Volatile Organic Compound Emission from Marine Oil Loading Operations

Volume 1 of 1

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Abstract

Marine oil loading operations release enormous volumes of oil vapours into the atmosphere. Releasing oil vapours causes direct economic loss and localised environmental pollution. Prolonged exposure to Volatile Organic Compounds (VOCs) can cause acute and chronic effects on human health. The adverse health effects of toxic VOCs from oil vapour emission (OVE) have been widely discussed in the literature. The current marine oil tanker design does not require equipment to be part of the standard design to stop this evaporative emission. Current procedures to load oil tankers affect the health of seafarers onboard and pollute the local environment, as tanker loading ports handle many ships simultaneously every day. This thesis aims to address the monetary loss, environmental pollution, and health risks to seafarers due to OVE during marine oil tanker loading operations and to make the loading operations sustainable and carbon neutral. There are no regulations in International Maritime Organization (IMO) conventions and coastal states to address this economic loss and environmental pollution. The research analysis is conducted for a crude oil and gasoline loading operation using Aspen HYSYS Chemical Process Simulator. Crude oil loading operation is analysed for an Aframax tanker and an Ultra Large Crude Carrier (ULCC), whereas gasoline loading is simulated in a product tanker. Results reveal an annual monetary loss of \$1.2 to 5.5 million for an Aframax tanker loading crude oil between the temperature range of 25℃ to 45℃, whereas for a ULCC, the annual monetary loss was found in the range of \$1.6 to 11.2 million for the same temperature range. OVE increases with an increase in oil temperature and decreases when higher cargo tank pressure is maintained during tanker loading operations. Hence, OVE can be reduced by adopting a working practice of maintaining elevated tank pressure of 120 kPa instead of the current practice of 108 kPa. Furthermore, the hydrocarbon (HC) emission was found to reduce by 4% to 10% for both crude oil and gasoline loading operations of 25℃ to 45℃ and cargo tank pressure of 120 kPa. The results also indicate that VOC emission is lower for a tanker with a higher loading rate (ULCC) during crude oil loading operations. Toxic VOCs, the current research identifies, include hexane, benzene, toluene, ethyl benzene, and xylene. Solutions are proposed to safeguard the health of seafarers due to toxic VOC exposure and reduce or stop the monetary loss and environmental pollution. This includes the amendments to the current regulations in SOLAS and MARPOL conventions such as the mandatory provision of vapour return line during oil tanker loading operations and conducting VOC Toxicity Hazard Assessment (VOCTHA) during ship design for oil tanker loading and ship bunkering operations.

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Dedication and Acknowledgements

Dedicated to my wife Sandeep, and children, Mehak and Harnoor.

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a	Energy parameter	(Equation 3.1)
b	Co-volume	(Equation 3.1)
C_n	Compounds containing 'n' carbon atom	
C_{10+}	Compounds containing more than ten carbon atoms	
C_A	Arrival emission factor, contributed by vapours in the empty tank compartment before loading, $lb/10^3$ gal loaded	(Equation 2.4)
C_G	Generated emission factor, contributed by evaporation during loading, $lb/10^3$ gal loaded	(Equation 2.4 and 2.5)
C_i	Unknown molar concentration of species 'i' in the mixture, in k-mol/m^3	(Equation 2.7)
C_L	Total loading loss, $lb/10^3$ gal loaded	(Equation 2.4)
CO	Carbon monoxide	
CO_2	Carbon dioxide	
D_{im}	Effective diffusion coefficient for species 'i' in the mixture, in m^2/s	(Equation 2.7)
D_{Unr_Vel}	Diffusion coefficient due to all unresolved velocities	(Equation 2.7)
E_G	Generated emission factor, $lb/10^3$ gal loaded	(Equation 2.6)
G	Vapour growth factor	(Equation 2.5)
H_2S	Hydrogen sulphide	
i	Component index	(Equation 3.1)
K_S	Saturation Factor	(Equation 2.1)
kg	Kilogramme	
kL	Kilo litre	
kPa	Kilo pascal	
k	Binary parameter	(Equation 3.1)
L_L	Loading loss	(Equation 2.1)

M	Molecular weight of the vapour	(Equation 2.5)
M_{Total}	Total mass of vapours vented to the atmosphere during loading operation, in kg	(Equation 3.2)
M_V	Molecular weight of the vapour	(Equation 2.1)
M_{VOC}	Mass of VOCs vented to the atmosphere, in kg	(Equation 3.3)
m	Mass loaded, in tonnes	(Equation 3.3)
mg/L	Milligram per litre	
mt	Metric tonnes	
N_2	Nitrogen	
NO_x	Nitrogen oxide compounds	
n	Mole number	(Equation 3.1)
O_2	Oxygen	
O_3	Ozone	
P	TVP of loaded crude oil, in psi_a	(Equation 2.5)
PM	Particulate matter	
P_{VA}	True vapour pressure of loaded crude oil	(Equation 2.1 and 2.6)
p	Pressure (Pa)	(Equation 3.1)
R	Gas constant	(Equation 2.1, 3.1)
SO_2	Sulphur dioxide	
SO_x	Sulphur oxide compounds	
T	Temperature of the vapour (R)	(Equation 2.5)
T	Temperature of the vapour (K)	(Equation 3.1)
T_c	Critical temperature (K)	(Equation 3.1)
T_V	Absolute temperature of the ullage (K)	(Equation 2.1)
V_L	Volume of the liquid loaded	(Equation 2.1)
V_m	Molar volume without correction factor	(Equation 3.1)
W	Vertical velocity of gas, m/s	(Equation 2.7)

ω	Acentric factor	(Equation 3.1)
x	Mole fraction	(Equation 3.1)
z	Vertical distance, m	(Equation 2.7)

List of Abbreviations

ACGIH	American Conference Of Governmental Industrial Hygienists
Aframax	An oil tanker with a deadweight between 80,000 to 120,000 metric tonnes, based on Average freight rate assessment
API	Index of density of crude oil, as per American Petroleum Institute
AR	Activity Rate
Aspen HYSYS	Chemical process simulator used in the research work
AV	Air Vent
BAT	Beat Available Technology
bbl	Barrels
CAA	Clean Air Act of U.S.A.
CCR	Cargo Control Room
CFD	Computational Fluid Dynamics
CFR	Code Of Federal Regulations, in U.S.A.
CII	Carbon Intensity Indicator
CPP	Clean Petroleum Products
CRUCOGSA	The physical behaviour of crude oil influencing its carriage by sea
CTMS	Custody Transfer Management System
CVA	Carbon Vacuum-Regenerated Adsorption
CVE	Crude Oil Vapour Emission
CVOC	Direct absorption of VOC in the crude oil
dwt	Deadweight tonnes
EEA	European Environment Agency

EC	European Commission
ELSA	Emergency Life Support Appliance
EOS	Equation of State
EPA	Environment Protection Agency (U.S.A.)
EF	Emission Factor
EI	Energy Institute
EU	European Union
FPSO	Floating Production and Storage Offshore
FSO	Floating Storage Offshore
FSS	Fire Safety System Code
GHG	Green House Gas
HAP	Hazardous Air Pollutant
HC	Hydrocarbon
HVV	High Velocity Vent
IAPH	International Association of Ports and Harbours
ICS	International Chamber of Shipping
IG	Inert Gas
IGS	Inert Gas System
ISGOTT	International Safety Guide for Oil Tankers and Terminals
IMO	International Maritime Organisation
KLIM	Norwegian Climate and Pollution Agency
KVOC	Cargo pipeline partial pressure control system
LNG	Liquefied Natural Gas
LRTAP	Convention On Long Range Trans Boundary Air Pollution
MARPOL	Convention On Prevention of Marine Pollution
MATLAB	Programming and numeric computing platform

MEPC	Marine Environment Protection Committee
MW	Molecular Weight
NAAQS	National Ambient Air Quality Standards
NEA	Norwegian Environment Agency
NESHAP	National Emission Standards for Hazardous Air Pollutants
MACT	Maximum Achievable Control Technology
MSC	Maritime Safety Committee
MSDS	Material Safety Data Sheet
mt	Metric tonnes
NAAQS	National Ambient Air Quality Standards
NGL	Natural Gas Liquid
NMVOC	Non-Methane Volatile Organic Compound
OCIMF	Oil Companies' International Marine Forum
OSHA	Occupational Safety and Health Administration
OVE	Oil vapour emission
PEL	Permissible Exposure Limit
PGM	Personal Gas Monitor
PIC	Person In Charge
PLC	Programmable Logic Controller
POCP	Photochemical Ozone Creation Potential
PPE	Personal Protective Equipment
P-V	Pressure-vacuum
RACT	Reasonably Achievable Control Technology
RVP	Reid Vapour Pressure
SD	Sounding pipe
SEEMP	Shipboard energy efficiency management plan

SIRE	Ship Inspection Control Programme, Under OCIMF
SOLAS	Convention On Safety of Life at Sea
Suezmax	Maximum size of a laden tanker which can pass through Suez Canal, typically around 160,000 dwt
SVP	Saturated Vapour Pressure
TEA	Toxic Exposure Assessment
THA	Toxic Hazard Assessment
TLV	Threshold Limit Value
TVP	True Vapour Pressure
ULCC	Ultra Large Crude Carrier, usually 320,000 dwt and above
UNCTAD	United Nations Conference on Trade and Development
UNECE	United Nations Economic Commission for Europe
USA	United States of America
UV-DOAS	Ultra-Violet Differential Optical Absorption Spectroscopy
VECS	Vapour Emission and Control System
VLCC	Very Large Crude Carrier, usually 200,000 dwt
VOC	Volatile Organic Compound
VOCIC	VOC Industry Co-Operation
VOCON	Vapour pressure release control valve
VOCTHA	Volatile Organic Compound Toxic Hazard Assessment
vol	Volume
WG	Water Gauge

Journal Paper

Details of the research papers published or in the process of being accepted

a)   Published

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Chapter 1. Introduction

1.1 Background

The world economy is heavily dependent upon the use of oil. Oil is primarily used as fuel in the transport sector, and its derivatives are used in other sectors such as the pharmaceutical and chemical sectors. The oil used in the transportation sector is refined from crude oil. Crude oil is shipped worldwide using marine oil tankers, referred to as 'Oil Tankers' in this thesis. Currently, most of the ships in the world use oil as fuel for their propulsion.

Oil is mainly used as fuel and lubricant for ship machinery, though a minor percentage uses 'Liquefied Natural Gas' (LNG). Crude oil production is only available in specific geographic locations. It needs to be shipped across various consumer countries, primarily using oil tankers. Crude oil wells located over land or offshore locations either pump crude oil to shore-based oil tanks via pipelines in nearby ports or refineries or directly transfer it to oil tankers in offshore locations. Crude oil and refined products, widely known as Clean Petroleum Products (CPP), are loaded onboard oil tankers for shipment to various consumer countries. Transferring crude oil and CPP onboard oil tankers is known as 'Loading Operation', and transferring fuel oil onboard ships is known as 'Bunkering Operation'. Oil vapours are mostly vented freely to the open atmosphere from the respective ship tank's venting pipes during loading operations onboard oil tankers and bunkering operations on all types of ships.

During loading and bunkering operations, the 'Oil Vapour Emission' (OVE) exposes ship personnel to the toxic substances present in this emission. A significant portion of OVE contains volatile compounds of various hydrocarbons, known as Volatile Organic Compounds (VOCs). The presence of toxic VOCs in this OVE around the ship's surrounding environment is a cause for concern due to their well-known adverse health effects, as well as them causing local air pollution. Continued exposure to VOCs can cause acute and chronic effects on human health, affecting respiratory, nervous, immune, and reproductive systems. Adverse health effects of toxic VOCs from OVE have been widely discussed in the literature (Ellis, 1989; Lin *et al.*, 2004; Ras *et al.*,

2009; Claxton, 2014b; Tamaddoni *et al.*, 2014; Wei *et al.*, 2014). Inhalation and dermal exposure to workers may occur during crude oil transportation (API, 2011). Knowing the toxic properties of petroleum products and constituents is undoubtedly important for understanding the carcinogenicity of carbon-based fuels (Claxton, 2014b)

Volatile compounds can escape from the oil mass during all steps of the crude oil industry, from extraction sites and transportation facilities to storage tanks and refineries. Therefore, the production sites and oil refineries have been recognised as the second major origin of the VOCs after vehicle exhausts in the transportation sector (Rajabi *et al.*, 2020). Hence, VOC emission during tanker loading and ship bunkering operations must be minimised or altogether stopped to safeguard air quality and human health.

The primary fossil fuels (crude oil or petroleum, natural gas, and coal) remain society's primary energy sources. They are the feedstocks for a vast assortment of synthetic materials and products. Nearly 3000 different compounds, primarily organic, resulting from human activity, have been identified in the atmosphere. This complex mixture of pollutants can have an impact on health and the environment. The search for alternative fuels to reduce dependence on petroleum and the emission of pollutants into the atmosphere has stimulated many scientific studies. Pollution and the health effects of fuel-based pollution are a worldwide problem (Claxton, 2014b). Crude oil exploitation industries have been classified by several regional regulations as one of the primary sources of VOCs so far. However, a comprehensive standard is still missing to control crude oil vapour emission (CVE) on a global scale and to pose restrictive policies on OPEC (Organization of Petroleum Exporting Countries) nations as well as industrial countries with high crude oil imports (Rajabi *et al.*, 2020). Numerous studies conducted in various countries to analyse air pollution near petroleum refineries indicate elevated levels of harmful VOCs in the surrounding regions and near storage tank farms (Kalabokas *et al.*, 2001; Lin *et al.*, 2004; Paulauskiene *et al.*, 2009).

In early 2019, the total world fleet stood at 95,402 ships, accounting for 1.97 billion deadweight tonnes (dwt) of capacity. Oil tankers' share in this dwt was 28.7 per cent.

The capacity dwt almost trebled from 1980 to 2019 (UNCTAD, 2020). Total oil supply in the world, which includes crude oil, natural gas liquids (NGLs), and non-conventional sources, increased from 66.5 million barrels per day (mbpd) in 1991 to 100.5 mbpd in 2019, an increase of over 50% in the last three decades (IEA, 1991; IEA, 2020), as shown in Table 1.1.

Year	World Fleet Thousands dwt	Total oil supply Million barrels per day
1990	651,282	66.5
2019	1,976,491	100.5
Increase	203%	51%

Table 1.1 Increase in world fleet and oil supply from 1990 to 2019

The lack of a comprehensive international standard on air pollution from ships has prompted local action in port cities and states where people bear the brunt of ship pollution. The growing patchwork of local rules and regulations is not a proper manner for regulating environmental protection in the shipping industry (Luttenberger *et al.*, 2013). Volatile organic compounds (VOCs) play an important role in the tropospheric atmospheric chemistry for the production of photochemical ozone (O_3) and other oxidants, which increase the atmospheric oxidising ability and adversely influence the air quality and human health (Wei *et al.*, 2014).

The quantities of oil transported by oil tankers are the highest because they are the most economical option. In the current world economy, this mode of oil transportation has become an integral and essential component. Due to the increasing volume of oil transportation and an increase in the capacity of the world fleet, it is imperative that the mechanism of OVE from tanker loading operations and ship bunkering operations be analysed in detail to understand its toxic potential as well as the resulting economic loss (Jurušs and Seile, 2017; Virdi *et al.*, 2021). However, research on financial loss is scarce, and more work needs to be done.

Current rules and regulations under international conventions such as SOLAS and MARPOL concerning the OVE from loading operations and bunkering operations are almost ineffective at the local and global levels. Although there are various rules and regulations to minimise the air pollution from the ship's engine exhaust emissions (DeLuchi, 1993; Agrawal *et al.*, 2008), a similar approach for vapour emission from oil tanker loading operations and ship's bunkering operations is lacking. Current tanker and ship design, such as siting of vapour vents and sounding pipes, does not consider the probability of toxic VOCs and their exposure risk to ship's personnel during tanker loading operations and ship bunkering operations. Venting of OVE also causes the economic loss of valuable hydrocarbons that can be recovered with existing technologies, thus enhancing the overall efficiency of tanker loading and the ship's bunkering operations.

1.2 Ship and oil tanker design and operation

Hence, there is an urgent need to analyse design, equipment, and work practices related to tanker loading and ship bunkering operations. This will enhance the efficiency and sustainability of using oil in the world economy and reduce the carbon emission from the current processes.

To understand the impact of toxic VOCs during OVE, the arrangement and location of fuel tanks and cargo tanks are described in the following sections.

1.2.1 Ship design

Ships are designed to carry containers, dry bulk cargo, liquid bulk cargo such as oil, chemicals and liquefied gases, vehicles such as cars, trucks and buses, passengers etc. The ship's hull acts as a container to load various cargo, and oil fuel tanks are also part of the hull. Only liquified gases are carried in extra independent containment inside the hull. Usually, the ship is divided into two main portions, the cargo area and machinery space with the superstructure, as shown in Figure 1.1 (a) and (b). Ship's fuel tanks, traditionally known as 'Bunker tanks', are located near the machinery space.
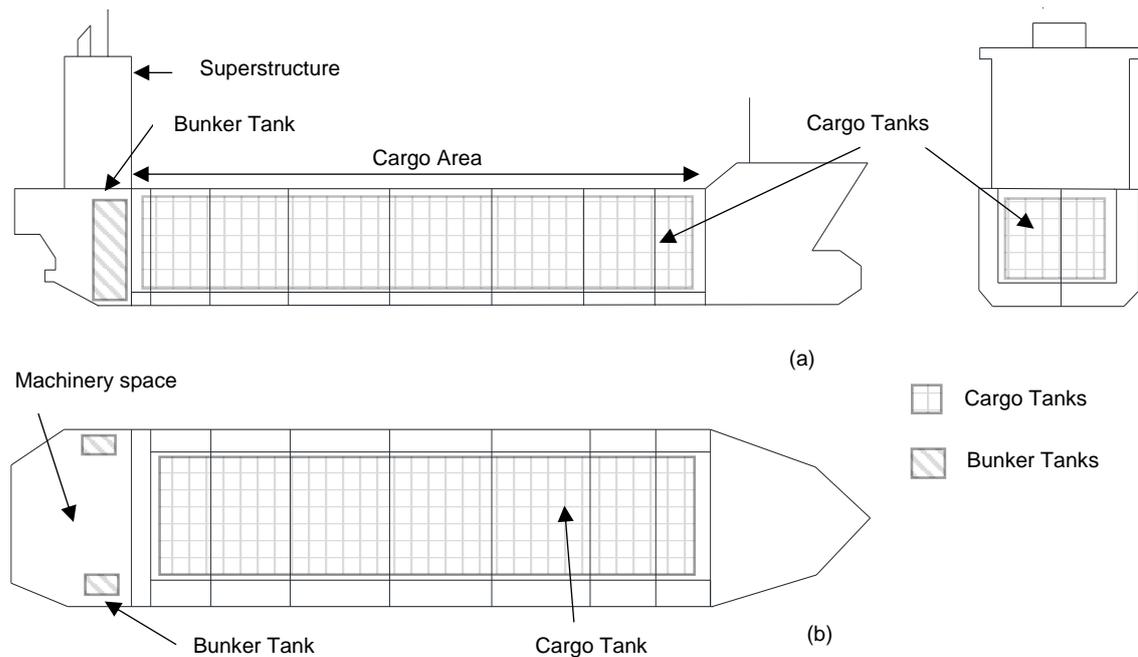
Figure 1.1 (a) Side view and Midship section of a typical oil tanker (b) Top view showing the arrangement of cargo oil tanks and bunker tanks

1.2.2 Oil tanker design

An oil tanker uses the ship's hull as a container to carry oil in massive quantities. The side view and midship section of a typical marine oil tanker are shown in Figure 1.1 (a), and the top view is shown in Figure 1.1 (b). The hull of the ship is used as a containment for transporting oil. The compartments which carry crude oil or CPP are known as 'Cargo 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 and loading points (known as manifolds) by a network of steel pipelines for loading and inter transfer of liquids and vapours. The liquid pipelines, situated at the bottom level of each tank, are used to load, and unload oil in the tanks.

Each cargo tank is connected to a typical vapour pipeline, known as 'Inert Gas Line' or 'Ventilation Line' (Ventilation Line is used for ships that are not required to have an Inert Gas System). This typical vapour pipeline is connected to a standard venting pipe, known as a 'Mast Riser.' (Figure 1.2 and Figure 1.3)

5

Each cargo tank has an automatic 'Pressure – Vacuum Valve,' known as 'P-V Valve' or 'High-Velocity Vent.' (HVV). This is a simple weight-activated relief valve to govern the maximum allowable pressure and vacuum setting for each cargo tank (MSC.380(94), 2014).
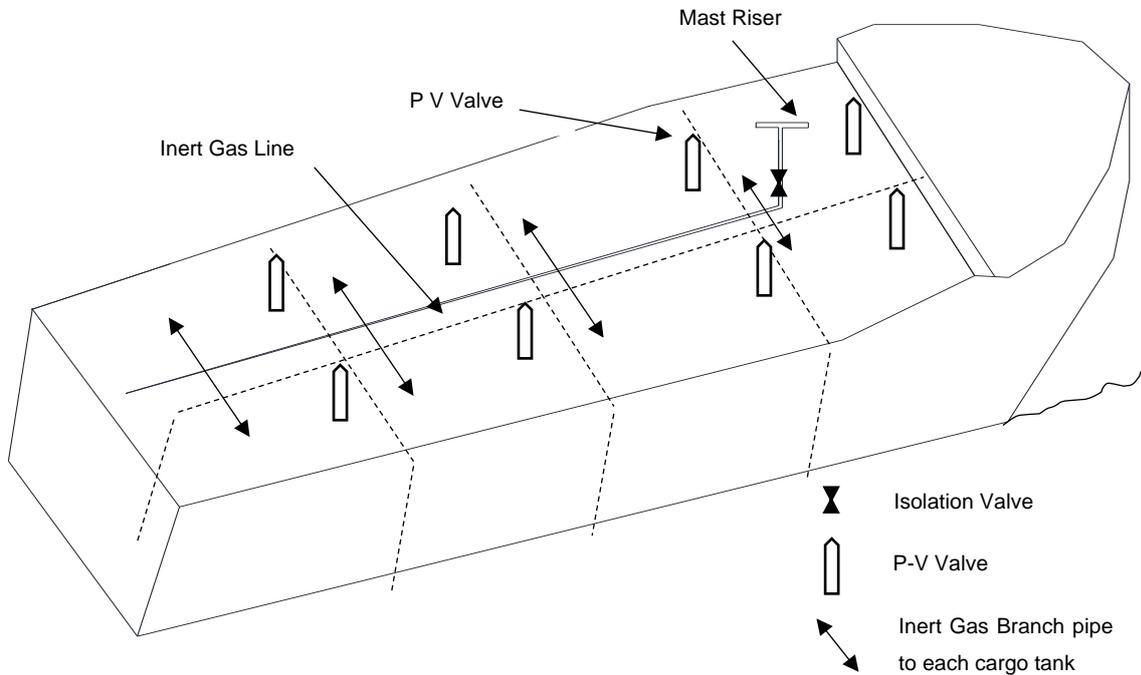
Figure 1.2 Location of Inert Gas Line, P-V Valves and Mast Riser on an Oil Tanker

Figure 1.3 Main cargo deck of a crude oil tanker (MEPC.1/Circ.680, 2009)

During oil loading operations in a CPP tanker, vapours are freely vented to the atmosphere from P/V Valves either continuously via manual setting or auto operation. In crude oil tanker loading operation, vapours are intermittently vented to the atmosphere from Mast Riser, usually maintaining a fixed tank pressure per the respective guidelines.

