>3</sup>/h

The total vapour emission in filling one tank of 5000m<sup>3</sup>, for different crude oil temperatures for various samples is shown in Figure 9. It can be seen clearly that more vapours are generated when the crude oil temperature is higher. It is seen that vapour generation is higher when crude oil temperature ranges from 30°C to 45°C than between 10°C to 30°C. Total vapour emission increased by more than 60% for a crude oil temperature at 45°C, as compared to vapour emission for crude oil at 10°C. The vapour generation increased by about 25% when compared for filling operation with crude oil temperature at 10°C and 25°C respectively, rising to more than 40% for variation in crude oil temperature from 30°C to 45°C, respectively.

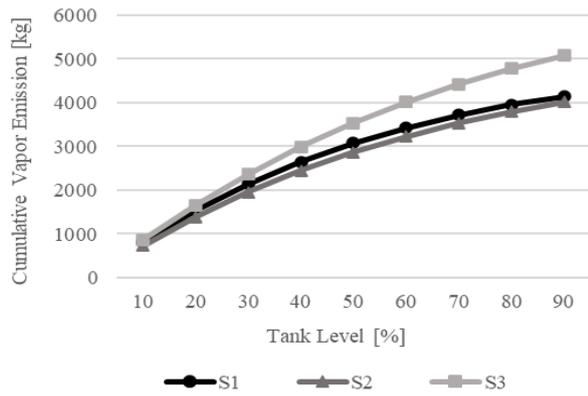


Figure 10: The rate of change of total vapour emission with a change in tank filling levels, for three crude oil samples at 25°C

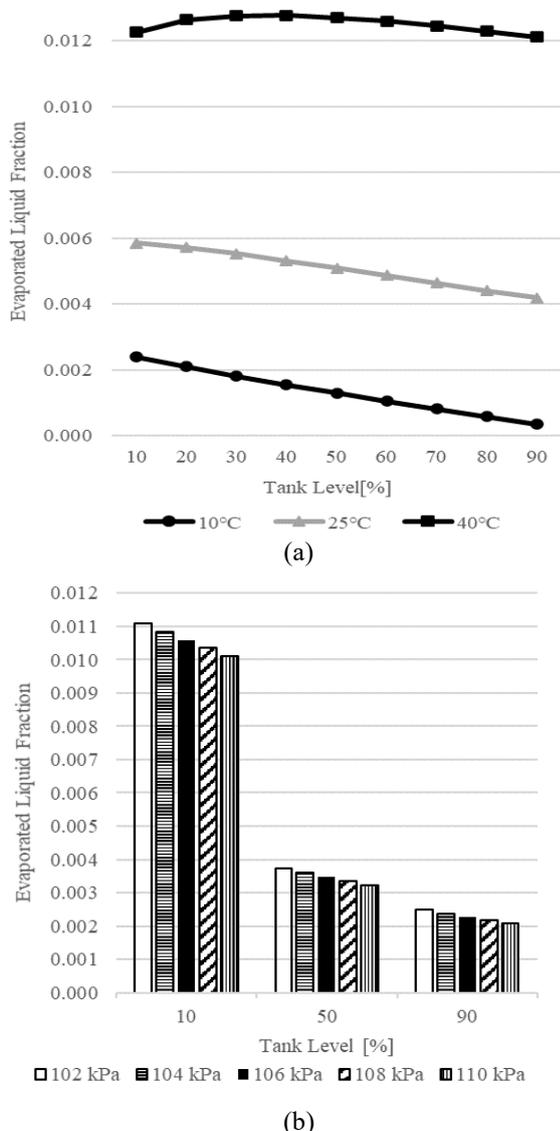


Figure 11: Vapourisation of crude oil with (a) an increase in crude oil temperature, for tank pressure 101.3 kPa, and (b) an increase in tank pressure, for 'Crude Oil Sample 2', for crude oil temperature 25°C

The crude oil loading terminals situated in warmer regions will tend to have higher crude oil temperatures and hence, more vapour emission as compared to the oil terminals situated in the colder regions. The variation in total vapour emission with the rise in tank level was analysed in the simulation study.

Figure 10 shows the variation in total vapour emission with the tank filling level, for the three samples, for crude oil temperature at 25°C. More vapour emission occurs in the first half of the loading operation.

Currently, there is no similar data in the available literature; detailed field measurements are required to validate the findings.

Two parameters that could affect the vaporisation of crude oil were crude oil temperature and the pressure in the receiving tank. The effect of crude oil temperature and the tank pressure on the amount of crude oil evaporation is shown in Figure 11 (a) and 11 (b). The higher temperature of the crude oil leads to the greater evaporation, and higher tank pressure leads to lower vapour generation.

Table 4: Reduction in monetary loss with increase in tank pressure, Flow rate 535m<sup>3</sup>/h, Crude Oil Temperature 25°C, Duration: 9 hours, Crude oil price \$60 per barrel

Pressure	Volume evaporated in m <sup>3</sup>	BBIs	Monetary Loss	Reduction
102 kPa	18	115	\$ 6,885	0%
104 kPa	18	111	\$ 6,630	4%
106 kPa	17	106	\$ 6,387	7%
108 kPa	16	103	\$ 6,155	11%
110 kPa	16	99	\$ 5,933	14%

Table 4 provides the details of crude oil evaporation for 'S2' at tank pressure from 102 kPa to 110 kPa. For every 2-kPa increase in tank pressure, the monetary loss due to vapour emission can be reduced by 3 to 4%, respectively. The higher temperature of crude oil during loading operation will result in higher evaporative loss, as per the trend shown in Figure 9 and Figure 11 (a).

The information shown in Figure 8 to Figure 11 is useful to evaluate the impact of vapour released in the surrounding environment. The data indicates that marine transfer points located near the populated areas are a steady point source of emission requiring emission control strategies to minimise air pollution due to the presence of toxic VOCs.

The data from vapour emission was correlated to find the amount of VOCs emitted for every tonne of crude oil

loaded into the tanker. The resulting analysis is shown in Figure 12. The total amount of VOCs generated for every tonne of crude oil transferred was calculated for various temperatures of the crude oil. Figure 12(a) shows a variation in VOC emission from a low of 0.1 kg/tonne to a high of 2.0 kg/tonne for the three samples of crude oil modelled in the study.

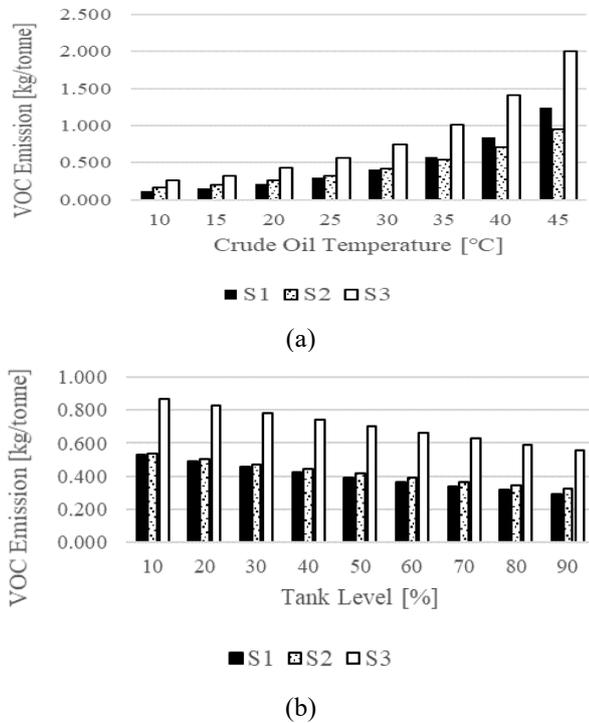


Figure 12: (a) VOC emission for crude oil transfer, at different crude oil temperature and (b) VOC emission for crude oil at 25°C with the level of filling

For crude oil temperature between 25°C to 35°C, the average VOC emission is about 0.8 kg/tonne, which is in close resemblance to the value of 1 kg/tonne accepted in the EU report (Hill, 2001). Figure 12(b) analysed the variation of total VOC emission for a crude oil temperature of 25°C with a change in tank level. The VOC emission falls uniformly as tank level rises. More detailed field measurements are required to validate the finding, and such information in the existing literature is not available.

### 3.2 QUALITATIVE ANALYSIS

The simulation output data can provide the details for various components in total vapour emission for crude oil loading at various temperatures. The vapours originated either from the initial inert gas present in the tank or from the evaporation of lighter hydrocarbon components in the crude oil.