1.2.3 Bunkering operations

Filling of fuel oil such as Heavy Oil, Gas Oil, and Lubricating Oil in the ship's fuel tanks is known as Bunkering operations. Oil is received from the barges or shoreside terminals via pipelines in the ship's tanks. Oil vapours are freely vented via venting pipes on the main deck during these bunkering operations, typically situated near the fuel tank top around the ship's accommodation areas.

The close siting of air vents and sounding pipes can potentially cause toxic exposure to VOCs during the bunkering operations, which can last for up to 6 to 8 hours for a medium-size ship of 50,000 dwt, and more for bigger ships.

Moreover, the air pipes are situated very close to the entrance door of the accommodation, as shown in Figure 1.4, which also has the potential to admit OVE to the accommodation. Bunker tank air vents (AV) and their respective Sounding Pipes (SD), as shown in Figure 1.5, are also located in proximity. During the bunkering operations, free venting of Fuel Oil vapours exposes the Duty Engineer to the toxic fumes in OVE while checking the tank sounding during the ship's bunkering operations. The distance between the air vent and sounding pipe is around 2200 mm, as shown in Figure 1.6, as an example from one of the ship's detailed drawings.
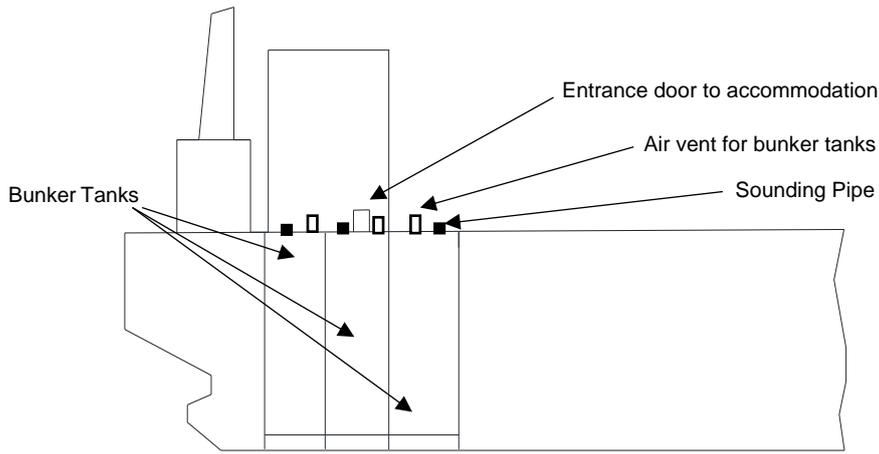
Figure 1.4 Arrangement of bunker tank and their air vent and sounding pipe

Bunker Tank Air Vent

Bunker Tank Sounding Pipe

Distance between Sounding Pipe and Air Vent = (380+230) = 610 mm

(a)

| AV and SD for No. 1 HFO Bunker Tank (P) |
| AV and SD for No. 2 HFO Bunker Tank (P) |
| AV and SD for No. 2 HFO Bunker Tank (S) |
| AV and SD for No. 1 HFO Bunker Tank (S) |

Engine Room

Cargo Tanks

▯ – Air Vent (AV)
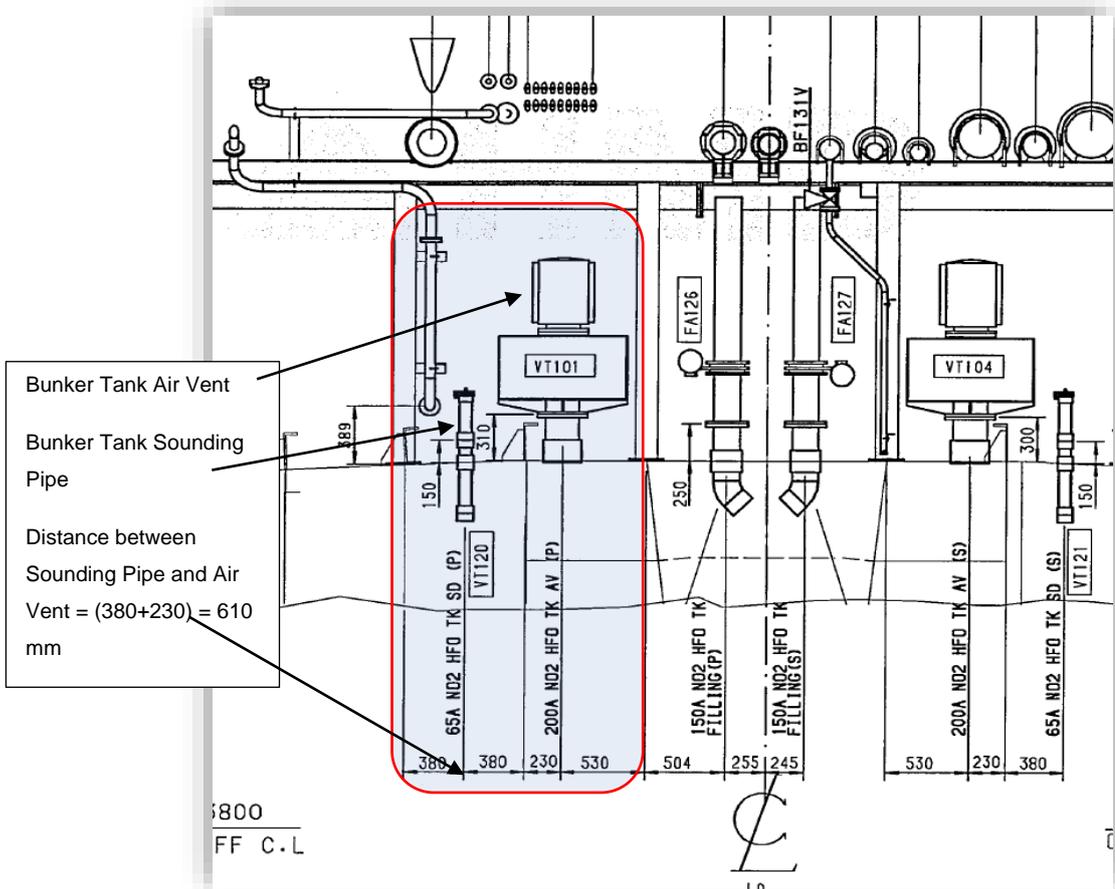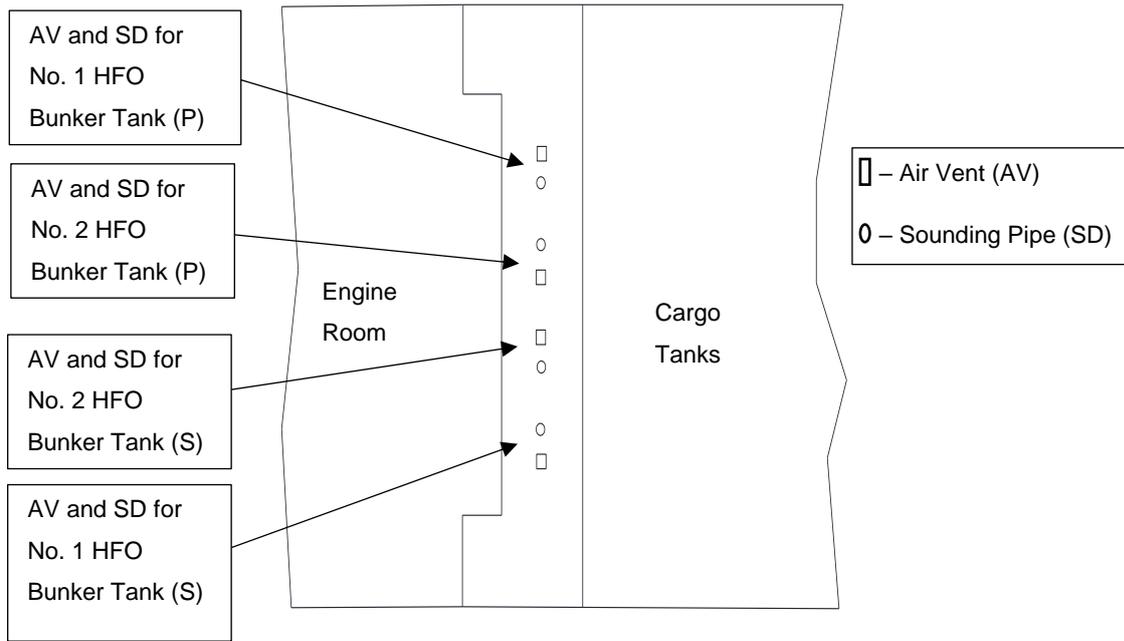
0 – Sounding Pipe (SD)

(b)

Figure 1.5 Location of bunker tank air vents and sounding pipes (a) Ship's Plan (b) Simplified sketch (Piping, 2006)
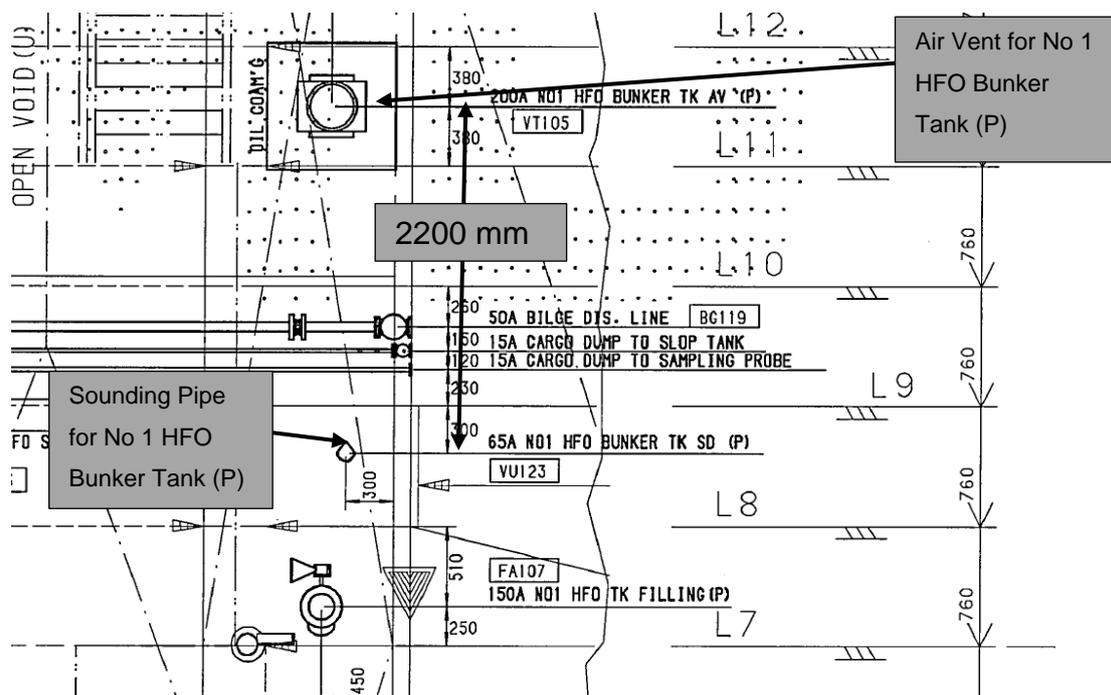
Figure 1.6 Ship's plan showing the distance between a bunker tank air vent and sounding pipe – detailed view (Piping, 2006)

1.2.4 Oil tanker loading operations

OVE from cargo tanks in an oil tanker can occur in two stages.

a) During the time of oil transfer, and

b) During the transportation

The thesis focuses only on the OVE during the oil tanker loading and ship bunkering operations.

Before an oil tanker commences loading operations, the tanks usually contain inert gas (IG). Inert gas is composed of mainly nitrogen and carbon dioxide, with an 8% or below oxygen content. This composition is used to make the tank atmosphere non-flammable. Smaller tankers, usually with 8,000 dwt or below, may have fresh air in the tanks instead of the IG (SOLAS, 2023). The safety onboard smaller tankers, having fresh air in the tanks, is ensured by following safe working practice of not allowing any dipping of

any object such as sounding rod during loading and at least waiting for 30 minutes on completion of loading. Another safety procedure to follow during gas freeing is maintaining the tank atmosphere below 50% LEL by regular monitoring of tank atmosphere for LEL reading using the portable gas monitoring equipment (OCIMF, 2006).

During tanker loading operations, the existing tank atmosphere must be vented to keep the safe pressure within the tank. Most ships use free or controlled venting methods, from single standard Mast Riser or individual Pressure-Vacuum (P-V) valves to carry out this venting, as shown in Figure 1.7 and Figure 1.8.

Oil tankers are also fitted with Vapour Emission Control Systems (VECS), which complies with the standards for VECS as per IMO MSC Circ.585(MARPOL, 2023). This system assists in collecting oil vapours when such a system is available in shore terminals where loading operations is being carried out. It is not mandatory to have VECS fitted onboard tankers, but most tankers engaged in international trade install the VECS system due to commercial considerations such as charterers' requirements. As per information available from IMO, only South Korea and The Netherlands have some oil terminals where this system is being used. Additionally, there are very few oil loading terminals in Norway, the USA, and Europe, where VECS is used due to strict local environmental regulations (Energy, 2008b).

As an example, from the ship's drawing, the Cargo tank sounding pipe or ullage pockets are sited very near the cargo tank venting pipe, as shown in Figure 1.9. The close siting of the sounding pipe exposes the Duty officers and deck crew to toxic components present in OVE from these vents when regular soundings or ullages need to be taken during tanker loading operations. Furthermore, a massive volume of VOCs present in this OVE also causes concentrated local air pollution, particularly in petroleum exporting terminals where numerous loading operations may happen in the vicinity.
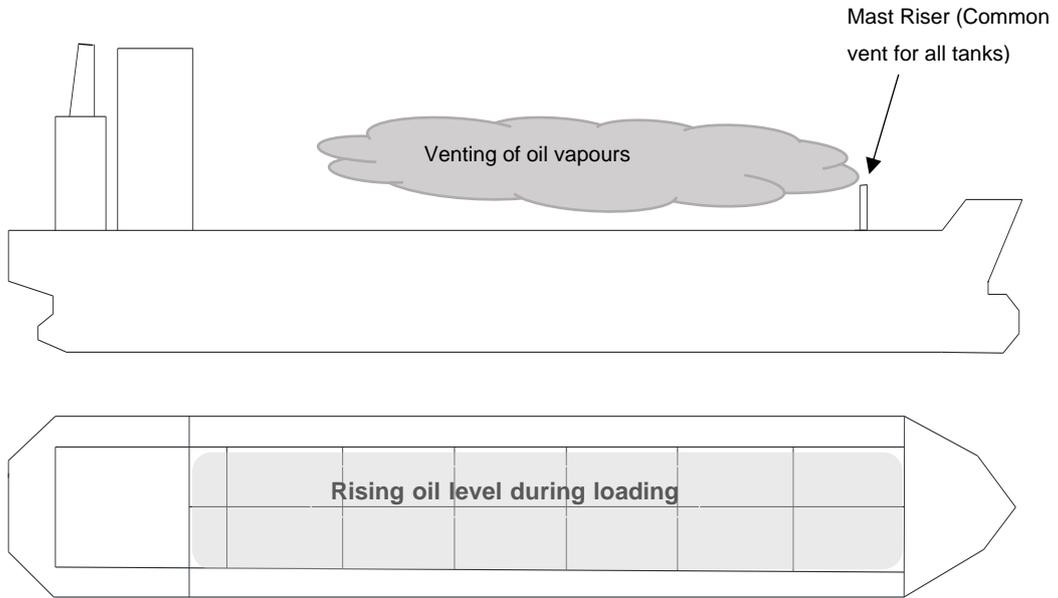
Figure 1.7 Venting of oil vapours from Mast Riser during loading operations in a crude oil tanker
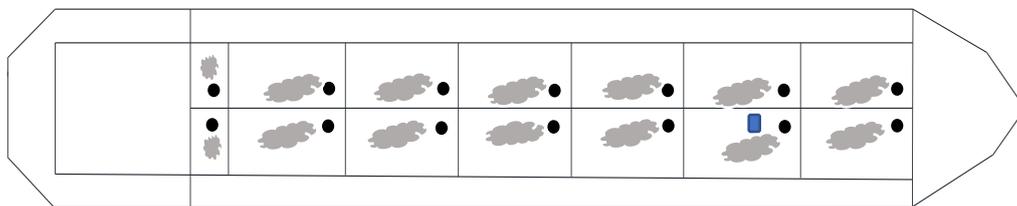
■ Mast Riser, Common Vent

● Pressure-Vacuum Valve, one for each
   Vented vapours

Figure 1.8 Venting of oil vapours from P-V Valve during loading operation in a CPP tanker
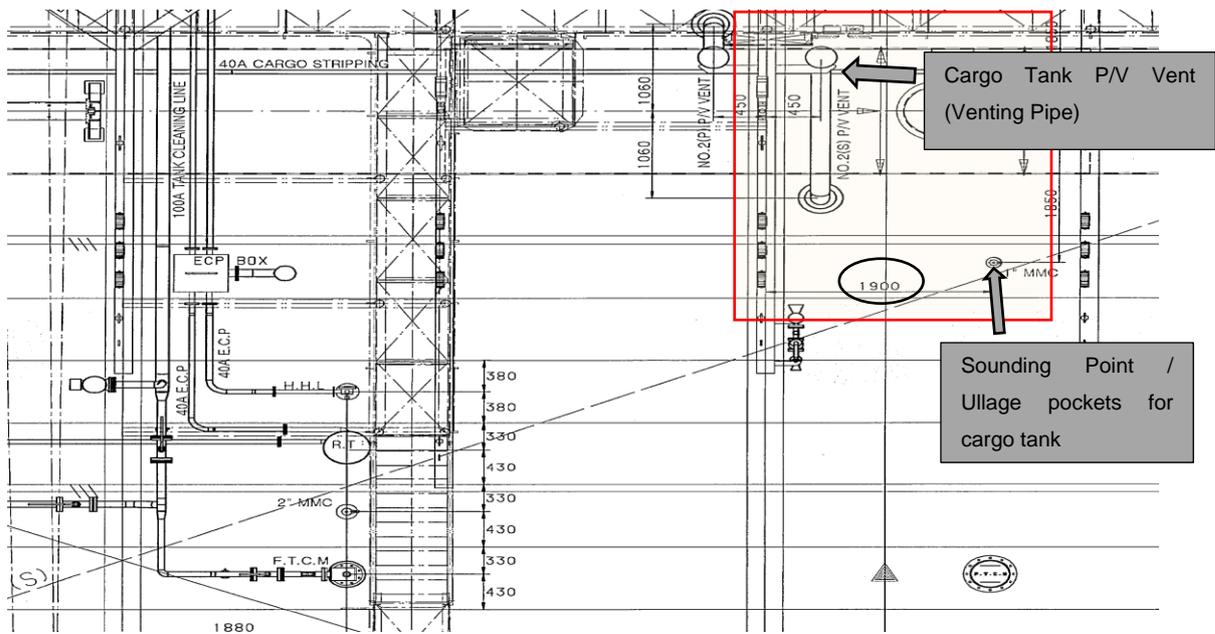
Figure 1.9 Location of cargo tank Air Vent (V) and Sounding pipe (SP) for a cargo tank in an oil tanker (Piping, 2006)

1.3 Problem statement

Oil vapours are vented in the surrounding environment during the loading operations onboard oil tankers and bunkering operations on all ships. This OVE, which may contain toxic VOCs, can degrade air quality onboard ships and the surrounding environment of loading terminals and bunkering locations due to the enormous volume of OVE. The regular exposure to the toxic VOCs presents in OVE in the surrounding atmosphere may affect their health in the long run. There are no regulations related to the design of tankers and ships to account for the Toxic Exposure Assessment (TEA) of VOCs in this OVE, nor are there any standardised industry work practices for monitoring their toxic exposure. Ship personnel are currently being provided with 'Personal Gas Monitors' (PGM) while working on deck during loading operations for monitoring the concentration of 'Hydrogen Sulphide' (H_2S) and 'Hydrocarbon' (HC) vapours only. The provision of PGM is to comply with the charterer's requirements, such as vetting by major oil companies under the OCIMF (Oil Companies International

Marine Forum) regime. There is no legislative requirement to monitor the concentration of toxic VOCs present in such OVE. Similar concerns arise during bunkering operations when oil vapours are vented freely from low-level air pipes near the deck and accommodation areas. The amount of oil vapours being released can vary from a few hundred to a few thousand cubic meters, depending on the volume of bunker tanks in a few hours. These volumetric losses of oil vapours also depend upon the volatility and the ambient temperature of the oil loading terminals, resulting in a direct monetary loss.

The abundant release of oil vapours during tanker loading and ship bunkering operations globally has neither been acknowledged nor been evaluated for its contribution to local air pollution and its effect on the health of seafarers. There is an urgent need to quantify such release and assess the impact on the environment to safeguard human health. Most of the oil-exporting countries and bunkering locations worldwide do not have any stringent rules and regulations for control of OVE containing toxic VOCs. The design requirement for oil tanks vents and air pipes, for oil tankers and ship's bunker tanks, under IMO (International Maritime Organization) conventions such as SOLAS (Safety of Life at Sea) as well as current work practices based on current MARPOL (International Convention for prevention of pollution from ships) convention need to be critically analysed for their adequacy in addressing 'Toxic Hazard Assessment' (THA) of these VOCs. Thus, there is an urgent need to amend the current ship design rules in the SOLAS convention. Similarly, relevant regulations in the MARPOL convention and current industry practices need to be reviewed to stop OVE during tanker loading operations and ship bunkering operations.