Figure 13 shows the variation of the average proportion of hydrocarbon mole fraction in the total vapour emission, at various crude oil temperatures. Higher crude

oil temperature has a higher proportion of hydrocarbons in the total vapour emission, almost a linear rate of rise. The amount of hydrocarbon components (VOCs) increases with the increase in the temperature of crude oil. The mole fraction of hydrocarbon in total vapour emission varied from a low of 0.14 to a high of 0.51 for S1, 0.2 to 0.48 for S2, and 0.26 to 0.62 for S3.

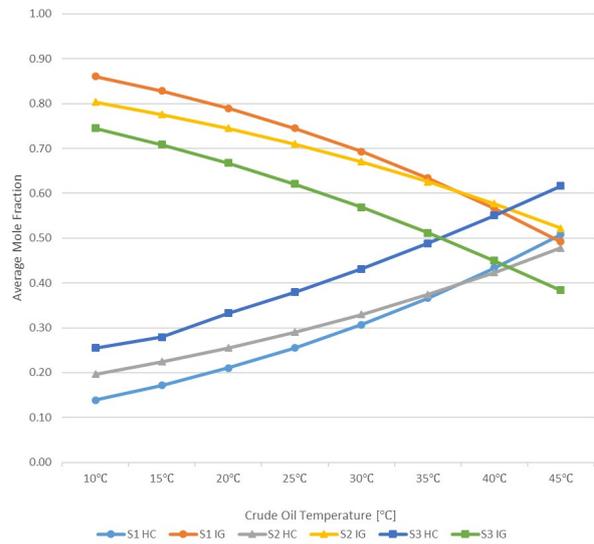


Figure 13: Variation of hydrocarbon components in the total vapour emission at different temperatures, for three samples of crude oil

The trend of evaporation of VOCs is useful for the design and operation of 'Vapour / VOC Recovery Systems' for devising the strategy on its operating period leading to the enhancement of the efficiency of crude oil transfer operations for oil terminals. The recovery of the lost fraction can assist in improving the environmental impacts such as Greenhouse Gas Emission and carbon footprint. The resulting monetary loss is highlighted later in the article.

The detailed simulation data is analysed further to identify the most significant VOCs in total vapour emission for the three samples. The component with the highest average proportion in the total hydrocarbon emission is selected.

Figure 14-16 summarises the significant VOCs in total HC emission, for the three different crude oil samples. The simulation results can identify dominant VOCs in the total vapour emission for the three samples modelled in the simulation. Significant components in the vapour emission resulting from 'S1' of the crude oil contains n-Pentane, Cyclopentane, and n-Hexane, 'S2' of the crude oil contains Cyclopentane, Methane, Ethane, Propane, and Benzene, whereas 'S3' of the crude oil contains Cyclopentane, Methane, Ethane, and Benzene. The identification of significant VOCs in vapour emission is in direct relationship with their respective average boiling points. It can be concluded that the lower boiling point VOCs, as well as the

initial mole fraction in the crude oil, play a dominant role in the resulting vapour emission.

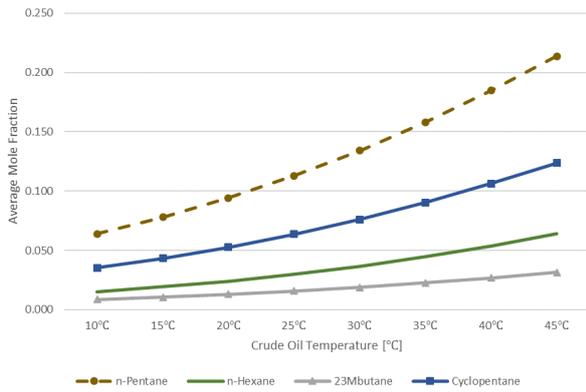


Figure 14: Average mole fraction of significant VOCs in total vapour emission, for 'S1' filling