1.4 Aims and Objectives

The research aims to analyse loading operations in crude oil and gasoline tankers and ship bunkering operations. The reasons and brief description are as follows:

1.4.1 Aim and Objective 1

Aim 1: Quantify the volume of crude oil and gasoline lost during the tanker loading operation to measure economic loss and suggest a feasible solution to enhance the efficiency of the current tanker practices.

Objective 1: The modelling of crude oil and gasoline flow will be done using Aspen HYSYS ® chemical process simulator. The simulation data output will calculate the fraction of crude oil and gasoline lost during tanker loading operations. The volume of the liquid pumped from the shore tank and the volume of the liquid received in the ship's tank will be compared to quantify the crude oil and gasoline lost to the evaporation. The data will be used to calculate the monetary loss. Modifications in tanker design and loading practices will be proposed to stop or minimise this financial loss.

1.4.2 Aim and Objective 2

Aim 2: Quantify the volume of vapours (VOCs) emitted during tanker loading operations to understand the impact on the air quality. Propose amendments to stop or minimise VOC emission to preserve air quality.

Objective 2: Aspen HYSYS ® chemical process simulator will be used to find the volume of OVE during crude oil loading operation in an Aframax Tanker (dwt 110,000 tonnes) and an 'Ultra Large Crude Carrier (ULCC) (dwt 320,000 tonnes) and gasoline loading in a product tanker (dwt 37,000) (Aspentech, 2024b; Aspentech, 2024a; Ivana Lukec, 2024). The composition analysis will be able to identify toxic VOCs in the OVE, which have a direct impact on air quality around the oil tanker terminals. The simulation output results will be verified by comparing the results obtained from an alternative chemical process simulation software, namely DWSIM (DWSIM, 2023). Amendments to ship design and working practices will be proposed to minimise VOC emission to preserve air quality.

1.4.3 Aim and Objective 3

Aim 3: Identify and analyse the composition of vapour emission (VOCs) for toxicity hazard assessment of tanker loading and ship bunkering practice. Propose

amendments to ship design and working practice to minimise toxic VOC exposure to safeguard health of seafarers.

Objective 3: Output from Aspen HYSYS ® chemical process simulator will identify the toxic components in VOC emission. The concentration of toxic components will help establish the exposure above the 'Permissible Exposure Level'. This is essential to propose additional safeguards to protect the health of seafarers. Related amendments to ship design and working practices will be proposed.

1.4.4 Aim and Objective 4

Aim 4: Critical analysis of the current international conventions (SOLAS and MARPOL) and local rules related to VOC emission from OVE due to oil tanker loading and ship bunkering operations, with reference to toxic vapour exposure to seafarers and localised air pollution. Propose amendments to minimise carbon emission from tanker loading and ship bunkering operations.

Objective 4: A detailed analysis of the international conventions related to the control of of VOC emission from tanker loading and ship bunkering operations will be conducted to limit GHG and carbon emission. Ship's design rules, such as siting and location of air vents and sounding pipes for oil tanks onboard tankers and ship's bunker tanks, will be analysed. The adequacy of the existing design parameters in the SOLAS convention and operational regulations in the MARPOL convention to safeguard the health of seafarers and the impact on local air quality will be analysed, supported by findings from the Aspen HYSYS ® chemical process simulator. New amendments will be proposed to modify ship design to minimise or stop VOC emission and amend current tanker loading and ship bunkering practices based on the revised arrangements.

1.5 Outline

The details of the 'Literature Review' are presented in Chapter 2. It analyses the status of the ship's design and working practices related to oil tanker loading operations and bunkering operations. Based on the analysis, gaps are identified as per the research aims and objectives. Current literature related to the quantum of OVE and its resulting

air pollution, followed by current technology in use for vapour recovery, is analysed, and gap analysis is conducted as per the aims and objectives of the research. This chapter also provides critical analysis of the existing regulations in international conventions such as SOLAS and MARPOL, regional rules and national initiatives as per Aim and Objective 4, Sub-section 1.4.4.

As the research aims to analyse OVE, Chapter 3 provides details on the methodology used to model crude oil and gasoline in Aspen HYSYS Chemical Process Simulator. The simulation output provides the details on the quantity and quality of OVE. The basis of selection of the assumed chemical composition of crude oil and gasoline, rate of loading, tank pressure and temperature of the oil are also described.

The evaporative loss for crude oil and gasoline during loading operations, and proposed amendments to minimise it are described in Chapter 4 to address Aim and Objective 1, Sub-section 1.4.1.

Chapter 5 provides a detailed analysis of the volume of VOCs in the OVE due to tanker loading and ship bunkering operations, affecting the local air quality surrounding tanker terminals. The chapter provides information on proposed amendments to ship design and working practices to preserve local air quality, as per Aim and Objective 2, Sub-section 1.4.2.

In Chapter 6, Simulation results related to the composition of OVE are presented, to identify the presence of toxic VOCs, as per Aim and Objective 3, Sub-section 1.4.3. This is followed by the proposed amendment to ship design and best practices to minimise exposure to toxic VOCs and to preserve air quality.

Lastly, Chapter 7 provides details on the proposed new regulations, the amendments to the existing regulations in SOLAS and MARPOL conventions, and unique regional or local regulations to minimise or stop VOC emission from the oil tanker loading and ship bunkering operations. This chapter addresses Aim and Objective 4, Sub-section1.4.4, whereas the critical analysis of the regulations is included in Chapter 2, Section 2.4.

Chapter 8 provides the Conclusion, and future work is included in Chapter 9.

The overall summary of the outline is shown in Table 1.2.

Aims and Objectives Chapter 1	Literature Review Chapter 2	Description
1 – 1.4.1	Section 2.1	Chapter 4
2 – 1.4.2	Section 2.2	Chapter 5
3 – 1.4.3	Section 2.3	Chapter 6
4 – 1.4.4	Section 2.4	Chapter 7

Table 1.2 Summary of research aims and objectives as described in respective chapters.

Chapter 2. Literature Review

The transport of crude and petroleum products by sea is a major primary driver and a facilitator of international trade, of which some 90% is carried by sea (Fulbright, 2018). Marine oil tankers worldwide ship oil from oil-producing countries to oil-consuming countries. Each tanker loading operation directly emits oil vapours into the atmosphere. Similarly, oil vapours are continuously vented into the atmosphere whenever a ship's tanks are filled with fuel (bunkering operations). In total, the emission of VOC from global sea transportation accounts for a total of more than 5 million tonnes per year (Wartsila, 2022a). This chapter analyses the status of the ship's design and working practices related to oil tanker loading operations and bunkering operations. Based on the analysis, gaps are identified as per the research aims and objectives. Current literature review has very limited work which is directly related to oil tanker loading operations. The data is presented from the currently published papers on handling petroleum products in oil tankers and terminals and oil refineries, where some co-relations can be drawn as per the objectives of the thesis.

2.1 Evaporative loss during loading and bunkering operations

Crude oils originate from different geographical sources around the world. Every crude oil from a specific geographical source contains different quantities of the various compounds that make up its composition (PujadÛ and Jones, 2006). During loading operations and bunkering, vapours are vented freely to the atmosphere to maintain the tank pressure, intermittently or continuously, using designated venting arrangements as per the current ship design and working practices. As the vapours are generated from the oil (crude oil, gasoline, or bunker fuel) being loaded, it results in a direct monetary loss.

The emission of oil vapours, or Volatile Organic Compounds (VOCs), to the atmosphere from tankers worldwide is not known to have been measured and assessed systematically. However, limited research papers have been published due

to local environmental regulations. One prominent example, which can be quoted here, is the national objectives of VOC emission reduction from tanker loading operations in Norway (Martens *et al.*, 2001; Hansen *et al.*, 2008; Wartsila, 2017). Martens *et al.* conducted a detailed study on various alternatives to capture the VOC emission during the offshore loading of crude oil tankers in Norway. The emission represented a loss of considerable monetary value and harmful environmental consequences (Martens *et al.*, 2001).

Similarly, Statoil in Norway has been investigating the loss of oil since the mid-1980s on shuttle tankers operating near the Norwegian coast. In 1987 and 1989, observations on these tankers found that the difference in the quantity delivered in the field and the amount received at the terminal was almost 0.2% by weight. For a shipment of 100,000 tonnes, there is a loss of about 200 tonnes (Wartsila, 2022). It can be assumed that most of this loss can be a loading loss as transit time from the offshore field to the terminal ashore is typically less than two days. This is useful to document that the loss of oil has been a concern for a long time.

Oil tanker owners in Norway have participated in numerous projects since 2003 to meet the national goal of a 70% reduction in VOC emission during offshore loading of crude oil to meet emission targets as per LRTAP Convention and Gothenburg Protocol (Hansen *et al.*, 2008). Tanker owners and oil field operators worked together under VOC Industry Cooperation (VOCIC) to find economical ways to achieve the VOC reduction targets. Under this VOCIC project, Hansen *et al.* investigated alternative low-cost solutions to achieve VOC emission reduction during loading operations. As installing a VOC recovery plant was considered expensive and complex to operate, another two new options were investigated in detail. One was an increase in the cargo tank operating pressure, and the other was installing a VOC absorbing system in crude oil in the cargo tank itself. Measurements were done for VOC emission reduction for both the options onboard shuttle tankers operating in the Norwegian offshore region. Volumetric oil flow, cargo tank pressure, temperature and composition of the gas flowing out of the tank were measured. These measurements were used to calculate the mass of emitted VOCs at the end of the loading operation, which was found to be 0.2% of the loaded mass of cargo, equalling 230 mt, for an oil shipment in an Aframax tanker. (Hansen *et al.*, 2008).

The findings do not provide details on the composition, or the density of crude oil being loaded, which can be an important parameter affecting the evaporation rate. The

investigation by Martens *et al.* reported a loss of 230 mt of crude oil during a specific loading operation. The monetary loss is calculated using API = 39.4 for Statfjord blends crude oil from a Norwegian basin, which is the type of crude oil mentioned in the investigation. The average crude oil price for 2020 and 2021 is US $70/bbl (Price, 2022). The calculated monetary loss is US $122,290 for every loading operation. As a conservative estimate, a tanker engaged in the shuttle trade usually conducts 36 loading operations annually, resulting in an annual loss of $4.4 million (ExxonMobil, 2018). The evaporative loss could be even higher if more frequent loading operations are conducted. However, the investigation did not provide any data on the actual difference between the crude oil pumped to the ship and the volume received. It could be due to high uncertainty in the measurement due to open sea conditions in the offshore loading area where the vessel is rolling and pitching due to prevailing weather conditions in the North Sea.

Grant and Mike provided information on the option of VOC recovery in crude oil loading operations. As they are engaged in a company providing solutions for VOC recovery from crude oil, it was estimated that approximately 2000 barrels of crude oil could be recovered for a total loading of 2 million barrels of crude oil in a 'Very Large Crude Carrier' (VLCC) (Todd, 2016). Using similar data for the cost of crude oil, it could be an economic loss of US $140,000 for a single loading operation. Based on a typical loading pattern, assuming 18 voyages for a VLCC in a year will amount to an annual loss of US $2.52 million. The authors neither provided the basis of their findings nor accounted for the variability in the results due to the different composition and temperature of crude oil.

Wartsila has provided information on a new concept of a shuttle tanker designed for reduced emissions for Teekay Tankers. The new concept can potentially reduce the CO_2 emission of a tanker by 42% (Wartsila, 2017). It is claimed that loading 850,000 bbls in North Sea installation can yield 100 tonnes of liquefied hydrocarbons and 10 tonnes of lighter hydrocarbons as vapours, both of which can be used as fuel in the ship's machinery. Another tanker design solution to minimise emission quotes a yearly emission of 3300 tonnes of VOCs for every offshore loading in transporting crude oil (Wartsila, 2018). This quantity may have included VOC emissions during loading and transit time. These developments in recent years have helped establish that shuttle tanker owners are taking innovative steps to minimise or stop VOC emissions during

loading operations. Technology is available to provide alternative solutions to capture and utilise these VOCs to enhance the efficiency of tanker operations.

Evaporative losses for loading operations with open venting involving petroleum products on ships and barges are dealt with in mathematical, empirical formulae in a common standard prepared by 'Energy Institute (EI) Hydrocarbon Management Committee and 'American Petroleum Institute' (API) Committee on Petroleum Measurement (EI, 2009). The standard estimating loading losses during loading crude oil and gasoline on ships and barges; there are tabulated values for Emission Factors (EF) to estimate emissions from typical loading operations. Loading loss is determined using the general expression for the volume of the liquid, saturation factor and vapour density at equilibrium. The loss from an uncontrolled petroleum liquid loading episode L_L is:

$$L_L = \frac{(V_L * K_S * P_{VA} * M_V)}{(R * T_V)}$$
Equation 2.1

where

L_L is Loading Loss;

V_L is the volume of liquid loaded;

K_S is the Saturation Factor, which is a function of the type of cargo and compartment condition before loading, a dimensionless quantity tabulated in the standard;

P_{VA} is the True Vapour Pressure (TVP) of the liquid;

M_V is the molecular weight of the stock vapours;

R is the ideal gas constant;

T_V is the absolute temperature of the ullage

Using SI units, Equation 2.1 is modified as below:

$$L_L \left(\frac{kg}{1000\ l}\right) = 0.1203 * \left[\frac{K_S * P_{VA} * M_V}{T_V}\right]$$
Equation 2.2

where units for P_{VA} is in kPa, M_V in kg/kg-mole and T_V in Kelvin.

The standard does not address evaporative loss for Very Large Crude Carriers (VLCC) and Ultra Large Crude Carriers (ULCC) unless Saturation Factor (K_S) is determined. Saturation Factor K_S depends on the previous cargo's volatility and whether the compartment was cleaned, uncleaned, or gas freed before loading. Annexe F of this

publication provides specific volumetric evaporative cargo loss factors as per Table 2.1 and Table 2.2.

Equation 2.2 is helpful in estimating the evaporative loss if the TVP, the vapours' molecular weight, and the temperature of the ullage space are known. However, the accuracy will depend upon the certainty of the Saturation Factor in use. The equation does not account for the flow rate, which could also be an influencing parameter.

Stock / Vessel	Typical Loss Factors (vol. %)
Crude oil tankers	
Non-lightered	0.03
Lightered	0.05
Gasoline tankers	0.05
Gasoline barges	0.08

Table 2.1 Volumetric Evaporative Cargo Loss Factors (EI, 2009)

Crude Oil Vessel Operation	P_{VA} (psi$_a$)	M_V (lb/lb-mole)	Estimated loss (vol%)
Non-lightered	1	70	0.01
	1	40	0.02
	4	58	0.03
	7	70	0.04
	7	40	0.08
Lightered	1	70	0.01
	1	40	0.02
	4	58	0.05
	7	70	0.07
	7	40	0.12

Table 2.2 Example of Predicted Crude Oil Evaporative Cargo Loss Factors (EI, 2009)

Jurus *et al.* studied the correct implementation of custom duties during the transhipment of liquid petroleum products transported by railway in Latvia (Jurušs and Seile, 2017). The study argued that if the loss of petroleum products has occurred due

to the nature of the goods, then the customs authorities should apply the only standard rate of loss. The study elaborated that the overall loss of petroleum products in rail transport due to natural wastage is affected by losses during loading and transit, amongst other factors such as breathing, working, and storage losses. The authors quoted the local Railway Agreement for the transportation of petroleum products, which states that railway administrations are not liable for loss of cargo mass up to 2% loss of mass for liquid products, products that must be transported in their liquid or fresh state, as well as wet cargo. The analysis included the working practice in the Netherlands, where customs authorities treat the evaporative loss as an irretrievable loss resulting from the nature of the goods. Still, relevant documentation is required to prove this loss. The law in the Netherlands does not establish a standard rate for irretrievable loss. Rates for loss that are being applied are based on practical observations. 0.2 – 0.3% is the most common loss rate applied in practice (Jurušs and Seile, 2017). The study also concludes that a 0.3% loss rate for petroleum products is a standard rate in business deals. The study acknowledges that the loss of petroleum products during various modes of transportation is well known. Although multiple mechanisms are being applied to account for the evaporative loss during the transportation of petroleum products, this research does not elaborate on the composition and temperature of the oil, which are essential parameters to understand the evaporative loss.

Marine Environment Protection Committee (MEPC) under 'International Maritime Organization' (IMO) has issued various information papers on preventing air pollution from ships. The information paper on 'The physical behaviour of crude oil influencing its carriage by sea (CRUCOGSA) and subsequent project' is a summary of a three-year research programme aimed at obtaining better knowledge of the physical properties of crude oils and developing new operational procedures for more efficient transportation of crude oil by sea as well as the limitation of maritime pollution from crude oil. CRUCOGSA study determined the physical behaviour of various crude oils whilst being transported such that increased efficiency can be obtained for controlling its volumetric loss. The preliminary measurement during this study found a loss of 0.4 to 0.6% of cargo volume for volatile crude oils, which was initially estimated to be at about 0.17% (MEPC47/INF.6, 2001). However, this loss is very close to 0.2% of data found in the study by Hansen *et al.* quoted above. The data provide preliminary

estimates of the volume being lost to evaporation. The data also does not specify the type and composition of crude oil or the temperature of crude oil.

Endresen did the modelling of VOC emissions from crude oil transport for ships. The modelling was done for crude oil carriers greater than 50,000 dwt, primarily involving Aframax, Suezmax and VLCCs, with an assumed average size of 75,000, 150,000, and 250,000 dwt, respectively. Twenty-nine main crude oil routes comprising 88% of 1466 Mt crude oil transported during 1996 were identified. The study tabulated the loss of crude oil during loading as 0.1% of the loaded weight (Endresen, 2003). The study does not provide details of the methodology used to estimate the loading loss emissions from tankers. Also, the quoted details in the study are not available publicly to verify.

Energy Institute (EI) database has been selected as the best option to estimate the emission of VOCs from the transport of crude oil in the second IMO GHG study 2009 (IMO, 2009). The Emission Factor for bunkering was shown to be 0.00233 kg/tonne in a study conducted to understand the total life cycle emissions of containerships powered by conventional fuel or natural gas (Hua *et al.*, 2018). This study has also quoted the values tabulated by Endresen for loss of crude oil during loading as 0.1% of the loaded weight. No data is available for bunker oil as it is traded in much smaller volumes and has not been investigated.

Only limited information is available on the volume of oil lost due to evaporation for marine tankers. More in-depth data is needed to understand this evaporative loss which depends upon the rate of loading, composition and temperature of the oil, as well as the design of the equipment (Komar *et al.*, 2010). A detailed understanding of this evaporative loss, leading to an economic loss, will be able to justify a proposal for modifications to tanker design and work practices to enhance the sustainability of petroleum transportation by ships.

For the evaporative losses to be considered effective and structured, there is a need to simulate tanker loading operations in detail. The simulation should be able to account for specific crude oil and gasoline based on their composition or origin, at a particular flow rate and their respective temperature to have a realistic estimation of the economic loss.

2.2 Quantum of vapour emission during loading and bunkering operations affecting local air quality

As crude oil and gasoline volume shipped using tankers is steadily rising annually, the volume of oil vapours being introduced in the surrounding atmosphere is also increasing annually, as oil vapours are vented freely in the environment. Tanker loading operations and ship bunkering operations involve venting the current vapours in the tank to the atmosphere from 'Pressure – Vacuum' (P-V) valves, 'Mast Risers' or designated vent pipes. Table 2.3 provides information on the world oil supply from 2016 to 2019.

Year	World Oil Supply (Million barrels per day)
2016	96.9
2017	97.5
2018	100.3
2019	100.5

Table 2.3 World oil supply data

This section deals with the volume of oil vapours released into the surrounding environment, which affects local air quality. There are currently 10,240 tankers transporting 3.8 billion gallons of crude oil worldwide (Wartsila, 2019). Literature indicates that very few countries in the world restrict the release of oil vapour emissions from tanker loading operations as per their national objective (EU, 1994; Environment, 2020; EPA, 2020e; Gothenburg, 2020; USA, 2020). It is also observed that international conventions have almost no regulations to limit such release to the environment (MEPC.1/Circ.680, 2009; MARPOL, 2020; SOLAS, 2023). However, local laws in certain countries dictate limitations on oil tanker loading operations, such as in the EU, USA, and Norway. An analysis is presented further for such measures.

Emission Factors (EFs) have been used as a fundamental tool for air quality management in European Union (EU) states and the United States of America (USA). EFs are quoted in European Environment Agency (EEA) report 13/2019 and US Environmental Protection Agency (EPA) issued document 'AP-42: Compilation of Air Emission Factors' (EEA, 2019; EPA, 2020b).

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with releasing that pollutant (EPA, 2020b). The regulatory bodies, consultants, and industry use EF to estimate emissions, develop control strategies, and ascertain the effect of sources and appropriate mitigation strategies. Though source-specific emission monitoring is preferred for evaluating emissions, the data are not always available and sometimes may not show the variability of actual emissions over time. Thus, despite their limitations, EF is frequently the best or the only method for estimating emissions.

The source category's activity rate (AR) is multiplied by the appropriate EF to estimate the emission of the specified pollutant, as per Equation 2.3.

$$E_{Pollutants} = AR_{Production} \times EF_{Pollutant} \qquad\qquad \text{Equation 2.3}$$

The EEA report only cites the EF for 'Non-Methane VOC' (NMVOC) for gasoline loading in a marine tanker, which is quoted as 4 g/m^3 throughput/kPa TVP (0.18 kg/kL). The report does not provide any data for crude oil loading in a marine oil tanker. The report mentions that data collected in 2001 in a study undertaken by European Commission concluded that, at that time, the cost to retrofit marine tankers with vapour collection systems and install shoreside vapour recovery units was not cost-effective (AEAT, 2001; EEA, 2019).

US EPA AP-42 EF, extracted from Table 5.2-2 (AP-42) for VOC emission from gasoline loading in the marine tanker, specifies 0.18 kg/kL transferred for clean tanks for volatile cargo. Similar information for crude oil loading operations, provided in Table 5.2-6 of the document, specifies total organic emission as 0.073 kg/kL transferred (EPA, 2020b). For a more detailed EF to calculate, the AP-42 document recommends using the following equations, Equation 2.4, and Equation 2.5, for marine crude oil loading:

$$C_L = C_A + C_G \qquad\qquad \text{Equation 2.4}$$

where:

C_L = total loading loss, lb/10^3 gal of crude oil loaded

C_A = arrival emission factor, contributed by vapours in the empty tank compartment before loading, lb/10^3 gal loaded

C_G = generated emission factor, contributed by evaporation during loading, lb/10^3 gal loaded

The average arrival emission factors (C_A) are quoted in Table 2.4.