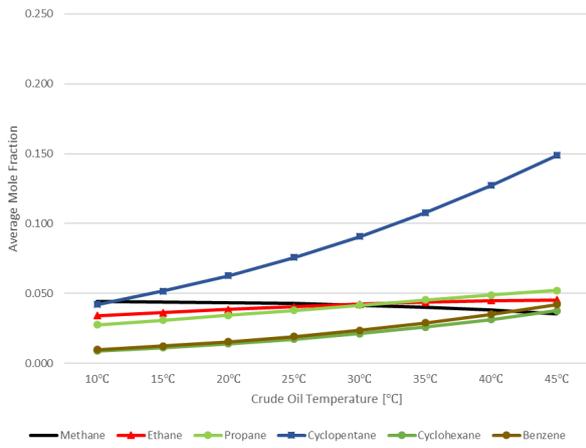


Figure 15: Average mole fraction of significant VOCs in total vapour emission, for 'S2' filling

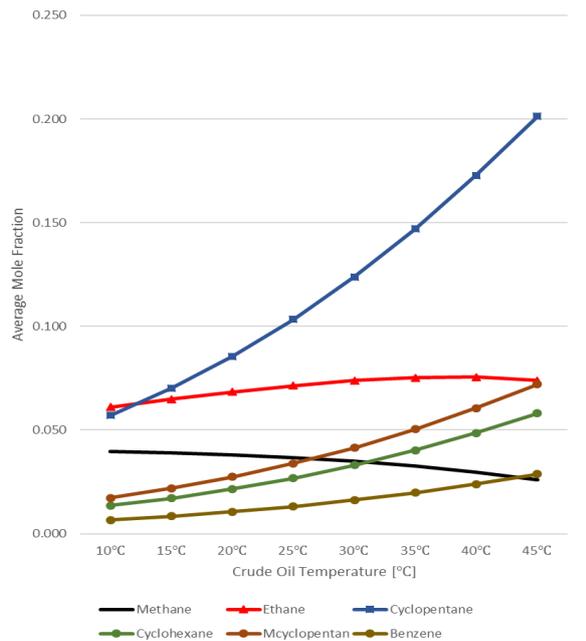
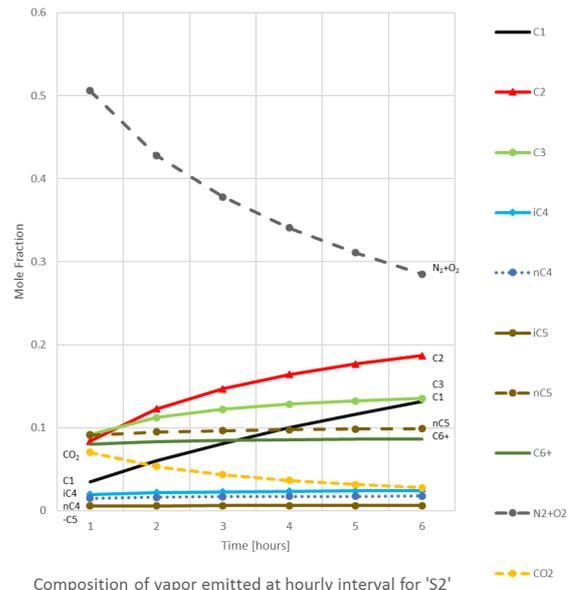


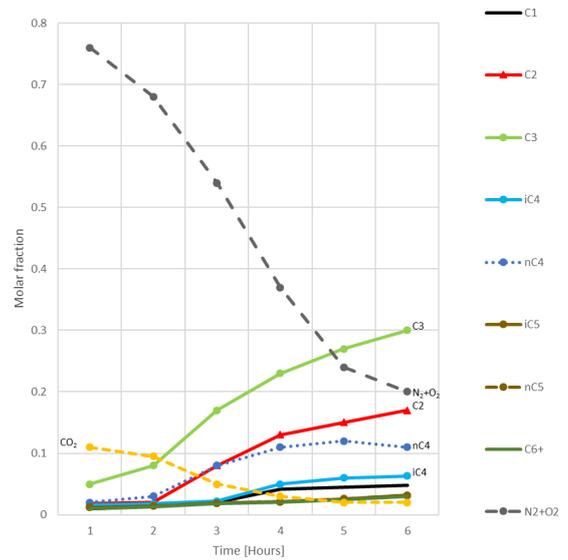
Figure 16: Average mole fraction of significant VOCs in total vapour emission, for 'S3' filling

The study analysed the composition of vapour emission from the current case to draw a comparison with the simulated vapour emission study done by Martens et al. (2001). The vapour emission resulting from filling a tank with 'S2' was compared with the similar tank filling level. The resulting data is presented in Figure 17. The pattern of variation of various components in the vapour emission resembles quite closely with the current simulation results.



Composition of vapor emitted at hourly interval for 'S2'

(a)



Composition of vapors emitted at hourly interval by study conducted by Otto M. Martens

(b)

Figure 17 (a) and (b): Comparison of vapour emission composition at the hourly interval (Martens et al., 2001)

The results of the vapour composition in the emission by the current study were further compared with the field study conducted by Tamadonni et al. (2014). The present study identified C1, C2, and C3 as major VOCs, whereas the results demonstrated by Martens et al. (2001) and Tamadonni et al. (2014) identified C2, C3, and C4 as the highest concentration in the total vapour emission, shown in Figure 18.

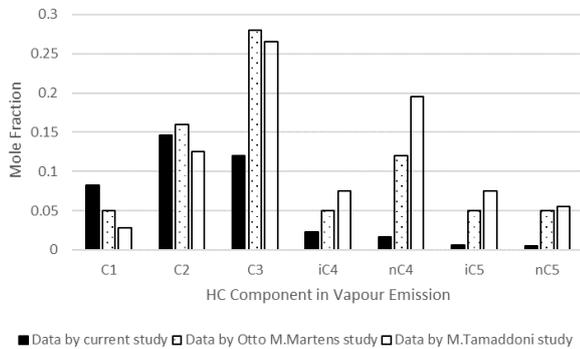


Figure 18: Comparison of vapour emission composition at a 30% filling level with similar studies (Martens et al., 2001, Tamadonni et al., 2014)

There is a close similarity in the results obtained in the current study and the study conducted by Martens et al. (2001), and Tamadonni et al. (2014). Both studies were based on different samples of crude oil, and hence the results are expected to vary. The available literature does not identify the individual components in the crude oil, so it is challenging to validate the findings at this stage. More experimental data with detailed crude oil composition is needed to validate the methodology.

The identification of the proportion of various VOCs in vapour emission is useful to identify the toxic VOCs in the ambient air onboard the ship or nearby refinery areas for maintaining a safe and healthy environment. e.g., personnel handling operations on crude oil tankers or refinery areas need to be evaluated for exposure risks for the relevant significant VOCs in the vapour emission.

The current simulation results identify benzene from the aromatic component, Cyclopentane from the naphthenic component, and Pentane from the paraffinic component as significant VOC in the vapour emission.

The simulation data can provide the information to highlight toxic VOCs for exposure control. The identified toxic VOCs in the vapour emission from each crude oil sample and 'Permissible Exposure Limit' (PEL) are shown in Table 5. E.g., for crude oil sample 'S1', the concentration at the vent outlet, of n-Pentane (1140-150 ppm), Cyclopentane (640 ppm), and n-Hexane (300 ppm) exceed PEL values, and exposure controls should be exercised to safeguard the health of the watch keeping personnel on deck. Similarly, exposure controls are necessary for 'S2' due to the concentration of Cyclopentane (760-770 ppm) and Benzene (190 ppm), and for 'S3', the concentration of Cyclopentane (1040-

1050 ppm) and Benzene (130 ppm), exceeding the PEL values. The molecular weight of the vapour emission is found to be 34, which is slightly higher than the molecular weight of air (29), this may cause the vapours to settle near deck in case of weak wind condition. The information provides a concrete basis for the exposure risk assessment of the surrounding personnel for managing their health at such work sites.

Table 5: Significant VOC emission and PEL data

Component	Crude Oil Sample	Mole fraction	PPM	Mole fraction	PPM	PEL
		50 % full		90% full		
n-Pentane		0.114	1140	0.115	1150	600
Cyclopentane	S1	0.064	640	0.064	640	600
n-Hexane		0.03	300	0.03	300	50
23Methyl butane		0.02	200	0.02	200	600
Methane		0.042	420	0.065	650	1000
Ethane		0.043	430	0.048	480	1000
Propane	S2	0.039	390	0.041	410	1000
Cyclopentane		0.076	760	0.077	770	600
Benzene		0.019	190	0.019	190	1
Cyclohexane		0.02	200	0.02	200	300
Methylcyclopentane		0.02	200	0.02	200	500
Methane		0.029	290	0.056	560	1000
Ethane		0.07	700	0.086	860	1000
Cyclopentane	S3	0.104	1040	0.105	1050	600
Benzene		0.013	130	0.013	130	1
Cyclohexane		0.02	200	0.02	200	300
Methylcyclopentane		0.02	200	0.02	200	500

Table 6 provides the pattern of change in the significant components in VOC emission with a rise in tank level. It is noticed that low boiling point components such as Methane, Ethane, and Propane have the concentration increased. In contrast, other components, such as n-Pentane and Cyclopentane, remained steady in their concentration. This data can be used to decide on the operation of the VOC recovery plant.