Ship/Ocean Barge Tank Condition	Previous Cargo	Arrival Emission Factor, C_A (kg/kL)
Uncleaned	Volatile (TVP > 10 kPa)	0.103
Ballasted	Volatile	0.06
Cleaned or gas freed	Volatile	0.04
Any condition	Non-volatile (TVP < 10kPa)	0.04

Table 2.4 Arrival Emission Factors, C_A (EPA, 2020b)

The quantity C_G can be calculated using Equation 2.5, developed empirically from test measurements of several vessel compartments:

$$C_G = \frac{(1.84(0.44\,P - 0.42) * M * G)}{T}$$
Equation 2.5

where:

P = true vapour pressure of loaded crude oil, psi_a

M = molecular weight of vapours, lb/lb-mole

G = vapor growth factor = 1.02 (dimensionless)

T = temperature of vapours, °R (°F + 460)

Arrival emission factors (C_A) are to be added to generated emission factors (C_G) calculated in Equation 2.5 to produce total crude oil loading loss (C_L). EF are for total organic compounds in table 2.4. When specific vapour composition information is unavailable, the VOC emission factor can be estimated by taking 85% of the total organic factor. It is about 15% lower due to the VOC, as it does not include methane or ethane, which are exempted from the regulatory definition of VOC by EPA (EPA, 2020a).

Another document, 'HM65', jointly issued by 'American Petroleum Institute' (API) and the 'Energy Institute' (EI) under the title, 'Atmosphere hydrocarbon emission from marine vessel transfer operations', also provides a similar EF for crude oil and gasoline loading operations. The quoted value is 1.5 lb/1000 gallon (0.18 kg/kL) for gasoline (Table 4 / HM65) and 0.6 lb/1000 gallon (0.073 kg/kL) for crude oil (Table 7 / HM65) (Institute, 2009). The values for EF are the same in the EEA report, AP-42 and HM65 document. The document provides an empirical method, using an equation based on TVP of crude oil, to find generated EF value for crude oil loading as below:

$$E_G = 0.205 * [0.44\,(P_{VA}) - 0.42]$$
<div align="right">Equation 2.6</div>

where

E_G is generated EF (lb/1000 gal) loaded,

P_{VA} is the True Vapour Pressure (TVP) of loaded crude oil in psi_a

Equation 2.6 is recommended to estimate emission if the TVP of crude oil is known. However, it does not consider the temperature of crude oil and the flow rate.

Matsumara conducted an in-depth study on evaporative losses of hydrocarbons from refinery plants, oil terminals and gas stations in Japan. He developed a mathematical relationship between the oil level and the concentration of HC in discharged vapours. EF was calculated for crude oil and gasoline as 0.12 kg/kL and 0.19 kg/kL loading, respectively, for the average temperature of the discharged gas as 30^0C (Matsumura, 1974). However, there were no specific details on crude oil and gasoline composition.

Otto M.Martens *et al.* (2000) participated in a VOC control project initiated by Norway at the national level to measure VOC emission and develop a simulation program to model evaporation rate and VOC emission for loading operations onboard shuttle tankers in Norwegian offshore areas. The project's main goal was to prepare and evaluate a set of concepts for VOC emission controls. One dimension diffusion-convection equation was used to develop the Simulation program. The target efficiency is given as 75% compared to a case when no controls are applied, based on national rules in Norway.

$$\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial z}(W C_i) - \frac{\partial}{\partial z}\left(D_{im} + D_{Unr\_vel}\right)\frac{\partial C_i}{\partial z} = 0$$
<div align="right">Equation 2.7</div>

where

C_i is an unknown molar concentration (k-mol/m^3) of species' i' in the mixture,

t is time (s),

W is the vertical velocity (m/s), and

z is vertical directions (m).

D_{im} is the (effective) diffusion coefficient (m^2/s) for species 'i in the mixture, and

D_{Unr_Vel} may be considered a diffusion coefficient due to all unresolved velocities.

Equation 2.7 is solved for the following species:

C_1 to C_{10+}, N_2, CO_2, and O_2, by approximating the partial derivatives with finite differences.

The development of the simulation program made it possible to compute the gas flow (Figure 2.1) and composition (Figure 2.2) during a tanker loading operation. The simulation program computed the gas flow between a tank and the environment by solving the mass continuity equation in each tank together with an equation of flow for each pipe. Several observations taken during shuttle tanker loading operations in offshore areas were matched with the simulation program, and the Diffusion coefficient for unresolved velocities was found by trial and error. The results were compared and verified with the actual observations. The actual measurements of the mass flow of vented vapours and their composition provide helpful information on the necessity to control such emissions, which occur regularly during tanker loading operations. The authors analysed additional power requirements and the cost analysis of other equipment required for various options to reduce VOC emission on shuttle tankers and 'Floating Production and Storage Offshore (FPSO) for different scenarios. Some VOC control concepts could apply to marine oil tankers with a gas return to shore terminals. The study does not include detailed information on the flowrate of crude oil, its chemical composition, and temperature.
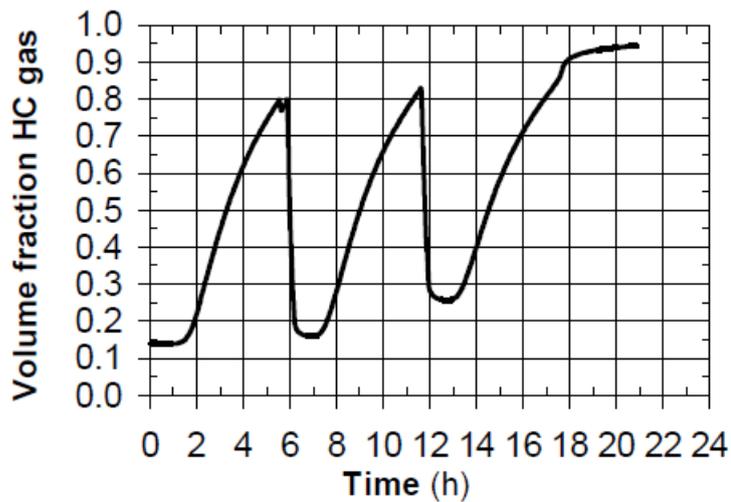
Figure 2.1 Volume fraction of hydrocarbon gas emitted from the tank – base case (Martens *et al.*, 2001)
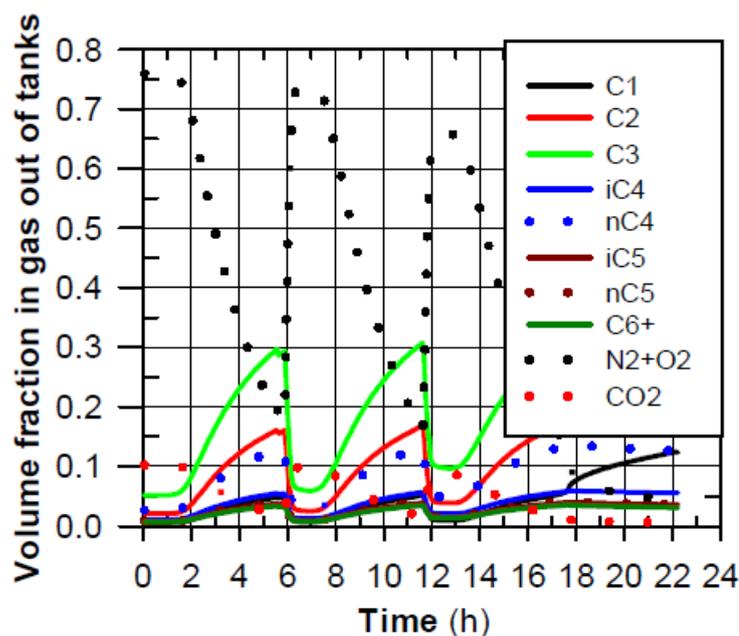
Figure 2.2 Composition of gas out of tanks – base case (Martens *et al.*, 2001)

DeLuchi (1993) evaluated the future emission of VOCs, NO_x, SO_x, PM, CO and toxic air pollutants during the production, storage and transport of gasoline and crude oil in the USA for the year 2000. The evaluation was done for emissions occurring in or near the continental US but excluded the emission associated with producing imported oil and gasoline and VOC emission from ships on high seas. The emissions from loading operations in a marine oil tanker were calculated using EPA issued AP-42 table; the

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data showed that uncontrolled loading loss, uncontrolled breathing, standing, and evaporative emissions contribute significantly to surrounding air pollution and are worth analysing further. VOC emissions from the loading of crude oil and gasoline were tabulated as 292 mg/L for Alaskan crude, 73 mg/L for Lower 48 crude, and 240 mg/L for gasoline. The paper analysed the data and summarised that most crude oil life cycle emissions starting from oil wells are from the storage of crude oil in the field and at refineries. This study also did not elaborate on crude oil and gasoline composition and temperature. It was concluded that gasoline production, storage, and transport are and will be a significant emission source, in some cases, greater than the tailpipe emission of new vehicles (DeLuchi, 1993).

An EU report (AEAT, 2001) prepared for Directorate General – Environment analysed the measures to reduce VOC emission during the loading and unloading of ships in EU states. The report provided a basis for estimating crude oil and gasoline VOC emission. The analysis used the guidance provided by US Environmental Protection Agency EPA). A cost-benefit analysis was carried out based on the amount of crude oil and gasoline loaded in EU states. It was concluded that costs incurred to fit VOC recovery equipment are not justified, given the limited amount of crude oil and gasoline loading operations in EU states. The report chose to use the Emission Factors (EF) for crude oil as 1 kg(emitted)/tonne (loaded) and for gasoline as 0.24 kg(emitted)/tonne (loaded), respectively. The same information has been quoted in the 2019 report issued by European Environmental Agency (EEA) (EEA, 2019).

Tamaddoni *et al.* (2014) conducted an experimental study on the nature of gases emitted from crude oil tankers docked in a large-scale oil export terminal in Iran. The data was gathered from the vapour stream composition in the cargo tanks of the crude oil tankers. Various factors such as cargo tank conditions, nature of crude oil, oil temperature, and tank pressure were analysed, which could minimise VOC emission in marine terminals. Using crude oil to absorb the vapour emission was also investigated as a strategy to reduce the VOC emission and enhance the efficiency of loading operations. The collected data from the vapour stream showed almost 13% of emitted gas are hydrocarbons, propane and butane being the major constituent in the vent stream. A mathematical model was developed using a mass conservation equation, and the diffusion-convection equation resembled the experimental data. The results were compared with other vapour emission studies conducted in similar conditions and reported closely. The increase in crude oil temperature showed

increased evaporation and higher emission. In contrast, an increase in the pressure of the ship's storage tank reduced the vapour emission, as shown in Figure 2.3 (Tamaddoni *et al.*, 2014).
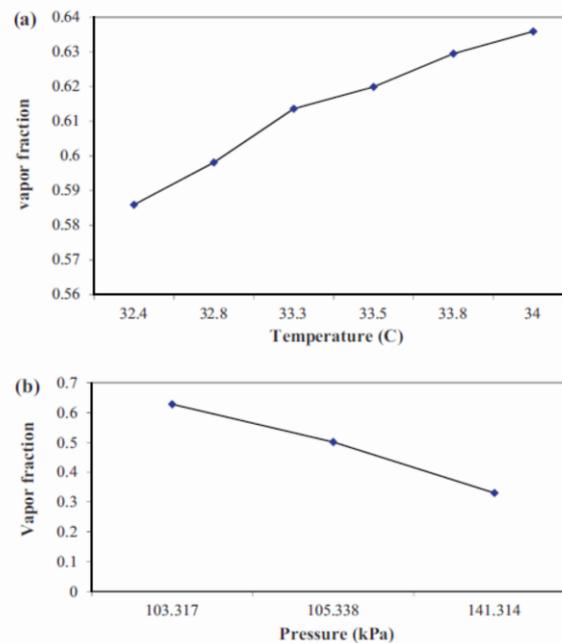
Figure 2.3 Vaporization of crude oil in (a) tank operating temperature and (b) operating pressure (Tamaddoni *et al.*, 2014)

The paper showed viable solutions which could be adopted in an oil-exporting terminal to limit the release of VOCs during crude oil tanker loading operations. The results from the study did not provide any details on the composition of crude oil as well as the resulting 'Oil Vapour Emission' (OVE) during loading operations, such as the concentration of paraffinic, naphthenic, and aromatic components in the crude oil.

Deligiannis *et al.* (2016) investigated the vapour growth rate during the loading operations in their crude oil tanker fleet. They presented a theoretical methodology combined with actual emission measurements for accurately quantifying VOC emissions during loading operations. Hydrocarbon (HC) vapour generation from liquid cargo was explained to occur with two separate mechanisms as chemical (evaporation) and mechanical (nucleation). The study showed a rise in HC content with loading. HC content increased as the loading progressed, paused when loading was stopped and increased again when loading was resumed, as shown in Figure 2.4. The actual measurement of vapour emission during loading and laden passage was taken onboard an Aframax tanker and a VLCC operated by their company.
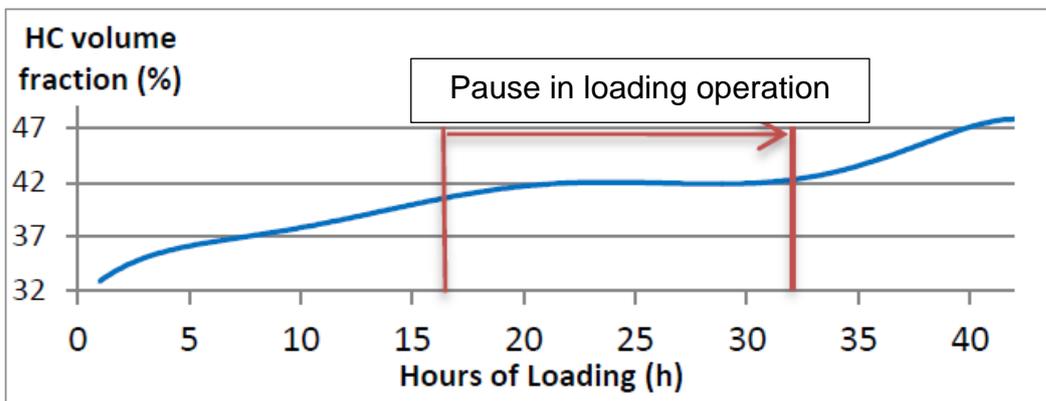
Figure 2.4 Variation in HC with loading and pause in loading operation (Deligiannis *et al.*, 2016)

The authors have compared VOC emission from four types of different crude oils with EF quoted by EPA USA and concluded that generic EF is relatively inaccurate. It was also proposed that specific operation parameters and cargo types be considered for analysing loading operations. Details to provide a conclusion in this study were based on certain assumptions of molecular weight of cargo vapours and API of the crude oil, which may not be the same if data for other crude oil is used.

EF for crude oil and gasoline quoted in documents issued by EPA USA, EEA EU, and the review done by various authors with consolidated information are summarised in Table 2.5.

Table 2.6 summarises the data relevant to the objective of the current research and identifies gaps in calculating the volume of OVE.

It can be concluded that the use of EF and other experimental or empirical approaches taken to estimate the OVE from loading and bunkering operations does not consider the detailed composition, flow rate and temperature of the crude oil and gasoline. The lack of this information in estimation makes this approach more of an estimate and not a definitive conclusion, which is necessary to do an in-depth analysis to assess air quality and its impact on human health. A detailed analysis is needed to propose amendments to international conventions related to tanker design and work practices to limit these VOC (carbon) emissions and enhance the sustainability of oil loading and bunkering operations.

Petroleum commodity	Reference	EF value / VOC emission	Remarks
Crude Oil	EEA	No data quoted	
	EPA USA	73 mg/L	Basis Crude Oil Density 0.83 tonne/m^3, 73 mg/L = 0.10 kg/tonne Excludes Methane and Ethane in OVE
	EI Hydrocarbon Management HM65	73 mg/L	Basis Crude Oil Density 0.83 tonne/m^3, 73 mg/L = 0.10 kg/tonne Excludes Methane and Ethane in OVE
	Matsumara report	0.12 kg/kL	Vapour temperature 30^{0}C Basis Crude Oil Density 0.83 tonne/m^3, 0.12 kg/kL = 0.14 kg/tonne
	DeLuchi	292 mg/L for Alaskan crude 73 mg/L for Lower 48 crude oil	Basis Crude Oil Density 0.83 tonne/m^3, 292 mg/L = 0.35 kg/tonne, 73 mg/L = 0.10 kg/tonne Excludes Methane and Ethane in OVE
	EU AEAT report	1 kg(emitted)/tonne (loaded)	
	Deligiannis report	Arabian Heavy Crude oil 0.07 kg/ tonne loaded @ 40^{0}C	Data is for different crude oil at different temperatures.

		Arabian Medium Crude oil 0.24 kg/ tonne loaded@ 29^{0}C Arabian Super light Crude oil 0.32 kg/ tonne loaded@ 42^{0}C	The detailed composition of crude oil is not described.
Gasoline	EEA	4 g/m^3 throughput/kPa TVP (180 mg/L)	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne
	EPA USA	180 mg/L	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne
	EI Hydrocarbon Management HM65	180 mg/L	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne
	Matsumara report	0.19 kg/kL	Vapour temperature 30^{0}C Basis Gasoline density 0.76 tonne/m^3 0.19 kg/kL = 0.25 kg/tonne
	DeLuchi	240 mg/L	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3

			240 mg/L = 0.32 kg/tonne
	EU AEAT report	0.24 kg(emitted)/tonne (loaded)	The temperature range used varies from 3^0C to 25^0C RVP ranges from 50 to 90 kPa The molecular weight of vapours is 62 to 68
	Deligiannis report	Condensate EF 0.76 kg/ tonne loaded@ 30^0C	Data is for condensate, which has a similar API as Gasoline.

Table 2.5 Summary of EF for crude oil and gasoline

S.No	Authors	Title	Data relevant to the objective of the current research	Identified gaps and helpful information for the aim of the research
1.	EEA Report, 2019	EMEP / EEA air pollutant emission inventory guidebook	Gasoline loading facility using marine tankers, NMVOC EF 4g/m^3 throughput/kPa TVP (180 mg/L) Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne	No data is available for crude oil loading operations, as the report states that EF for the distribution of non-gasoline oil products is unavailable. EF for crude oil loading is necessary to estimate air pollution potential.
2.	EPA EF information	AP-42 Compilation of EF, table 5.2-2 and 5.2-6	Gasoline EF 180 mg/L Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne Crude Oil EF 73 mg/L Basis Crude Oil Density 0.83 tonne/m^3, 73 mg/L = 0.10 kg/tonne	Data for gasoline and crude oil EF exclude methane and ethane in the emission. Different crude oil may have different EF, and emission depends upon the flow rate and temperature of the oil. EF data is applicable for a dispensed product of 16^{0}C. Quoted EF for crude oil assumes RVP = 5 psi$_a$ (34 kPa); in reality, RVP varies between 1 to 10 psi$_a$. RVP for gasoline is assumed to be 10 psi$_a$ (69 kPa).
3	Matsumara	Evaporation loss of hydrocarbon in handling petroleum	Gasoline EF 0.19 kg/kL Basis Gasoline density 0.76 tonne/m^3 0.19 kg/kL = 0.25 kg/tonne	Different crude oil may have different EF, and emission depends upon the flow rate and temperature of the oil.

			Crude Oil EF 0.12 kg/kL Basis Crude Oil Density 0.83 tonne/m^3, 0.12 kg/kL = 0.14 kg/tonne Light Naphtha EF 0.34 kg/kL	
4	Otto Martens *et al.*	Control of VOC emission from crude oil tankers	Shows variation in HC concentration with loading time, as well as the concentration of HC species in vapour emission	Data are presented only for one type of crude oil, which is relatively volatile, as per the comments in the report. Require more detailed information on variation in EF based on the type of crude oil.
5.	DeLuchi	Emissions from the production, storage and transportation of crude oil and gasoline	Uncontrolled loading loss from AP-42 was cited for two different types of crude oil. NMVOC EF for Alaskan crude 292 mg/L Crude Oil (Lower 48) 73 mg/L Basis Crude Oil Density 0.83 tonne/m^3, 292 mg/L = 0.35 kg/tonne, 73 mg/L = 0.10 kg/tonne	RVP for crude oil is assumed equal to 5, whereas RVP for each crude oil will be different, EF does not consider the crude 'il's temperature and flow rate.

			Gasoline 240 mg/L Basis Gasoline density 0.76 tonne/m^3 240 mg/L = 0.32 kg/tonne	
6.	EU report	Measures to reduce emissions of VOCs during the loading and unloading of ships in the EU	EF for crude oil loading 1 kg(emitted)/tonne (loaded) and EF for Gasoline loading 0.24 kg(emitted)/tonne (loaded)	Different crude oil may have different EF, and emission depends upon the flow rate and temperature of the oil.
7.	Tamaddoni *et al.*	Experimental study of the VOC emitted from crude oil tankers	Composition of vented gas during loading; Effect of temperature and tank pressure on OVE	Only two specific types of crude oils were used in the study.
8.	Deligiannis *et al.*	VOC emission assessment from the cargo area of tanker vessels	Calculated EF for specific cargo, loading temperature and rate of loading shows that generic EF are not accurate for policy-making. A steady increase in HC content in OVE as the loading progresses.	The detailed composition of the crude oil is not shown. The approach for calculating EF using a specific example of crude oil, API, temperature, and molar weight of crude oil vapours from one agency may not be the same for comparing data from other agencies where such values may have been different.

Table 2.6 Summary of identified gaps for EF for crude oil and gasoline

2.3 Quality of vapours in the vicinity of VOC emission affecting the health of seafarers

During tanker loading and ship bunkering operations, OVE introduces a vast amount of VOCs in the surrounding air, especially near oil terminals. Numerous studies are related to emissions from storage tanks in petroleum refineries, and limited literature is related to actual marine oil terminals.

Benzene, Ethyl benzene, Toluene, Xylene, Hexane, and Cyclo-hexane were identified in OVE from crude oil, which was processed in oil refineries or from or near petroleum storage tanks such as crude oil and gasoline in various countries (Kalabokas, 2001; Cetin *et al.*, 2003; Lin *et al.*, 2004; Liu *et al.*, 2008; Paulauskiene *et al.*, 2009; Ras *et al.*, 2009; Krol *et al.*, 2010; Wei *et al.*, 2014).