The simulation can show the fraction of crude oil lost to evaporation, and the detailed data are presented in Table 7. The fraction lost due to evaporation for S1 and S2 is more in the first half of the loading. Also, more evaporation occurs when the temperature of crude oil is higher. For S3, at a higher temperature, such as 40°C, there is more evaporation loss even as the tank level rises, which could be due to a higher rate of VOC evaporation.

Table 6: Detailed variation of mole fraction of significant VOC components with change in tank level for S1, S2, and S3, at 25°C, as per Figure 14 to 16

Tank Level /Component	10%	20%	30%	40%	50%	60%	70%	80%	90%
<b>n-Pentane</b>	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
<b>Cyclopentane</b>	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
<b>n-Hexane</b>	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
<b>2,3Methylbutane</b>	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
<b>Methane</b>	0.01	0.02	0.03	0.03	0.04	0.05	0.05	0.06	0.07
<b>Ethane</b>	0.02	0.03	0.04	0.04	0.04	0.04	0.05	0.05	0.05
<b>Propane</b>	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.04	0.04
<b>Cyclopentane</b>	0.07	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.08
<b>Benzene</b>	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
<b>Cyclohexane</b>	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
<b>Mecyclopentane</b>	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
<b>Methane</b>	0.01	0.02	0.02	0.03	0.04	0.04	0.05	0.05	0.06
<b>Ethane</b>	0.04	0.05	0.06	0.07	0.08	0.08	0.08	0.08	0.09
<b>Cyclopentane</b>	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.11
<b>Benzene</b>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
<b>Cyclohexane</b>	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
<b>Mecyclopentane</b>	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

Table 7: Evaporation loss of different crude oil samples at different temperatures with the change in tank filling level

Percentage Liquid evaporated with the rise in tank level

Temp		Tank Filling Level [%]								
		10	20	30	40	50	60	70	80	90
15°C	S1	0.4	0.4	0.3	0.3	0.3	0.2	0.2	0.2	0.1
25°C		0.8	0.8	0.7	0.7	0.6	0.6	0.6	0.5	0.5
35°C		1.4	1.4	1.4	1.3	1.3	1.3	1.2	1.2	1.1
45°C		2.4	2.5	2.5	2.5	2.5	2.5	2.4	2.4	2.4
15°C	S2	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.1
25°C		0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.4	0.4
35°C		1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9
45°C		1.5	1.6	1.7	1.7	1.7	1.7	1.7	1.7	1.7
15°C	S3	0.6	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.4
25°C		1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9
35°C		1.6	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
45°C		2.6	2.8	3.0	3.1	3.2	3.3	3.3	3.4	3.4

A literature review of similar studies included studies conducted for the identification of toxic VOCs in the tank farms and refinery areas. The significant VOCs identified include Pentane, hexane, and benzene, which have been identified in field measurements near petroleum tank farms and refinery areas (Milazzo *et al.*, 2017, Kalabokas *et al.*, 2001, Ras *et al.*, 2009, Lin *et al.*, 2004).

Ras *et al.* (2009) conducted VOC levels in ambient air near petrochemical complexes in southern Europe, toluene, i-pentane, 1-pentene, and n-pentane were identified as the most abundant compounds followed by benzene, ethylbenzene, and xylenes. Lin *et al.* (2004) detected benzene and toluene as the most abundant VOC around the petroleum refinery. Kalabokas *et al.* (2001) measured vapour concentration around the refinery areas and detected benzene, toluene, ethyl benzene, xylenes, trimethylbenzene, hexane, heptane and octane, hexane and toluene being the highest. Milazzo *et al.* (2017) detected benzene and toluene as the highest concentration of VOCs near a refinery and marine loading terminal.

The vapours generated by crude oil transfer leads to a loss of crude oil. This data helps to devise various work practices to minimise evaporative loss or the installation of additional equipment to capture the fraction being lost to the evaporation process. As shown in Table 7, for three samples of crude oil modelled in the study, 1 to 3% of the crude oil volume being transported can be lost during the transfer process of 24 hours or less, not accounting for the transit loss across the voyage. For a crude oil tanker of 100,000 dwt, the 1% of tank volume being approximately 1000 m<sup>3</sup>, this loss could be \$340,000 at the crude oil rate of \$60 per barrel.

#### 4. CONCLUSIONS

In the present study, an approach is proposed to conduct a qualitative and quantitative analysis of vapour emission during crude oil tanker loading operations. Specific VOCs with toxic potential are identified in crude oil vapour emission using Aspen HYSYS ® Process Simulation Software. The simulation data provides a concrete basis to conduct health and environmental risk assessment for crude oil tanker loading operations. It can also be used for land-based bulk oil transfer facilities involving road tankers and railway wagons.

The vapour emission and the resulting VOC emission analysis was conducted for three different samples of crude oil. The simulation was performed at different crude oil temperatures from 10°C to 45°C, at steps of 5°C. The data was collected from an empty tank to 90% full, for each 10% change in tank level. It was found that a higher temperature of crude oil during loading operations has a higher volume of vapour emission. The crude oil temperature in the shore tanks is usually

influenced by the ambient temperature of the geographic location of crude oil loading operation. The rate of vapour emission is higher in the initial stage of loading and decreases as the tank level reaches the completion stage. The same trend was noticed for different crude oil samples at different temperatures. The effect of tank pressure on vapour emission was also analysed, and it was found that maintaining higher tank pressure in the loading tank leads to reduced vapour emission. The influence of crude oil temperature during loading operation and pressure in the cargo tank of an oil tanker on VOC emission are useful for the formulation of safe working practices to minimise or eliminate VOC emission. The data can conclude that maintaining higher tank pressure during crude oil loading operations leads to an overall reduction in vapour emission.

The analysis showed that total VOCs emitted for every tonne of crude oil loaded varied from a low of 0.1 kg/tonne to a high of 2.0 kg/tonne, as shown in Figure 12 (a). This data is useful in decision making for the installation of 'VOC Recovery Units' to reduce the monetary loss and environmental impact of crude oil tanker loading operations for sustainable operations.

The detailed analysis of the data obtained in the simulation study can identify the proportion of hydrocarbon components in the total vapour emission, as well as the ratio of individual VOCs in the hydrocarbon fraction. The identification and comparison of individual VOCs in the total hydrocarbon emission with PEL are helpful in monitoring compliance with local exposure regulations and industry best practice. The data analysis of the vapour emission justifies the adoption of exposure control measures, such as carriage of mandatory 'Personal Gas Monitors' to safeguard the health of marine personnel involved in tanker loading operations. The study can confirm some results with somewhat limited literature available in similar work sites, and more validation is required in the future.

It is considered that the study showed it is useful to evaluate the overall evaporative loss leading to direct monetary loss, during crude oil tanker loading operations. The simulated data can show the pattern of evaporative loss with change in tank filling level, for various crude oil temperatures for three crude oil samples. Higher evaporative losses are observed when the temperature of crude oil is more elevated. The data is also able to calculate the reduction in the evaporative loss by maintaining higher tank pressure in the loading tank. The efficiency of crude oil tanker loading operations can thus be enhanced by maintaining higher tank pressure in the loading tank and also by the installation of 'VOC Recovery Units.'

This research work is useful to quantify the VOC emission by crude oil tanker loading operations for global and local impact on air quality. The results can be used to highlight the environmental and health risks

when applied to the current work practices of crude oil tanker loading operations. The data output obtained from the simulation can justify the urgency to devise new strategies to amend the current work practices and crude oil tanker design to enhance the efficiency of crude oil tanker loading operations for health and environmental impact.

The study can further be extended to estimate similar results for clean oil product transfer such as gasoline, naphtha, kerosene, as well as various grades of ship bunker fuel oil. Transit losses can be estimated better with the above approach and can be used to validate with existing oil loss control reports.

## 5. ACKNOWLEDGMENTS

The authors acknowledge Newcastle University in Singapore for their support in providing the resources used in this research.

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