As per US Environmental Protection Agency (EPA), HAP (Hazardous Air Pollutants), also known as toxic air pollutants, are known, or suspected to cause cancer or other serious health effects, such as reproductive effects, birth defects, or adverse environmental effects. HAPs, such as Benzene, Toluene, Xylene, and Hexane, have been identified as present in the VOC emission resulting from crude oil loading operations (EPA, 2020d).

In the USA, 'National Emission Standards for Hazardous Air Pollutants (NESHAP), authorised under the 'Clean Air Act' (CAA), are generally the most stringent and extensive EPA regulation. Many VOCs are HAPs and hence potentially subject to NESHAP. Most of the significant VOC emission sources in crude oil and gasoline production emit both hazardous and non-hazardous VOCs. However, since the hazardous VOCs typically cannot be controlled separately from the non-hazardous VOCs, the NESHAP applying to HAPs from a given source effectively apply to all VOCs from the source (DeLuchi, 1993). As marine tanker loading operation is identified as an industrial source category, evaluated in risk and technology review, there are specific regulations to monitor VOC emission from marine terminals during crude oil and gasoline loading operations, specified in US Federal Register under 40 CFR Part 63 (USA, 2020; EPA, 2022).

The 'American Petroleum Institute' (API) report described occupational exposure from OVE during crude oil production in high volumes in the USA. It was reported that the individual constituents of crude oil volatilize by their unique physical-chemical properties. One of the two primary inhalations is from the VOCs similar to gasoline which can readily volatilise from crude oil, the other being from hydrogen sulphide. There are enforceable (from OSHA, as

PEL) and recommended occupational exposure standards (from ACGIH, as TLV) for numerous volatile constituents typically found in crude oil (API, 2011). Examples of the PEL and TLV as per OSHA and ACGIH are shown in Table 2.7.

Component in crude oil		OSHA PEL (ppm)	ACGIH TLV (ppm)
C_4	Butane		1000
	2-Methyl Propane		1000
C_5	Pentane	500	600
C_6	Benzene	1	1
	Hexane	500	50
	Cyclohexane	300	100
C_7	Toluene	200	20
C_8	Ethyl Benzene	100	100
	Xylenes	100	100
C_9	Cumene	50	50
	Trimethyl Benzene		25
Others	Hydrogen Sulphide	2 mg/m^3	1
	Methyl mercaptan		0.5
	Gasoline		300

Table 2.7 OSHA and ACGIH Occupational Exposure Standards for volatile constituents of crude oil (API, 2011)

This is clear evidence that personnel working near areas where crude oil is being handled and the resulting OVE needs to be monitored for safe exposure, which is currently lacking for marine personnel.

Komar *et al.* studied the various options to minimise VOC emission from tanker loading operations. It was mentioned that the VOC emission rates from crude oil and gasoline loading depend on the characteristics of the previous and the current cargo, temperature, loading rate, turbulence in the atmosphere of the storage tank, sea condition, and the elapsed time of unloading of the previous cargo. During the crude oil loading, a mixture of VOCs and inert gas is discharged from the cargo tank, and the new emission of VOCs is generated on the surface by the evaporation of the oil. This study highlighted the inclusion of regulations for controlling VOC emission in the 'International convention for Prevention of Pollution from Ships' (MARPOL). It summarised various available technical solutions to reduce VOC emissions, even though the reduction measures are not mandated under any international convention (Komar *et al.*, 2010).

Rajabi *et al.* analysed the overall scale of global VOC emission from all stages of oil processing. The authors summarised the significant detrimental effects of crude oil vapour emission (CVE) on human health in a diagram shown in Figure 2.5. The main challenges to accurately quantifying CVEs included the inherent limitations in the used analytical approaches, discrepancies in the types of crude oil and meteorological influences on CVEs. Among all VOCs emitted from crude oil, toluene, benzene, hexane, heptane, cyclohexane, and pentane were high-detected high-concentrated compounds. This study highlighted the importance of restrictive policies and regulations to control VOC emissions worldwide, particularly those related to the oil and gas industry (Rajabi *et al.*, 2020). Though the study focuses on crude oil processing, the analysis included comments about crude oil transportation and oil-exporting countries where VOC controls are reported to be severely lacking.
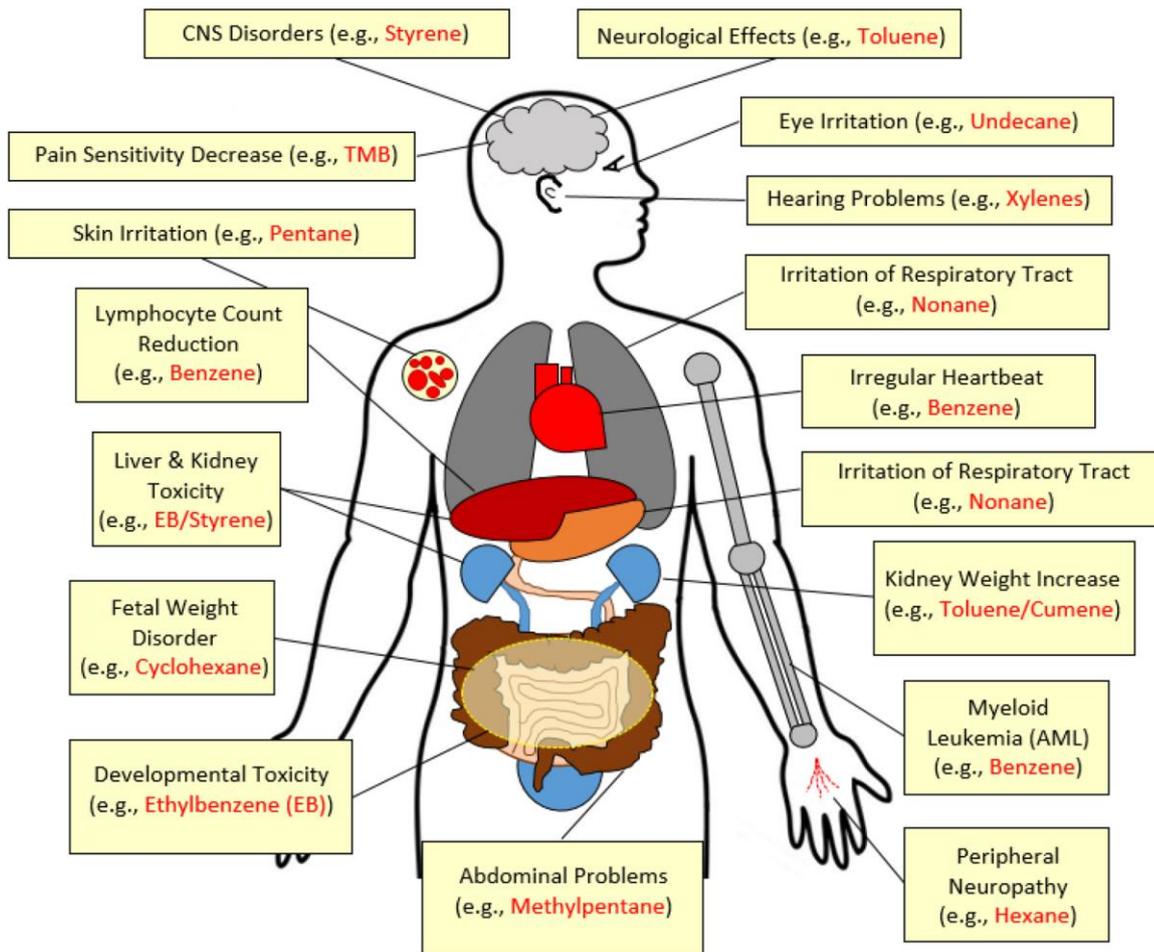
Figure 2.5 Major impacts of VOCs on human health (Rajabi *et al.*, 2020)

The study summarised the VOC emission control used in crude oil shipment and the transportation sector, shown in Table 2.8, as good practices.

Circumstances	Procedure	Remarks / Gap Analysis
Quoted from Rajabi *et al.*		
Crude oil loading	Vapour Emission Control System (VECS)	IMO MSC/Circ.585, the standard provided for the port which may use VECS not mandatory under any convention
	Vapour Pressure Release Control System (VOCON Valve)	IMO MEPC.1/Circ.680 is not mandatory under any convention
	Cargo Pipeline Partial Pressure Control System (KVOC)	IMO MEPC.1/Circ.680, Technical guidelines for VOC Management Plan, not mandatory under any convention
	Vapour Recovery Systems (VRS) such as Condensation systems, Absorption systems, Vacuum-Regenerated Adsorption (CVA), and Direct Adsorption of VOC in Crude Oil (CVOC systems)	IMO MEPC.1/Circ.680 and 719, Technical guidelines for VOC Management Plan, not mandatory under any convention
	Increased Pressure Relief Settings (Applicable also for transit conditions)	IMO MEPC.1/Circ.680, Technical guidelines for VOC Management Plan, not mandatory under any convention
Crude Oil Transit	Vapour Pressure Release Control System (VOCON Valve)	IMO MEPC.1/Circ.680, Technical guidelines for VOC Management Plan, not mandatory under any convention
	Recovery of excess VOC and tank adsorption (Venturi system)	
	Increased Pressure Relief Settings	

Table 2.8 Control procedures during oceanic tanker loading and transport (Rajabi *et al.*, 2020)

A review of the majority of the procedures to control VOC emission under the MARPOL convention indicates that these details are only technical guidelines by IMO and not enforceable by any international conventions(MSC/Circ.585, 1992; MEPC.1/Circ.680, 2009; MEPC.1/Circ.719, 2010; MARPOL, 2020). It limits their effectiveness for the intended purpose of restricting VOC emissions.

A current review of the various studies on the effect of VOC emissions on human health indicates that there should be specific regulations in international conventions to limit VOC emissions to safeguard the health of marine personnel and ship staff. A detailed analysis of the status of current regulations is discussed in the next section.

2.4 International and local regulations related to loading and bunkering operations

Various regulations on VOC emission from loading operations in oil tankers can be classified as international, national, and tanker industry-specific practices. The international regulations about tankers are covered under 'International Maritime Organization' (IMO) conventions such as 'The International Convention for Safety of Life at Sea' (SOLAS) and 'The International Convention for the Prevention of Pollution from the ships' (MARPOL). The regional and national regulations related to tankers can be regional and local conventions and acts such as the 'Long-Range Transboundary Air Pollution' (LRTAP) convention under 'United Nations Economic Commission for Europe' (UNECE), and the 'Clean Air Act' (CAA) in the USA. The tanker industry-specific practices are related mainly due to commercial considerations to seek tanker business, such as 'Oil Companies International Marine Forum' (OCIMF) led 'Ship Inspection Report Programme' (SIRE) inspections and following industry best practices under 'International Safety Guide for Oil Tankers and Terminals' (ISGOTT). This section deals with the status of international conventions, regional and national regulations, and tanker industry practices per the objectives of the thesis.

2.4.1 SOLAS Convention

Regulation 3-1 Chapter II-1 stipulates that the ships shall be designed, constructed, and maintained in compliance with the structural, mechanical and electrical requirements of a classification society recognized by the Administration (Flag State) (SOLAS, 2023). None of the regulations in SOLAS mentions the risk of inhaling oil vapours and its associated toxicity hazard of the carriage of oil as cargo or as fuel. As the current objective is to analyse the rules related to the carriage of oil and use of oil as fuel, it is observed that all the regulations associated with the design of ships and oil tankers address the flammability hazard of the

oil, e.g., SOLAS Ch II-2 entirely deals with Fire protection, fire detection and fire extinction issues. Ch II-2 Regulation 4.5.7, Gas measurement and detection, also details the carriage requirement to contain the flammability hazard of oil cargo.

A typical ship bunkering operation involves regular vapour venting and monitoring the oil level in the bunker tank using a sounding pipe. Vapour Vents and Sounding Pipes are generally located near each other. Ship staff engaged in monitoring filling levels of bunker tanks via Sounding Pipe are regularly exposed to VOC emissions from the bunker tank vapour vents. These vapour vents discharge freely to the surrounding air and have a typical height of only 600 mm from the main deck. Current SOLAS regulations for bunker tank designs have no minimum safe distance requirement between air vents and the sounding pipe of a bunker tank to prevent the inhalation of oil vapours by the ship's crew. Similarly, there is no requirement for a safe distance between oil tanker cargo tank venting arrangements and the location of sounding pipes for minimising inhalation of oil vapours, whether from cargo oil tanks or bunker tanks.

SOLAS Chapter VI, 'Carriage of cargoes', 'Regulation 3' deals with the carriage of Oxygen analysis and gas detection equipment to be carried when transporting bulk cargo. The regulation is applicable for the cargo liable to emit toxic or flammable gas; the regulation is not applicable for the carriage of liquids in bulk. This means that the regulations are for bulk solid cargoes and not for the carriage of oil as cargo.

In the same chapter, there is an anomaly between 'Regulation 1', 'Application', and 'Regulation 5-1', 'Material safety data sheets' (MSDS). 'Regulation 1' states that the chapter applies to the carriage of cargoes except for liquids in bulk, whereas 'Regulation 5-1' is for ships carrying 'Annex I' cargoes, which is oil.

Tanker loading and ship bunkering operations emit flammable and toxic vapours during loading and bunkering operations and in transit. There are no regulations to check the presence of VOCs, including toxic gases, when oil vapours are vented during the routine loading in oil tankers and ship bunkering operations. Further, Chapter VI, 'Carriage of Cargoes and Oil Fuels', 'Regulation 3', 'Oxygen analysis and Gas detection equipment', requires ships carrying solid bulk cargo to have an appropriate instrument for measuring the concentration of gas or oxygen in the air when carrying cargo which is liable to emit toxic or flammable gas.

'Regulation 5-1' of this 'Chapter VI' only mentions the ships to be supplied with appropriate 'Material Safety Data Sheet' for oil as cargo or oil as fuel before loading such cargoes. Though the regulation does not state the purpose of the requirement, a detailed analysis of the related IMO MSC Resolution states the purpose as recognizing the importance of providing seafarers with clear, concise, and accurate information on the health and the environmental effects of toxic substances carried onboard tankers (MSC.286(86), 2009). It has been reported in various research papers and publications about the toxic components in vapours emitted from crude oil and gasoline (Hansen *et al.*, 2008; Claxton, 2014a; Milazzo *et al.*, 2017; Rajabi *et al.*, 2020; Virdi *et al.*, 2021). There is no regulation in SOLAS prohibiting or limiting VOC emission during loading operations in oil tankers or any bunkering operations. Moreover, this regulation does not specify any reason for the mandatory carriage of MSDS, unlike SOLAS 'Chapter VI Regulation 5', which defines the basis for compliance as the carriage of cargo liable to emit toxic or flammable gas.

A similar inhalation risk is present in oil cargo and bunker fuels, but there is no regulation for such requirements during their handling. The mandatory carriage of MSDS does not ensure that the ship operator will necessarily provide additional safeguards to protect the health of seafarers from toxic vapour exposure. There is a clear gap in connecting the carriage of MSDS with the provision of personal gas measuring instruments in SOLAS regulations.

SOLAS Chapter XI-1 'Special measures to enhance maritime safety' mandate that all ships carry an appropriate portable atmosphere testing instrument, with a minimum capability of measuring oxygen concentrations, flammable gases or vapours, and hydrogen sulphide and carbon monoxide before entry into enclosed spaces (SOLAS, 2023). No such instrument is specified for oil loading or bunkering operations, which pose oil vapour inhalation risks.

Another regulation in SOLAS which addresses any health-related aspect of seafarers is the guidelines for controlling the noise from ship machinery, commonly referred to as 'The Noise Code', under 'Chapter II-1', 'Regulation 3-12' (SOLAS, 2023). The 'Noise Code' issuance under SOLAS mentions that high noise levels onboard ships could affect seafarers' health and impair the ship's safety (MSC.337(91), 2012). No health issue has been documented for handling oil as cargo or fuel in any regulation.

From the above analysis, it can be deduced that there are only two regulations which deal with the protection of the health of seafarers, one related to noise and one about MSDS, to inform about the toxicity hazard of oil. No regulations specifically acknowledge the inhalation

risk and associated toxicity hazard from oil as liquid and the resulting OVE, when tanks are filled up, e.g., oil tanker loading operations or ship bunkering operations.

'Ch II-2' 'Regulation 4.5.3' has detailed requirements for cargo tank venting, but the basis is only to address the flammability hazard. Current tanker cargo tanks and ship bunkering tank design drawings reveal that the tank venting and sounding pipes are sited in proximity. As there is a prudent operational, procedural practice to compare the manually taken tank soundings or ullages with remote tank level monitoring systems, the physical verification of soundings or tank ullages exposes the seafarer to the inhalation of toxic vapours which are being freely vented to the atmosphere during tanker loading or ship bunkering operation, as shown in Chapter 1 Sub-section 1.2.3 and 1.2.4.

It can be concluded from the above analysis that the inhalation risk and toxicity hazard of OVE needs to be included in the SOLAS regulations related to the ship's design; in the same way, the flammability hazard is addressed in various regulations in the SOLAS convention.

2.4.2 MARPOL Convention

Regulations covering the various sources of ship-generated pollution are contained in the six annexes of the MARPOL convention. The regulations related to the prevention of air pollution, contained in Annex VI of the MARPOL, are the latest addition to this convention, which entered into force on 19th May 2005.

As vapour emission from oil loading operations and ship bunkering contributes to air pollution, the related regulations are discussed in MARPOL Annex VI.

MARPOL Annex VI 'Regulations for the prevention of air pollution from ships' 'Regulation 15' 'Volatile Organic Compounds' (VOCs)' provides detailed guidance and requirements for regulating VOC emission from tankers. The current text leaves the decision to control VOC emission on individual tanker terminals per applicable local rules where the port or terminal is situated.

The countries ratifying the convention must report to IMO where such VOC regulations are being imposed (MEPC.509, 2006). Currently, only South Korea and the Netherlands are the only countries worldwide that have officially notified IMO about the list of ports and terminals where VOC regulation is in force (GISIS, 2020).

As per Regulation 15.6, every crude oil tanker shall have and implement a 'VOC Management Plan', which is approved by the administration, taking into account the relevant

IMO guidelines (MEPC.1/Circ.680, 2009; MEPC.185(59), 2009; MEPC.1/Circ.719, 2010). The analysis of MEPC guidelines leaves the decision with the ship operator about the scope of minimising or stopping the VOC emission by optimising operational procedures or providing devices to prevent VOC emission. There is no requirement to stop VOC emissions as per this regulation.

Moreover, Regulation 15.6 does not apply to tankers carrying clean oil products such as Gasoline, Kerosene, and Naphtha and does not cover VOC emissions during ship bunkering operations. Clean petroleum products are more readily prone to evaporation and can introduce more toxic VOCs into the environment. Still, there is no regulation to include such clean products to have any VOC Management plan.

During oil tanker loading operations, any excess pressure above the safe pressure limit of a cargo tank is vented to the atmosphere via approved venting devices such as 'Mast Risers' or 'P-V Valves'. Oil tankers carrying clean petroleum products vent the cargo vapours freely from P-V Valves. There is considerable VOC volume released in the environment during this venting as this emission may contain 30 – 60% hydrocarbons, especially when the tank level is between 50% to being full, as shown in Figure 2.6 (MEPC.1/Circ.680, 2009).

The literature review of various approved 'VOC Management Plans' (VOCMP, 1999; VOCMP, 2010; VOCMP, 2015) for different crude oil tankers concludes that crude oil tankers usually maintain 108 to 110 kPa tank pressure in their cargo tanks during loading operations. Any excess tank pressure is released into the atmosphere during loading operations via the 'Mast Riser'.
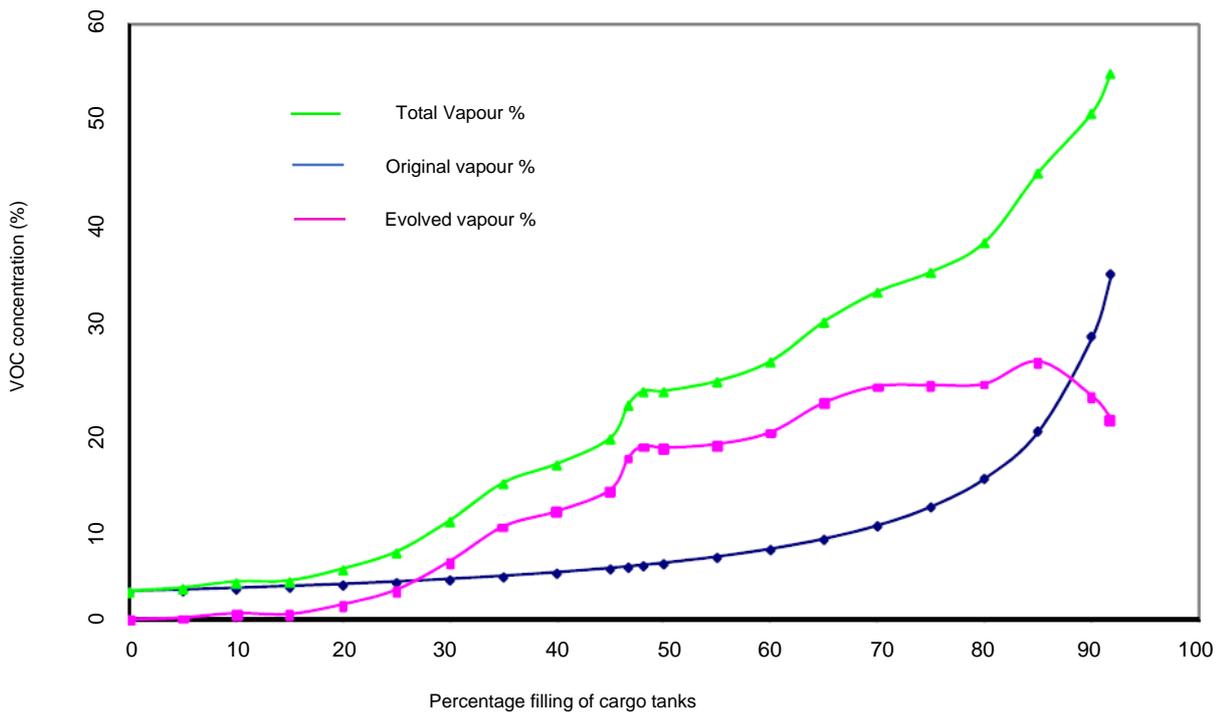
Figure 2.6 Hydrocarbon vapour concentration in the vapour phase during the loading operation (MEPC.1/Circ.680, 2009)

This current tanker loading and bunkering practice keep introducing VOCs into the surrounding environment, leading to local air pollution, and exposing the ship personnel to toxic VOCs. There is an urgent need to estimate the volume of such OVE, which contributes to continued VOC emissions daily in petroleum exporting terminals and bunkering locations in various countries worldwide. Having reasonably accurate data will assist in risk assessment and, if necessary, formulate regulatory controls to enhance air quality around oil exporting terminals and bunkering locations and stop or minimize toxic VOC exposure for seafarers and marine personnel.

MARPOL 'Annex VI' 'Regulation 22' requires ships to have a specific 'Ship Energy Efficiency Management Plan' (SEEMP) (MARPOL, 2020). This plan is developed as per IMO guidelines (MSC.282(70), 2016). The purpose of SEEMP is to have a ship management plan for improving energy efficiency, guidance on best practices for fuel-efficient operations, collect fuel oil consumption data and calculate direct CO_2 emissions due to ship operations. Listed factors to optimise efficiency include optimum use of ship machinery, propeller and hull cleaning, cargo and fuel heating, draft and trim optimisation, weather routeing and speed optimisation. The standardised data reporting format for CO_2 emissions focuses only on fuel

oil consumption, as shown in Figure 2.7. The guidelines do not reference any VOC emissions from oil loading and ship bunkering operations, contributing to CO_2 emissions. By having accurate OVE data, it is proposed to amend 'Regulation 22' to include VOC emissions from oil loading operations and bunkering in the standardized reporting for accurate results to capture 'Green House Gas' (GHG) emissions from ship's operations.

STANDARDIZED DATA REPORTING FORMAT FOR THE DATA COLLECTION SYSTEM

Column (top-to-bottom vertical headers, left to right)
Method used to measure fuel oil consumption[9]
Other(...........) (Cf:......)
Ethanol (Cf: 1.913)
Methanol (Cf: 1.375)
LNG (Cf: 2.750)
LPG (Butane) (Cf: 3.030)
LPG (Propane)
HFO (Cf: 3.114)
LFO (Cf: 3.151)
Diesel/Gas Oil (Cf: 3.206)
Fuel oil consumption (t)
Hours underway (h)
Distance Travelled (nm)
Power output (rated power) (kW)[8] — Auxiliary Engine(s) / Main Propulsion Power
Ice class[7] (if applicable)
EEDI (if applicable)[6] (gCO2/t.nm)
DWT[5]
NT[4]
Gross tonnage[3]
Ship type[2]
IMO number[1]
End date (dd/mm/yyyy)
Start date (dd/mm/yyyy)

Figure 2.7 Standardised data reporting as per SEEMP guidelines by IMO (MSC.282(70), 2016)

The above analysis concludes that the current MARPOL regulations in 'Annex VI' focus mainly on preventing air pollution due to exhaust gas emissions and monitoring energy efficiency through ship manoeuvring and fuel oil consumption. 'Regulation 15' of 'Annex VI' requires an amendment to restrict such VOC emissions and include all oil tankers, not only crude oil tankers. Also, there should be mandatory provisions to minimise or stop VOC emission by ship operations, and not on the choice by oil terminal.

2.4.3 Regional and national regulations

Only a few nations in the world have adopted air quality laws based on the local pollution levels. Examples include 'Clean Air Act' in the USA in 1963, and 'LRTAP Convention' under 'UNECE' in 1979, and the reduction in VOC emission in Norway under 'The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone' (Hansen *et al.*, 2008; UNECE, 2015; EPA, 2020b).

The current review indicates that national regulations in the USA and Norway and regional regulations in Europe have been the main drivers for adopting measures to regulate VOC emissions from tankers.

Federal laws in the USA are enforced through the 'Clean Air Act' (CAA), which has regulated air emissions from stationary and mobile sources since 1963 to control air pollution at the national level. 'Section 112' of the CAA addresses emissions of hazardous air pollutants (HAP), such as emissions from tanker terminals. The 1990 amendment of the act set new goals for achieving 'National Ambient Air Quality Standards' (NAAQS), established by the 'Environmental Pollution Agency' (EPA). The amendment requires the issuance of technology-based standards for 'Major Sources', defined as a stationary source or a group of stationary sources that emit or have the potential to emit 10 tons per year or more of a HAP or 25 tons per year or more of a combination of HAPs. HAPs are defined in federal regulations (EPA, 2020d).

Oil terminals engaged in loading tankers and barges fall under the stationary source category. 'Title 40 Part 63' of 'Federal Regulations' provides regulations for 'National Emission Standards for Hazardous Air Pollutants for source categories (NESHAP)', which covers marine loading terminals. 'Subpart Y' of this section provides detailed requirements of vapour emission controls from marine loading terminals under the heading 'National Emission Standards for Marine Tank Vessel Loading Operations'. The details include the applicability of the rules, definitions, vapour emission control standards, compliance and performance testing, monitoring, recordkeeping, and implementation of standards for marine tank vessel loading operations (USA, 2020).

The standards define two methods to control vapour emission, 'Maximum Achievable Control Technology' (MACT) and 'Reasonably Available Control Technology' (RACT), for all products (including gasoline and crude oil) at marine loading terminals, except for products having vapour pressure less than 10 kilopascals (kPa) at 20°C and 760-mm Hg.

The regulation requires each marine terminal to have either:

a) annual emission of 10 tons or more of each individual HAP (Hazardous Air Pollutants) or 25 tons of all HAP combined, follow 'MACT' standard, or

b) annual throughput of 10 million barrels of gasoline or 200 Million barrels of crude oil loading operations, follow the 'RACT' standard, shall be equipped with a vapour collection system, as per applicable standard.

For the 'MACT' standard, the system should be designed to collect VOC vapours displaced from marine tank vessels during loading and prevent their venting into the atmosphere.

A vapour collection system means any equipment located at the source, i.e., at the terminal, that is not open to the atmosphere; it may be led to a control device or for vapour balancing. A control device means a combustion device or vapour recovery device. Vapour balancing means routing the vapours back to the storage tank from where the loading product originated or using the vapours in feed at a refinery. Captured HAP shall be reduced by 97 to 98 weight per cent for existing and new terminals, respectively, using Combustion and Recovery Control Devices as described in CFR 63.565. For new offshore terminals, the reduction is 95 weight per cent. CFR 63.565 also provides a detailed methodology for emission estimation and performance test procedures for the 'Combustion and Recovery Control Devices' to ensure the required reduction in HAPs.

Combustion devices include thermal or catalytic incinerators, boilers, and process heaters used for the combustion or destruction of organic vapours and do not include flares. Recovery Control Devices include a carbon absorber, condenser/refrigeration unit, or absorber capable of removing vapours and recovering liquids or chemicals.

For 'RACT' standards, the terminal shall reduce captured VOC emissions from marine tank vessel loading operation by 98 weight-percent when using a combustion device or reduce captured VOC emissions by 95 weight-percent when utilising a recovery device (USA, 2020). Alternatively, the terminal can meet the requirement by reducing gasoline loading emissions to, at most, 1,000 ppm_v outlet VOC concentration. As per federal regulations, the terminals cannot operate if vapour collection or control devices are not fitted (USA, 2020).

The analysis of the above regulations in oil terminals in the USA concludes the following:

a) There are detailed specific federal regulations to limit VOC emission from tanker loading operations at tanker terminals,

b) The rules specify various standards to follow to regulate VOC emission from shore terminals, and

c) The standards also broadly specify available technological solutions to regulate VOC emission.

d) The federal rules in the USA may be used as guidelines by IMO member states to regulate VOC emissions.

e) Current standards in federal regulations do not cover ship bunkering operations.

The 'Long-range Trans Boundary Pollution' (LRTAP) convention guides air pollution control in the European Union (EU). Under the European Parliament, various directives are issued to advise the EU members on their implementation of obligations under the LRTAP Convention. The EU community was instructed to work closely for revisions in the MARPOL convention in 1996 (EU, 1994). EU Directive 94/63/EC on the control of VOC emission resulting from the storage of petrol and its distribution from terminals to service stations declares that the VOC emission during the loading of ships must be drawn at IMO level for vapour control and recovery systems to apply to both loading installations and ships, on the grounds of international standardization and of safety during the loading of ships. The Directive applies to vehicles such as road and rail tankers and inland waterway vessels transferring petrol from one terminal to another. It explicitly excludes the loading of the ships (tanker loading operation). There is no mention of air pollution due to ship bunkering operations.

Article 9, 'Monitoring and Reporting' of the Directive, invited the European Commission to look at extending the scope to include vapour control and recovery systems for loading installations and ships. A study was conducted in 2001 to support this obligation. The st'dy's objective was to identify and assess the cost and effectiveness of measures to reduce VOC emissions from loading and unloading ships' tanks in the EU (AEAT, 2001). The report analysed the VOC emission from crude oil tankers in Europe. It concluded that the impact on ozone in ambient air be assessed first before proceeding with measures for their abatement, as most loading operations occur in the North Sea. The study conducted in 2001 remains current as per the EEA report published in 2019 (EEA, 2019). As per this report, the local air quality issues in Gothenburg oil harbour have resulted in using vapour emission control systems in ship loading operations. It was concluded that the emissions resulting from the ship-loading of gasoline and crude oil in the EU represent 0.07% and 0.8%, respectively, of all VOCs emitted annually in the EU, and it would not be cost-effective for the relative gains obtained.

The following conclusions are drawn from the above analysis:

a) The current deciding factor for regulating VOC emission in the EU is still based on the study conducted in 2001 (AEAT, 2001).

b) VOC emission from tanker loading operations is a tiny percentage of total VOC emission in the EU, leading to cost ineffectiveness.

c) Major tanker loading operations emissions are in the North Sea, away from any populated area.

d) Gothenburg oil harbour has regulated VOC emission as a local rule to protect the surrounding population from the toxic effect of VOCs.

'Norwegian Environment Agency' (NEA), a government agency under the 'Ministry of Climate and Environment,' implements and advises on developing climate and environmental policy and exercises regulatory authority (NEA, 2020). In 2002, the 'Norwegian Climate and Pollution Agency' (KLIM) imposed regulations on oil companies to reduce the overall emissions from offshore loading by 30% in 2003, increasing to 70% in 2006 (Hansen *et al.*, 2008).

The primary sources of NMVOC emissions in Norway are the storage and loading of crude oil in offshore areas. Emissions from the petroleum sector are directly regulated through requirements on using the 'Best Available Techniques' (BAT) and specific emission limits in permits under the 'Pollution Control Act' (Petroleum, 2020). Since the early 2000s, NMVOC emissions from the petroleum sector have been substantially reduced, mainly because of investment in NMVOC recovery equipment. Under the Gothenburg Protocol of the LRTAP Convention, Norway has undertaken to reduce its overall NMVOC emissions by 40% by 2020, when compared with the 2005 VOC emission level. In 2018 the total NMVOC emissions were 40,500 tonnes.

Numerous shuttle tankers operating in Norwegian offshore waters were fitted with 'VOC Recovery Systems' or 'VOC Emission Control' technologies to meet these national targets between 2000 to 2010. The technologies were used in FSO, FPSO and shuttle tankers (Martens *et al.*, 2001; IPIECA, 2013). The techniques recommended by various IMO circulars were used in these projects, and a substantial reduction in VOC emission was achieved.

Thus, following conclusions are drawn:

a) Norwegian rules explicitly declared the reduction targets for regulating VOC emission from tanker loading operations since 2003,

b) The tanker operators designed and fitted various technologies onboard tankers to meet the targeted VOC emission reduction from loading operations, and

c) The national rules in Norway have significantly reduced VOC emissions from tanker loading operations.

2.4.4 Industry guidelines

Tanker owners and operators follow recommendations from OCIMF and Intertanko to ensure the commercial acceptability of tankers for continued commercial employment. The most important influence is the role of vetting inspection under SIRE and following tanker best practices as per the tanker safety guide 'ISGOTT'.

Major oil companies commercially employ tankers for global oil shipment. Due to the potential pollution liabilities of operating oil tankers, the oil companies manage their fleet on various charter parties instead of owning the ships. To assist in finding the best-managed tankers worldwide, a tanker vetting database, 'Ship Inspection Report Programme' (SIRE), is used. The tanker owners offer their fleet to be inspected by accredited vetting inspectors or vetting companies. The ship inspection programme lists an elaborate requirement to fulfil various criteria ranging from ship certification, manning levels, tanker safety features for cargo, ballast, and pollution controls to machinery operations. Some of the requirement under this inspection exceeds safety standards under SOLAS and MARPOL conventions.

A specific example related to the current study is the mandatory carriage and use of 'Personal Protective Equipment' (PPE) during oil loading operations. The ship's crew must carry and use 'Personal Gas Monitors' while working on deck during oil loading operations to safeguard their health against toxic gas exposures from cargo tank vapour vents. There is no requirement in SOLAS for mandatory carriage of such instruments during oil loading operations. The other examples include the detailed requirement for 'Enclosed Space Entry Procedure', carriage of mandatory 'Emergency Life Support Apparatus' (ELSA) during tank entry, carriage of multiple 'Personal Gas Analysers', Personal Gas Monitors' and carriage of sufficient spare parts and calibration requirements have been tanker industry-standard much earlier than that were added in SOLAS.

It can be concluded that the SIRE programme under OCIMF has been able to address the exposure risks of shipboard staff from toxic VOC emissions, which are currently not resolved by any regulations in the SOLAS and MARPOL conventions.

'International Safety Guide for Oil Tankers and Terminals,' popularly known as ISGOTT, is jointly prepared by 'The International Chamber of Shipping (ICS),' 'The Oil Companies International Marine Forum (OCIMF)' and 'The International Association of Ports and

Harbour (IAPH)' has been tanker industry standard for standard operating practices for oil tanker operations. The guide provides recommendations for tanker and terminal personnel on the safe carriage and handling of crude oil and petroleum products on tankers and terminals.

The IAPH guide does not make recommendations on the design and construction of the tankers. There is detailed guidance in ISGOTT on the various standard operating procedure for the operation of different gas measuring instruments, their use to check toxic exposure levels, venting systems and vapour emission control systems. The guide assists in filling up some gaps that have not been made to any reference in SOLAS and MARPOL conventions. Detailed guidance is available to marine personnel to safeguard against exposure risks.

Based on the above details for the international and national regulations, as well as industry guidelines, it can be concluded that:

a) The toxicity hazard of OVE needs to be included in the SOLAS convention to minimize or stop toxic VOC exposure for seafarers and marine personnel,

b) MARPOL convention Annex VI Regulation 15 and Regulation 22 be amended to minimise or stop VOC emission during loading operations in oil tankers and bunkering operations on all ships.

c) Local rules in the USA, EU states and Norway related to controlling VOC emissions from tankers should be studied in detail for their efficacy. That approach may be used to amend international conventions and national regulations.

d) Guidelines in ISGOTT may provide reference to control inhalation exposure risk of seafarers.

2.5 Gap analyses

Tanker loading and ship bunkering operations based on current ship design and operation procedures are inadequate for sustainable efficiency, preserving local air quality of oil loading and bunkering ports, and protecting the health of seafarers and marine personnel. To make a meaningful assessment of OVE, there is an urgent need for a robust methodology to be developed where the modelling of oil loading and bunkering operation can be conducted. The modelling should be able to accept inputs of oil composition, flow rate, and the temperature of the oil. The results should be compared with other experimental or actual measurements to validate and then use the results for proposing various solutions to address above mentioned issues, as follows:

a) Evaluate the volume of oil lost due to evaporation and calculate the monetary loss. Propose feasible modifications to tanker design and loading practices to increase the efficiency of current operations for the sustainability of tanker loading for reduced monetary losses.

b) Evaluate the volume of OVE and the composition of VOC to assess the impact on local air quality onboard ships, marine terminals, and bunkering locations for reducing local air pollution near marine oil terminals and bunkering ports.

c) Identify toxic VOCs in OVE during tanker loading and ship bunkering to conduct an objective toxic hazard assessment for proposing solutions to safeguard the health of seafarers and marine personnel.

d) Propose amendments to appropriate regulations in international conventions related to ship design and the related working practices to minimise and capture VOC emission from tanker loading and ship bunkering operations. The amendments should also protect health of seafarers and enhance local air quality surrounding marine loading terminals and bunkering locations.

Chapter 3. Methodology

3.1 Description

Oil tanker loading and ship bunkering operations are required to be analysed in detail to meet the aims and objectives of the research. The novel approach used for this research involves use of industry recognised Aspen HYSYS chemical process simulator which is widely used in oil and gas industry (ANSYS, 2019). To calculate monetary loss and the environmental and health impact from the resulting OVE, exact volume and chemical composition is required to be known. The required results can be obtained by modelling crude oil and gasoline correctly. The basis of oil modelling and selection of influencing parameters such as loading rate, tank pressure, and oil temperature are described in this chapter.

3.2 Gasoline and crude oil composition

Crude oil is a complex liquid mixture mainly consisting of hydrocarbon compounds containing different proportions of hydrogen and carbon. Other small amounts of organic compounds containing sulphur, oxygen, nitrogen, and metals such as vanadium, nickel, iron, and copper are also present. The hydrogen-to-carbon ratio affects the physical properties of crude oil. The hydrocarbon compounds' specific gravity and boiling point increase as the hydrogen-to-carbon ratio decreases. The composition of crude oil on an elemental basis is shown in Table 3.1 (Fahim *et al.*, 2010). This composition is relatively uniform even if the crude oil originates worldwide.

In petroleum refining, crude oil is separated into gases, kerosene, gasoline, diesel fuel, heavy gas oil, and lubricating oil. The components are produced based on the market demand, and the details of carbon atoms present in each product are shown in Table 3.2 (Delft, 2016b).

The major component of petroleum is hydrocarbons (compounds containing hydrogen and carbon). The different 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.'

Element	Composition (wt. %)
Carbon	83.0 – 87.0
Hydrogen	10.0-14.0
Sulphur	0.05 – 6.0
Nitrogen	0.1 – 0.2
Oxygen	0.05 – 2.0
Nickel	<120 ppm
Vanadium	< 1200 ppm

Table 3.1 Elemental composition of crude oil (Fahim *et al.*, 2010)

Carbon atoms	Component output
$C_1 – C_4$	Gas
C_5-C_{10}	Gasoline
C_{11}-C_{13}	Kerosene
C_{14}-C_{18}	Diesel fuel (light gas oil)
C_{19}-C_{25}	Heavy gas oil
C_{26}-C_{40}	Lubricating oil
>C_{40}	Residuum

Table 3.2 Distillation of petroleum (Delft, 2016a)

Crude oil systems from various regions around the world are analysed into the following categories:

a) Paraffinic
b) Naphthenic
c) Aromatic

Crude oil from the same region tends to belong to one of the above categories. Paraffinic hydrocarbons have open or straight molecular chains joined by single bonds. Examples are methane, ethane, propane, butane, which contain branched chains, including isomers of these compounds. The first four members of the paraffinic series are gaseous at room temperature and pressure. Compounds ranging from pentane through heptadecane (C_7H_{16}) are liquids, whereas the higher members are colourless, wax-like solids. Naphthenic

hydrocarbons are ringed molecules and are also called cycloparaffins. These compounds, like paraffin, are also saturated and stable. They make up the second primary constituent of crude oil. Aromatic hydrocarbons are also cyclic but derivatives of benzene. The molecular rings have alternate double bonds but are stable, though not as stable as paraffin. Crude oils are a complex mixture of these hydrocarbons, with paraffins and naphthenes being the predominant species. No crude oil has ever been wholly separated into individual components, although many can be identified. A detailed composition of Oklahoma crude oil is shown in Table 3.3 (Lake *et al.*, 2006).

Paraffins	Naphthenes	Aromatics
All normal paraffins to $C_{10}H_{22}$	Cyclopentane	Benzene
	Cyclohexane	Toluene
Isobutane	Methylcyclopentane	Ethylbenzene
2-Methylbutane	1,1-Dimethylcyclopentane	Xylene
2,3-Dimethylbutane	Methylcyclohexane	1,2,4-Trimethylbenzene
2-Methylpentane	1,3-Dimethylcyclohexane	
3-Methylpentane	1,2,3-Trimethylcyclohexane	
2-Methylhexane		
3-Methylhexane		
2-Methylpentane		
2,6-Dimethylheptane		
2-Methyloctane		

Table 3.3 Example of a detailed crude oil composition (Lake *et al.*, 2006)

The information on various primary components of the crude oil from multiple regions is shown in Table 3.4 (PujadÛ and Jones, 2006).

Component	Arabian Crude	Iranian Crude	Kuwait / Iraq	Libya / Algeria	Nigeria	North Sea	South America (Bachequero)
% vol. boiling below 350^{0}C	46.5-54	53.0-55.0	49.0-61.1	64.0-75.2	54.5	61.2	30.0
Gravity, API	28.2-33.4	30.8-33.5	31.2-35.9	40.4-44.7	26.0	36.3	16.8
Sulphur, weight %	1.8 -2.84	1.4-1.6	1.95-2.5	0.13-0.21	0.23	0.21	2.4
Paraffins	69.5 – 70.3	50-54	67-9-69	53-56.5	27.5	56.5	27.6
Olefins	-	-	265 ppm	20 ppm	1.5	-	-
Naphthenes	18.2-21.4	30-35	21-22.1	32.9-39.3	57	29.5	58.5
Aromatics	8.3-12.3	15-16	9.8-10	7.7-10.6	14	14	13.9

Table 3.4 Characteristics of some crude oils from various worldwide locations (PujadÛ and Jones, 2006)

For example, for a crude oil API = 34, the molecular composition is shown in Table 3.5 (Fahim *et al.*, 2010).

API gravity	34.00
Specific gravity	0.8550
Molecular weight	257.12
Light Fractions MW	70-200
Paraffin, mole %	53.83
Naphthene, mole %	15.03
Aromatic, mole %	31.14
Heavy Fractions MW	200-600
Paraffin, mole %	70.80
Naphthene, mole %	5.86
Aromatic, mole %	23.33

Table 3.5 Molecular composition of crude oil, API=34 (Fahim *et al.*, 2010)

Crude oil is generally assumed to be composed of paraffin, naphthenes, aromatics and asphaltic components, as shown in Table 3.6 (Jukic).

Component	Average (by weight)	Range
Paraffin	30%	15 – 60%
Naphthene	49%	30-60%
Aromatic	15%	3 -30%
Asphaltic	6%	

Table 3.6 Example of the composition of crude oil (Ante Jukic, 2016)

3.3 Modelling of crude oil and gasoline in Aspen HYSYS

Simulation of loading operation is carried out for an Aframax tanker, a ULCC for crude oil, and a clean petroleum product tanker for gasoline. The assumed composition and physical properties of the crude oil and gasoline used in the simulation are obtained from various research papers and petroleum publications, and as per the data in Table 3.3 to Table 3.6 (M A Fahim; Lake *et al.*, 2006; PujadÛ and Jones, 2006; Ante Jukic, 2016; Registry, 2017; Speight, 2017). The details of the selected composition of crude oil are shown in Table 3.7 and Table 3.8 and are used to analyse vapour emissions using Aspen HYSYS Simulation Software, which uses 'Equation of State' (EOS) for petroleum applications. The equation of state is described further.

3.3.1 Equation of state (Aspentech, 2001; Aspentech, 2017)

Petroleum-tuned EOS Property methods are based on equations of state for nonpolar compounds with built-in binary parameters. These property methods use the API/Rackett model for liquid density to overcome the drawback of poor liquid density calculated by cubic equations of state. Commonly used EOS property methods for hydrocarbons are Peng Robinson and RK-SOAVE. In this research, the Peng Robinson (PENG_ROB) property method is selected for the following reasons:

a) Recommended package for petrochemical applications involving hydrocarbons and light gases.
b) Use of binary parameters for accurate results in Vapour-liquid-equilibrium calculations.
c) Reasonable results at all temperatures and pressure range.

The Standard Peng-Robinson EOS (Equation 3.1) is the basis for the PENG-ROB property method, as used in the Aspen HYSYS Simulation Software. It is the Peng-Robinson EOS with the Boston-Mathias alpha function. It is recommended for hydrocarbon processing applications such as gas processing, refinery, and petrochemical processes (Aspentech, 2001).

The equation for the Boston-Mathias model is:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}$$
Equation 3.1

where

p is the pressure (Pa)

R is the gas constant (8.314 J mol^{-1} K^{-1})

T is the temperature (K)

V_m is the molar volume calculated by the equation of state without the correction (m^3 mol^{-1})

a is the energy parameter, a measure of attractive forces between the molecules

b is co-volume, related to the size of molecules

x is the mole fraction

T_c is the critical temperature (K)

p_c is the critical pressure (Pa)

ω is the acentric factor to account for the shape of the gas molecules

k is the binary parameter

n is the mole number

i is the component index

$$b = \sum_i x_i b_i$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$

$$b_i = f_{cn}(T_{ci}, p_{ci})$$

$$a_i = f_{cn}(T, T_{ci}, p_{ci}, \omega_i)$$

$$k_{ij} = k_{ji}$$

The parameter a_i is calculated according to the standard Peng- Robinson formulation. For best results, the binary parameter k_{ij} must be determined from phase equilibrium data regression, such as VLE data. The Aspen Physical Property System also has built-in k_{ij} for a large number of component pairs. These parameters are used automatically with the Peng Robinson property method (Aspentech, 2001; Aspentech, 2017).

Component	Type	Mole Fraction
Ethane	Paraffins 63.2%	0.0009
Propane		0.0103
i-Butane		0.0285
n-Butane		0.0650
i-Pentane		0.0297
n-Pentane		0.0418
n-Hexane		0.0287
n-Heptane		0.0211
n-Octane		0.0150
n-Nonane		0.0115
n-Decane		0.0012
n-C_{11}		0.0002

n-C$_{12}$		0.0002
n-C$_{13}$		0.0002
n-C$_{14}$		0.0002
n-C$_{15}$		0.0002
n-C$_{16}$		0.0002
n-C$_{17}$		0.0015
n-C$_{18}$		0.0015
n-C$_{19}$		0.0023
n-C$_{20}$		0.0023
n-C$_{21}$		0.0031
n-C$_{22}$		0.0031
n-C$_{23}$		0.0031
n-C$_{24}$		0.0031
n-C$_{25}$		0.0046
n-C$_{26}$		0.0054
n-C$_{27}$		0.0061
n-C$_{28}$		0.0612
n-C$_{29}$		0.1377
n-C$_{30}$		0.1377
23-Mbutane		0.0017
2-Mhexane		0.0014
2-Mheptane		0.0012
Cyclopentane	Naphthenes 15.3%	0.0459
Cyclohexane		0.0459
Mcyclopentane		0.0612
Benzene	Aromatics 21.5%	0.0058
Toluene		0.0159
E-Benzene		0.0036
m-Xylene		0.0182
Naphthalene		0.0803
Chrysene		0.0916

Table 3.7 Composition of crude oil used in the simulation

Parameter	Value
Molecular Weight	217.8
Mass Density [kg/m^3]	830.3
Reid Vapour Pressure at 37.8^{0}C [kPa]	75.1
True Vapour Pressure at 37.8^{0}C [kPa]	91.9

Table 3.8 Physical properties of crude oil sample

Before loading, the empty cargo tank in an oil tanker contains inert gas (IG), so as to reduce the flammability risk. The composition of the inert gas contained in the empty tank is shown in Table 3.9.

Component	Mole Fraction
CO_2	0.14
N_2	0.80
SO_2	0.01
O_2	0.05

Table 3.9 Inert gas composition in the cargo tank

Gasoline composition is shown in Table 3.10 and Table 3.11 (ATDSR, 1995).

Component	Type	Mole Fraction
n-Pentane	Paraffinic 48%	0.18
n-Hexane		0.04
n-Decane		0.22
n-C_{11}		0.04
Cyclopentane	Naphthenic 12%	0.07
Cyclohexane		0.05
p-Xylene	Aromatic 40%	0.16
Toluene		0.12
Benzene		0.12

Table 3.10 Composition of Gasoline (ATDSR, 1995)

Parameter	Value
Molecular Weight	100.3
Mass Density [kg/m^3]	752.7
Reid Vapour Pressure at 37.8^{0}C [kPa]	32.7
True Vapour Pressure at 37.8^{0}C [kPa]	33.0

Table 3.11 Physical properties of gasoline used in Aspen HYSYS simulation

The simulation of vapour generation for crude oil and gasoline loading operation is conducted using Aspen HYSYS process simulation software. Aspen HYSYS is a proven industry standard solution with over 25 years of success. The software improves engineering design and operations, energy efficiency, and capital costs. Numerous chemical and process-based companies use Aspen HYSYS software to optimise business performance, solve critical engineering and operating problems throughout the plant lifecycle, and accurately represent basic processes. This helps to reduce greenhouse gas emissions and supports environmental, health and safety policies and regulatory compliance, among others (Aspentech). The simulation modelling in Aspen HYSYS Simulation software used Peng Robinson thermodynamic package (Aspentech, 2001; Aspentech, 2017; Aspentech, 2024a; Aspentech, 2024b). This is the most widely used thermodynamic package as it applies to all hydrocarbon applications. It is the most enhanced model in this software with the most extensive applicability range regarding temperature and pressure.

Aframax and ULCC tankers are selected as representatives of commonly employed tankers for crude oil transportation. Simulation is performed in the Aspen HYSYS Chemical Process Simulator. Details related to each type of tanker, such as Deadweight, total volume of the cargo tanks at the ambient temperature, number of cargo tanks, duration of loading, rate of loading, temperature of the oil and pressure in the tank are shown in Table 3.12. The crude oil temperature set for the simulation is 25℃, 35℃ and 45℃. The temperatures are chosen to cover the average temperature of most of the crude oil exporting countries(OPEC, 2016; IEA, 2020). The tank pressure during loading operations selected for simulation is 108 kPa and 120 kPa. A literature review of the current tanker design and loading procedures indicates that a tank pressure is maintained at 108 kPa during tanker loading operations. A tank pressure of 120 kPa is chosen as recommended by IMO guidelines to analyse its effectiveness in minimising the evaporative loss as well as VOC emission (VOCMP; VOCMP, 1999; MEPC.1/Circ.680, 2009; VOCMP, 2010). Thus, a tank pressure of 108 kPa is a base case for the current simulation. Loading duration is based on the review of tanker loading terminals data and personal communication (ADNOC, 2022; Aramco, 2022). The above details are summarised in Table 3.12.

Type of tanker	Deadweight (tonnes)	The total volume of crude oil at the ambient temperature (m³)	Number of cargo tanks, excluding Slop Tanks	Loading duration (hours)	Loading rate in one tank (m³/hour)	Temperature of the oil	Tank Pressure
Aframax	113,458	126,772	12	12	880	25°C, 35°C and 45°C	108 kPa and 120 kPa
ULCC	308,492	341,879	15	15	1520		
Product	37,900	40,778	12	12	283		

Table 3.12 Tanker data and flow rate used in the simulation

For this methodology, one sample of crude oil and one sample of gasoline are selected for the detailed analysis.

The following assumptions are made for the simulation:

a) The composition of crude oil and gasoline as shown in Table 3.7 and Table 3.10.

b) The physical properties of crude oil and gasoline and the Flowrates is as per Table 3.8, Table 3.11, and Table 3.12.

c) The empty storage tank in an oil tanker initially contains Inert Gas, composition shown in Table 3.9.

d) Only two phases, i.e., liquid and vapour, exist in the tank.

e) No reaction takes place in the empty storage tank.

f) The temperature of Inert Gas and that of crude oil inflow is the same.

g) The temperature of crude oil and gasoline entering the tank is taken for three values of 25°C, 35°C, and 45°C, based on the general geographic location of export terminals in various countries.

h) Vapours are vented to the atmosphere to maintain the tank pressure of 108 kPa, as per current tanker practice; the amount of vapour vented is equal to the volume of liquid entering the cargo tank.

i) The tank pressure is 108 kPa as per usual tanker practice, and additional data is collected for elevated tank pressure of 120 kPa to understand the effect of high tank pressure on evaporative loss and VOC emission.

j) There is negligible heat transfer between the tank and the surrounding atmosphere.

k)   The software output is at steady-state conditions at each time step, which requires validation. This will be verified by an alternative chemical process simulation software, DWSIM (Section 3.4), since verification/validation by on-site / field tests is not possible.

The vapours are vented to the atmosphere continuously during the loading via the Mast Riser or individual P-V valves. A snapshot of the Flowsheet modelled in Aspen HYSYS Simulation is shown in Figure 3.1. Flow and composition data were collected for every 10% change in the liquid level.
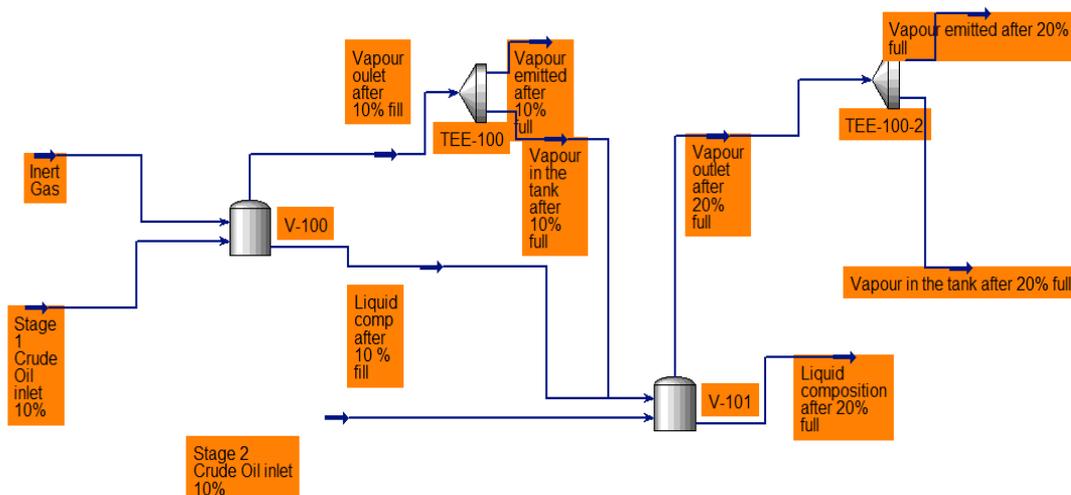
Figure 3.1 Snapshot of flow sheet in Aspen HYSYS Simulation

The primary objective of the simulation study is to calculate evaporative loss and VOC emissions during tanker loading operations. The volumetric results were used to determine the economic loss during tanker loading operation and its effect on local air quality, which contributed to carbon emission. Simulation results also identified the toxic components in the VOC emission, which can affect the health of seafarers. Furthermore, the results also helped to propose amendments to the current regulations to safeguard the health of seafarers.

The literature on the evaporative loss of oil during loading operations is unavailable. The validation of the results is conducted by calculating the 'Emission Factor (EF) as EFs have been quoted in the current literature dealing with evaporative loss and VOC emission (Matsumura, 1974; DeLuchi, 1993; AEAT, 2001; Deligiannis *et al.*, 2016; EEA, 2019; EPA, 2020b). Simulation output results include total volumetric OVE, the fraction of Inert gas (IG) and VOC in OVE, and the mass and volume of oil in the tank

at every 10% change in tank filling level. The methodology for calculating EF from loading operation first identifies the total mass of vapours (in kg) vented to the atmosphere to maintain the respective tank pressure (108 kPa or 120 kPa) during the loading operation, based on the simulation results.

EF is obtained as shown below, as per Equation 3.2 and Equation 3.3.

M_{VOC} = M_{Total} * VOC fraction   Equation 3.2

EF = M_{VOC} / m   Equation 3.3

where

M_{Total} is the total mass of vapour vented to the atmosphere during loading operation, in kg,

M_{VOC} is the mass of VOCs vented to the atmosphere, in kg,

VOC fraction is the fraction of VOCs in total OVE, and

m is the mass of oil loaded, in tonnes.

The EF values calculated in kg/tonne (kilogrammes of VOC emitted per tonne of oil loaded) are used to compare and validate the results with similar available literature.

3.4 Alternate Chemical Process Simulation Software, DWSIM

An alternate chemical process simulation software, 'DWSIM', is selected to compare the results obtained from the Aspen HYSYS simulation (DWSIM, 2023; Ivana Lukec, 2024; Wagner, 2024). This chemical process simulation software has also been widely used in the chemical industry. Kwanchanok.T *et al.* conducted a comparison study of Aspen HYSYS and DWSIM chemical process simulator. Chemical process related to the production of an offshore facility was selected to evaluate the thermal and chemical behaviour of the system to demonstrate the software capability, and the results were compared with the heat and mass flow diagram which was used as reference. The analysis found that the discrepancy between the simulation and the reported values was in general less than 5% (Kwanchanok Tangsriwong, 2020).

Crude oil tanker loading onboard an Aframax tanker, and a gasoline loading onboard product tanker, as per the details in Table 3.12, were simulated in Aspen HYSYS and DWSIM chemical process simulator. The simulation involved three temperatures of crude oil and gasoline 25℃, 35℃, and 45℃, at two different cargo tank pressure, 108 kPa and 120 kPa. The statistical analysis of the results obtained from both the simulation are shown in Table 3.13 to Table 3.15 for crude oil loading, and in Table 3.16 to Table 3.18 for gasoline loading operations.

Evaporative Loss Crude Oil/ Aframax	Aspen HYSYS	DW SIM	Mean	Standard Deviation
T25℃ P108kPa	0.18%	0.11%	0.15	0.05
T25℃ P120 kPa	0.13%	0.08%	0.11	0.04
T35℃ P108 kPa	0.38%	0.25%	0.32	0.09
T35℃ P120 kPa	0.27%	0.11%	0.19	0.11
T45℃ P108 kPa	0.84%	0.38%	0.61	0.33
T45℃ P120kPa	0.62%	0.06%	0.34	0.40

Table 3.13 Simulation results by Aspen HYSYS and DWSIM for evaporative loss for crude oil loading in an Aframax tanker

VOC Emission Crude Oil / Aframax	Aspen HYSYS	DW SIM	Mean	Standard Deviation
T25℃ P108kPa	0.73	0.41	0.57	0.23
T25℃ P120 kPa	0.56	0.37	0.47	0.13
T35℃ P108 kPa	1.46	0.74	1.10	0.51
T35℃ P120 kPa	1.09	0.64	0.87	0.32
T45℃ P108 kPa	2.90	0.80	1.85	1.48
T45℃ P120kPa	2.26	1.32	1.79	0.66

Table 3.14 Simulation results by Aspen HYSYS and DWSIM for VOC emission for crude oil loading in an Aframax tanker

Parameter		Evaporative Loss	VOC emission
Standard Deviation	Minimum	0.04	0.13
	Maximum	0.33	1.48
Confidence Level	Minimum	0.32	1.21
	Maximum	3.56	13.34

Table 3.15 Statistical analysis of Simulation results by Aspen HYSYS and DWSIM for crude oil loading in an Aframax tanker

Evaporative Loss Gasoline	Aspen HYSYS	DW SIM	Mean	Standard Deviation
T25℃ P108kPa	0.06%	0.03%	0.05	0.02
T25℃ P120 kPa	0.04%	0.01%	0.03	0.02
T35℃ P108 kPa	0.14%	0.25%	0.20	0.08
T35℃ P120 kPa	0.11%	0.21%	0.16	0.07
T45℃ P108 kPa	0.27%	0.75%	0.51	0.34
T45℃ P120kPa	0.22%	0.33%	0.28	0.08

Table 3.16 Simulation results by Aspen HYSYS and DWSIM for evaporative loss for gasoline loading in a product tanker

VOC Emission Gasoline	Aspen HYSYS	DW SIM	Mean	Standard Deviation
T25℃ P108kPa	0.37	0.35	0.36	0.01
T25℃ P120 kPa	0.31	0.31	0.31	0.00
T35℃ P108 kPa	0.64	0.61	0.63	0.02
T35℃ P120 kPa	0.54	0.51	0.53	0.02
T45℃ P108 kPa	1.17	1.11	1.14	0.04
T45℃ P120kPa	0.96	0.91	0.94	0.04

Table 3.17 Simulation results by Aspen HYSYS and DWSIM for VOC emission for gasoline loading in a product tanker

Parameter		Evaporative Loss	VOC emission
Standard Deviation	Minimum	0.02	0
	Maximum	0.34	0.04
Confidence Level	Minimum	0.19	0
	Maximum	3.05	0.38

Table 3.18 Statistical analysis of Simulation results by Aspen HYSYS and DWSIM for gasoline loading in a product tanker

The slight variations in the simulation results obtained from Aspen HYSYS and DWSIM are attributed to the fact that the binary coefficients used in the Peng Robinson EOS in both simulations are different. PR EOS package in HYSYS has been significantly enhanced by Hyprotech to extend their range of applicability. Additionally, literature review indicates difference in the results could be due to different computational methods and assumptions used in the code of respective software in Aspen HYSYS and DW SIM (Kwanchanok Tangsriwong, 2020). However, simulation results from Aspen HYSYS and DWSIM show the similar trend for both evaporative loss and VOC emission at the tested tank temperatures and pressures. The results are shown in Appendix Figures A1 to A6 and Table A.1 and Table A.2.

Based on the above finding, further analysis of evaporative loss and VOC emission is conducted using Aspen HYSYS Simulation Software due to wide use in the industry as well as academia and research work (Aspentech, 2001; Mondal *et al.*, 2015).

3.5 Safety considerations for filling tanks to 98%

Cargo tanks onboard oil tankers are filled to 98% by volume to ensure optimum usage of the tank space between the loading and unloading port (Hyundai Shipyard, 2007; Shipbuilding, 2009). The process of topping off tanks requires good planning and coordination with the shore terminal supplying the oil. The common precautions to be observed by the PIC in CCR and the ship's crew (OCIMF, 2016), are as follows:

a) The cargo loading operations is supervised by Chief Officer and the adequate number of officers (designated as PIC) in the CCR onboard.

b) The remote ullaging system and associated high-level and high-high level alarms are to be tested for proper functioning before every loading operation. (High Level (95% level), and High-High Level (98% level))

c) The PIC in CCR monitors the loading rate continuously during the loading operations, as per the cargo plan issued by the Chief Officer.

d) The PIC records and compares the oil quantity received on board with the shore supply on an hourly basis throughout the loading operation.

e) Tank levels are staggered so that the aft tanks are topped off first. Usually, it is planned to keep a difference of 1 meter in ullage between each set of cargo tanks.

f) The loading rate is reduced appropriately to top off each tank in a careful manner, as per the initial ship-shore loading plan.

g) The PIC ensures that the tank level readings obtained using manual alleging and remote readings match to minimise any automation error.

h) The ship's crew is to use a closed tank gauging device to minimise any oil vapour exposure.

i) Manual ullaging by the ship's crew is to be reported to the PIC in CCR for every 5 cm rise in oil level, as the ullage level exceeds 90% level.

j) Manual ullaging by the ship's crew is to be reported to the PIC in CCR for every 2 cm rise in oil level, as the ullage level exceeds 95% level.

k) No more than two cargo tanks are topped off simultaneously to avoid human error.

l) Tank valves are closed at the designated 98% volume, and any change in the ullage is closely after the tank valves are closed to ensure no overflow.

m) Repeat the above precautions for each tank till all tanks are topped off to 98% level.

Chapter 4. Evaporative losses from crude oil and gasoline

4.1 Crude oil and gasoline lost to evaporation

This chapter deals with the evaporative loss of crude oil and gasoline and proposes amendments to minimise it. The crude oil and gasoline model described in Chapter 3 is run through the simulation using the Aspen HYSYS chemical process simulator. The output from the simulation is used to establish the monetary loss due to OVE, quantify the volume of vapour emission, and identify toxic components in the OVE. The data on the emission volume and its toxicity potential will provide the basis for proposing regulations to restrict toxic VOC exposure to seafarers onboard and minimise carbon emissions from tanker loading and ship bunkering operations.

4.2 Evaporative loss

Crude oil and gasoline loading simulation results can provide the exact amount lost to evaporation. The difference between the total oil volume at the inlet and the actual oil volume received in the tank is calculated and analysed in detail. The results for the evaporation of crude oil for the Aframax tanker and ULCC are presented in Table 4.1 to Table 4.5, and the variation of evaporative loss with change in tank level is shown in Figure 4.1.

The following findings are summarised based on the simulation output:

a) The higher the crude oil and gasoline temperature during loading operations, the higher the resulting evaporative loss. For all tankers, the evaporative loss becomes almost double for every 10℃ rise in oil temperature. A similar trend is observed when data are compared for the same tank pressure in ULCC and gasoline tanker (Table 4.1, Table 4.2, Table 4.3). During crude oil loading in an Aframax tanker, for crude oil temperature 25℃ and tank pressure 108 kPa, the total evaporative loss as per simulation data in Table 4.1 is 0.18%. This loss becomes 0.38% when the crude oil temperature is 35℃ (an increase of 90% as compared to evaporative loss at 25℃) and 0.84% for crude oil temperature of 45℃ (an increase of 121% as compared to evaporative loss at 35℃). This trend may be explained to occur due to the more evaporation of lower boiling point components in crude oil and gasoline when the temperature is higher, as crude oil and gasoline are composed of numerous components, each with different boiling points that evaporate based on their respective proportions in crude oil and gasoline.

Crude Oil Temp. ℃	Tank Pressure kPa	Tank Level / Evaporative Loss									
		10%	20%	30%	40%	50%	60%	70%	80%	90%	98%
25	108	1.49%	0.89%	0.63%	0.48%	0.39%	0.32%	0.27%	0.23%	0.20%	0.18%
25	120	1.30%	0.74%	0.51%	0.39%	0.30%	0.25%	0.21%	0.17%	0.15%	0.13%
									90% increase		
35	108	2.14%	1.40%	1.06%	0.86%	0.72%	0.62%	0.54%	0.48%	0.43%	0.38%
35	120	1.88%	1.17%	0.86%	0.68%	0.55%	0.47%	0.40%	0.35%	0.31%	0.27%
									121% increase		
45	108	2.90%	2.08%	1.69%	1.44%	1.27%	1.15%	1.05%	0.96%	0.89%	0.84%
45	120	2.64%	1.82%	1.44%	1.20%	1.04%	0.92%	0.82%	0.74%	0.68%	0.62%

Table 4.1 Evaporative Loss, as a percentage of liquid volume loaded, for an Aframax loading operation

Crude Oil Temp. ℃	Tank Pressure kPa	Tank Level / Evaporative Loss									
		10%	20%	30%	40%	50%	60%	70%	80%	90%	98%
25	108	1.00%	0.56%	0.38%	0.28%	0.22%	0.18%	0.15%	0.12%	0.10%	0.09%
25	120	0.85%	0.45%	0.30%	0.21%	0.16%	0.13%	0.10%	0.08%	0.07%	0.06%
35	108	1.55%	0.97%	0.72%	0.57%	0.47%	0.40%	0.34%	0.30%	0.26%	0.23%
35	120	1.31%	0.78%	0.55%	0.42%	0.34%	0.28%	0.23%	0.20%	0.17%	0.15%
45	108	2.25%	1.59%	1.29%	1.10%	0.97%	0.87%	0.79%	0.73%	0.68%	0.63%
45	120	1.99%	1.34%	1.05%	0.86%	0.74%	0.65%	0.57%	0.52%	0.47%	0.43%

Table 4.2 Evaporative Loss, as a percentage of liquid volume loaded, for a ULCC loading operation

Gasoline Temp. ℃	Tank Pressure kPa	Tank Level / Evaporative Loss									
		10%	20%	30%	40%	50%	60%	70%	80%	90%	98%
25	108	1.16%	0.56%	0.35%	0.24%	0.18%	0.14%	0.11%	0.09%	0.07%	0.06%
25	120	1.02%	0.48%	0.29%	0.20%	0.14%	0.11%	0.08%	0.06%	0.05%	0.04%
35	108	1.83%	0.94%	0.61%	0.44%	0.34%	0.27%	0.22%	0.19%	0.16%	0.14%
35	120	1.61%	0.81%	0.52%	0.37%	0.28%	0.22%	0.18%	0.15%	0.12%	0.11%
45	108	2.78%	1.53%	1.03%	0.77%	0.60%	0.49%	0.41%	0.35%	0.30%	0.27%
45	120	2.46%	1.32%	0.88%	0.64%	0.50%	0.40%	0.33%	0.28%	0.24%	0.22%

Table 4.3 Evaporative Loss, as a percentage of liquid volume loaded, for a gasoline loading operation

b) The amount of evaporation is highest when the tank filling level is almost empty to 30% full. As the tank level rises, the evaporation fraction falls steeply in the first 30% of tank filling, as shown in Figure 4.1 . It may be explained due to the higher SVP (Saturated Vapour Pressure) of the crude oil when the vapour-to-liquid ratio in the cargo tank is lower, particularly in the range between 0.02 to 0.2, as shown in Figure 4.2 V. (MEPC.1/Circ.680, 2009). As the difference between SVP and tank vapour pressure tends to be higher in the initial loading stage, more liquid changes to vapour, leading to a higher evaporative loss in the initial stages of loading.

When the tank level increases, continuous evolution of vapours from oil surface in the cargo tank increases the tank pressure, leading to an increase in the SVP of the volatile components and hence the evaporation rate decline towards the end of the loading. The change in SVP in this range is due to influence of individual volatile hydrocarbon types and their varying proportion in both the liquid and vapour phases, that separately contributes to the final SVP under equilibrium conditions (Sutton *et al.*, 2006; MEPC.1/Circ.680, 2009; Elliott and Lira, 2012; Clark, 2023).
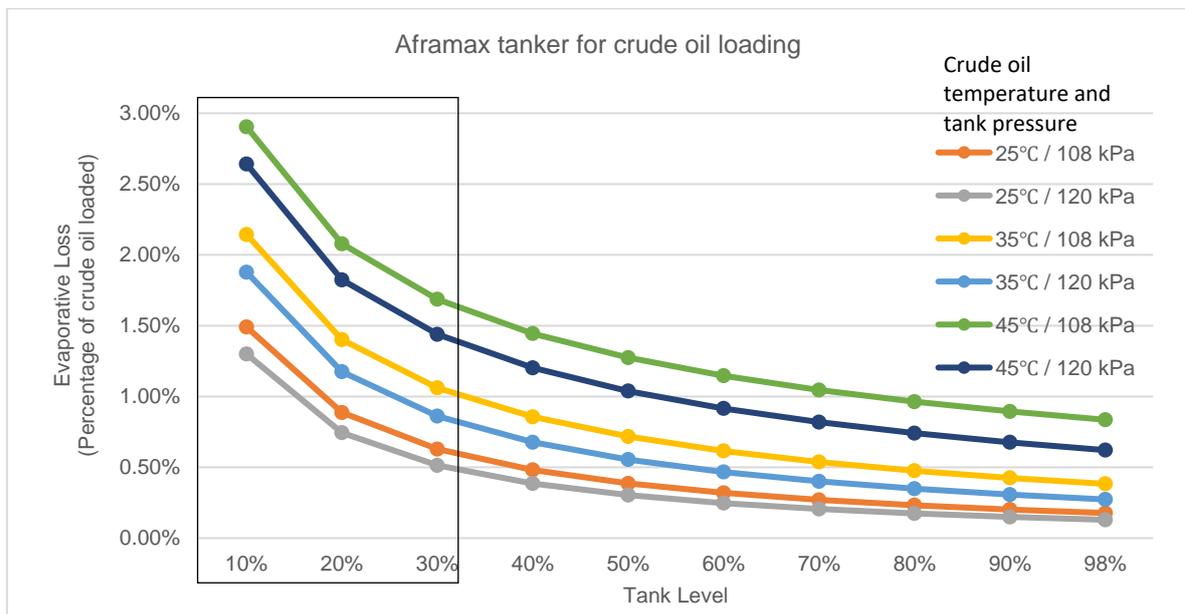
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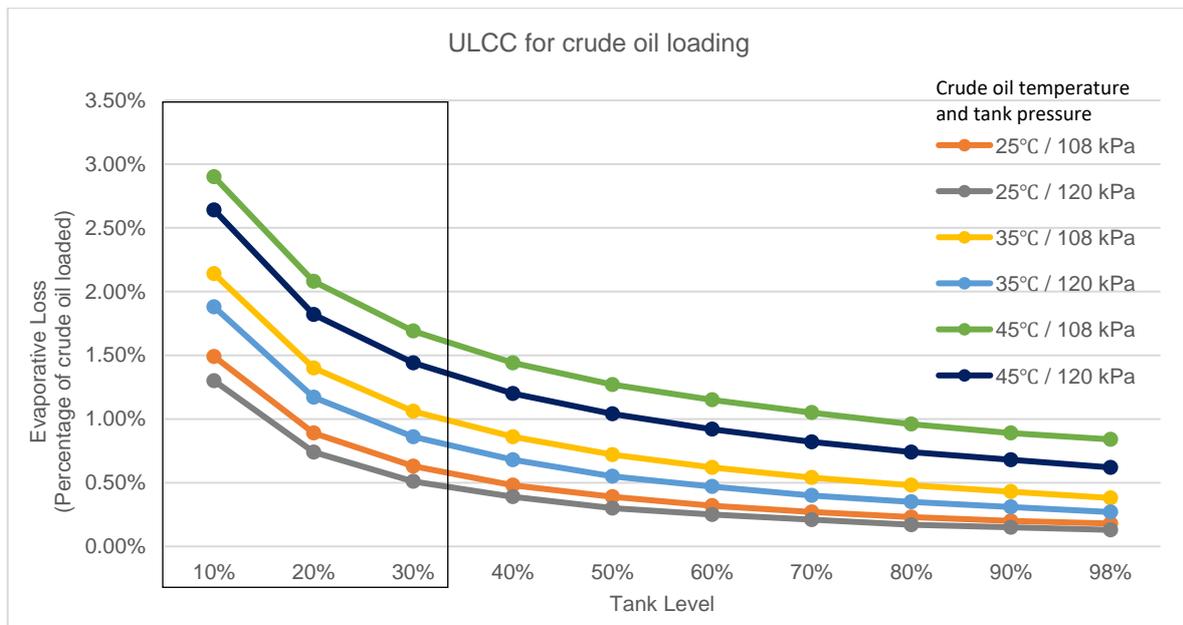
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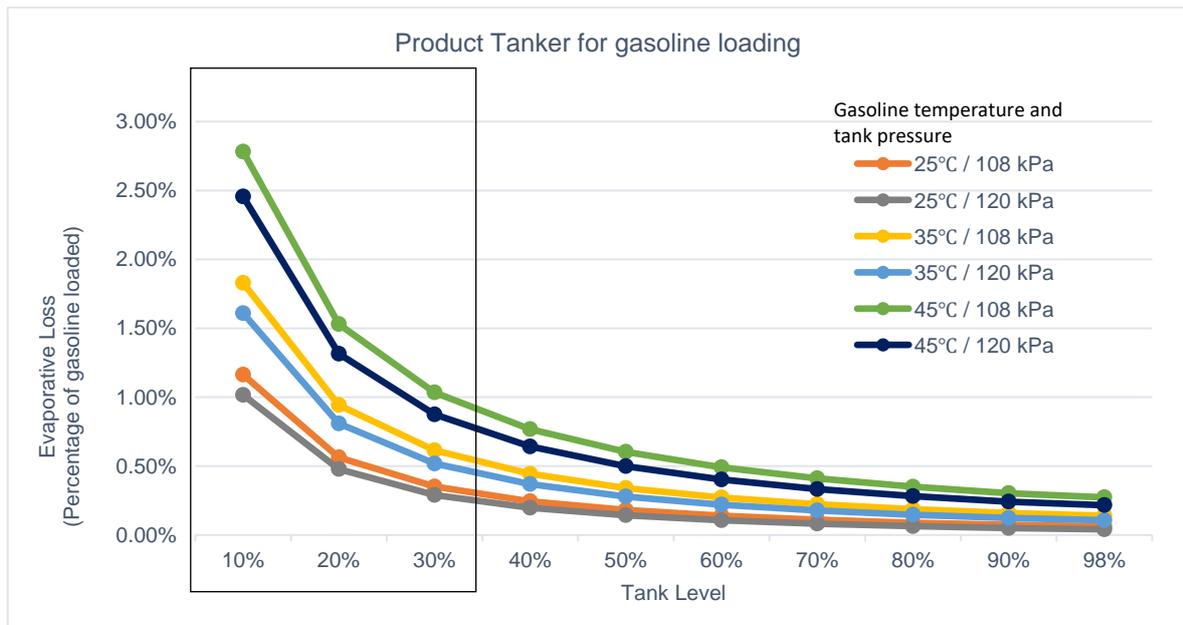
(c)

Figure 4.1 Evaporative loss, as a percentage of oil loaded, for a) a crude oil loading in an Aframax tanker, b) crude oil loading in a ULCC, and c) Gasoline loading operation in a Product tanker, with tank level, and various oil temperatures and tank pressures
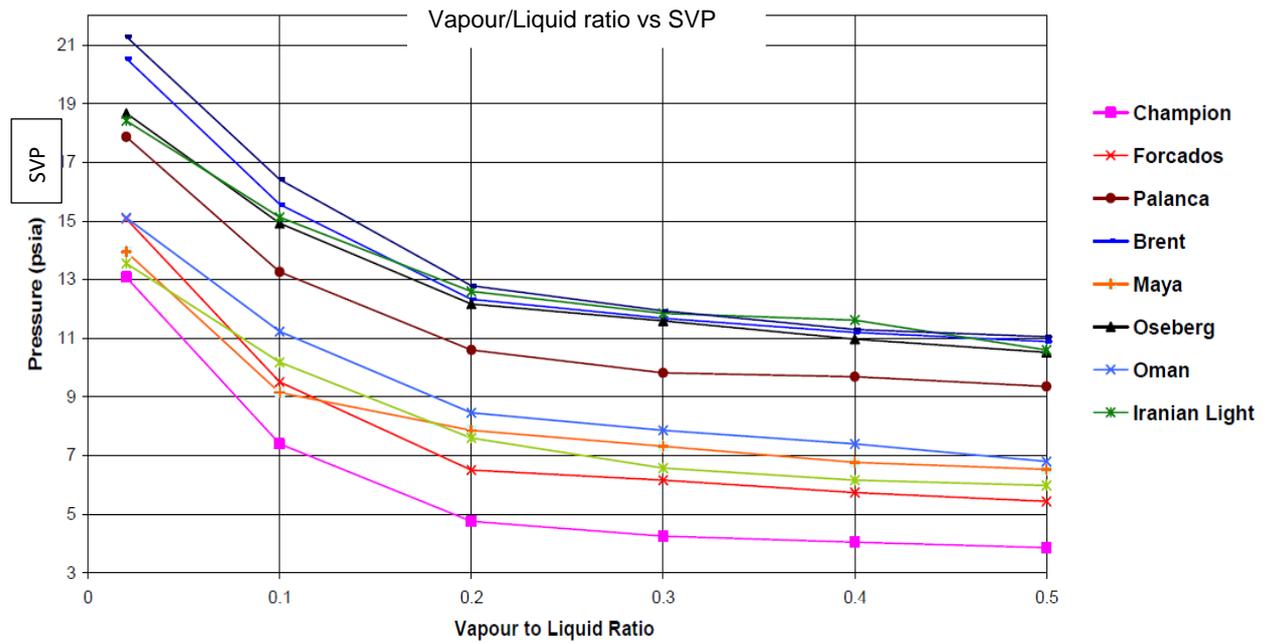
Figure 4.2 Variation in SVP of various types of crude oils (shown as Pressure on Y-axis) with 'Vapour to Liquid ratio' (MEPC.1/Circ.680, 2009)

c) Evaporative loss and VOC emission are reduced when higher tank pressure is maintained during the loading operations, as shown in Table 4.4 and Table 4.5. Simulation data showed that the evaporative loss is reduced by 26 to 29% for an Aframax tanker, 32 to 35% for a ULCC, for crude oil loading, and 21 to 34% for a gasoline tanker when loading is conducted by maintaining an elevated tank pressure of 120 kPa, instead of 108 kPa. Similarly, VOC emission was reduced by 23 to 26% for the Aframax tanker, 27 to 29% for a ULCC for crude oil loading, and 15 to 18% for a gasoline tanker when loading is conducted by maintaining an elevated tank pressure of 120 kPa, instead of 108 kPa. The decrease in evaporation and VOC emission may be explained by an expected rise in the boiling point of individual components in crude oil and gasoline with increased tank pressure. This observation is helpful to propose the adoption of maintaining higher tank pressure in cargo tanks during loading operations to achieve higher cargo outturn and reduced monetary loss. Additionally, this tanker practice of maintaining higher tank pressure during loading operation will also reduce carbon footprint during loading operation, as it reduces VOC emission. (Note: Current IMO GHG emission guidelines do not include controlling carbon footprint from tanker loading operations (IMO, 2021)).

d) Percentage evaporative loss is higher in an Aframax tanker than a ULCC, for same tank pressure and crude oil temperature. A higher loading rate in a ULCC tend to evaporate more liquid due to larger surface area available in the tank, leading to an increased cargo tank pressure. The resulting higher tank pressure increases the SVP of the volatile components, leading to overall reduced evaporative loss in ULCC (Elliott and Lira, 2012; Clark, 2023).

Tanker	Oil Temperature	Evaporative Loss (Percentage of oil loaded)		Decrease in evaporative loss
		108 kPa	120 kPa	
Aframax, Crude oil	25℃	0.18%	0.13%	28%
	35℃	0.38%	0.27%	29%
	45℃	0.84%	0.62%	26%
ULCC, Crude Oil	25℃	0.09%	0.06%	33%
	35℃	0.23%	0.15%	35%
	45℃	0.63%	0.43%	32%
Product, Gasoline	25℃	0.06%	0.04%	34%
	35℃	0.14%	0.11%	24%
	45℃	0.27%	0.22%	21%

Table 4.4 Evaporative loss, as a percentage of oil loaded, and the decrease in evaporative loss due to an increase in tank pressure from 108 kPa to 120 kPa

Tanker	Oil Temperature	Average VOC emission (kg/tonne)		
		108 kPa	120 kPa	Decrease in Average VOC emission
Aframax, Crude oil	25℃	0.71	0.55	23%
	35℃	1.44	1.07	26%
	45℃	2.92	2.26	23%
ULCC, Crude Oil	25℃	0.41	0.30	27%
	35℃	0.94	0.69	27%
	45℃	2.26	1.62	29%
Product, Gasoline	25℃	0.37	0.31	15%
	35℃	0.64	0.54	16%
	45℃	1.17	0.96	18%

Table 4.5 Average VOC emission and a decrease in VOC emission with an increase in tank pressure from 108 kPa to 120 kPa

The rate of flow in the pipeline governs the time taken to load the tanker. This rate of flow, which is commonly referred to as Tanker Loading Rate is analysed further. Additional Simulation is conducted to understand the evaporative loss with loading rate for crude oil and gasoline operations, the results are shown in Figure 4.3.
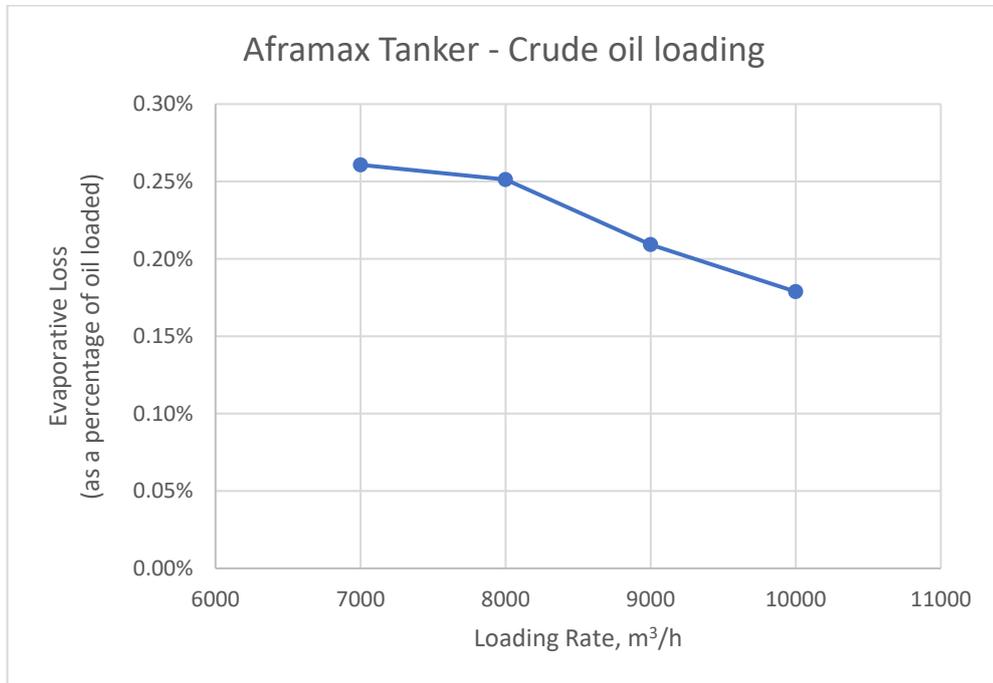
(a)
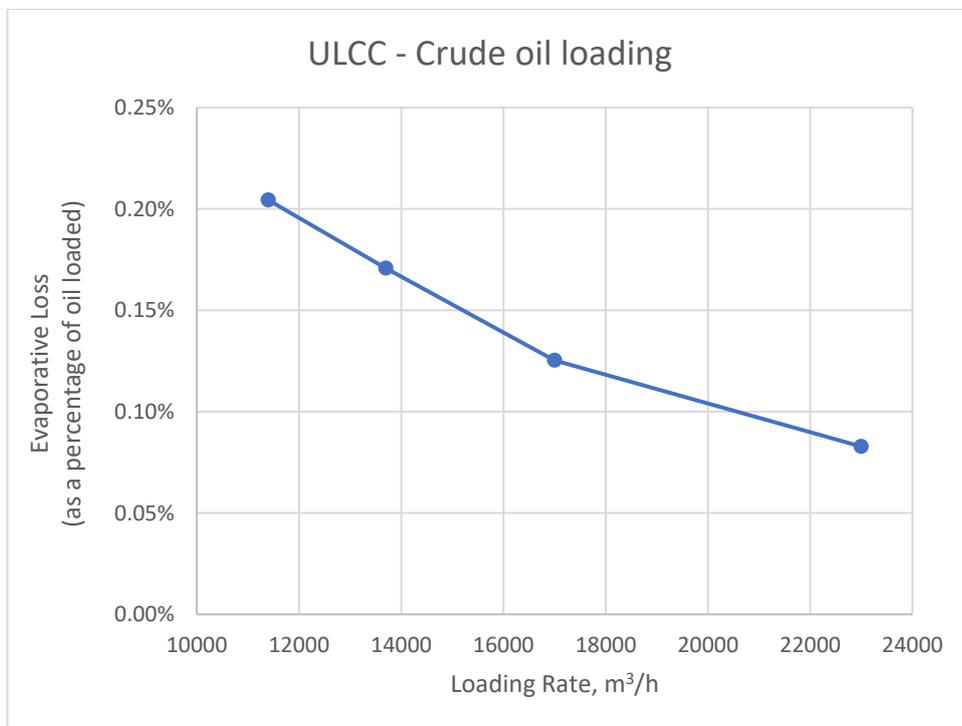
(b)
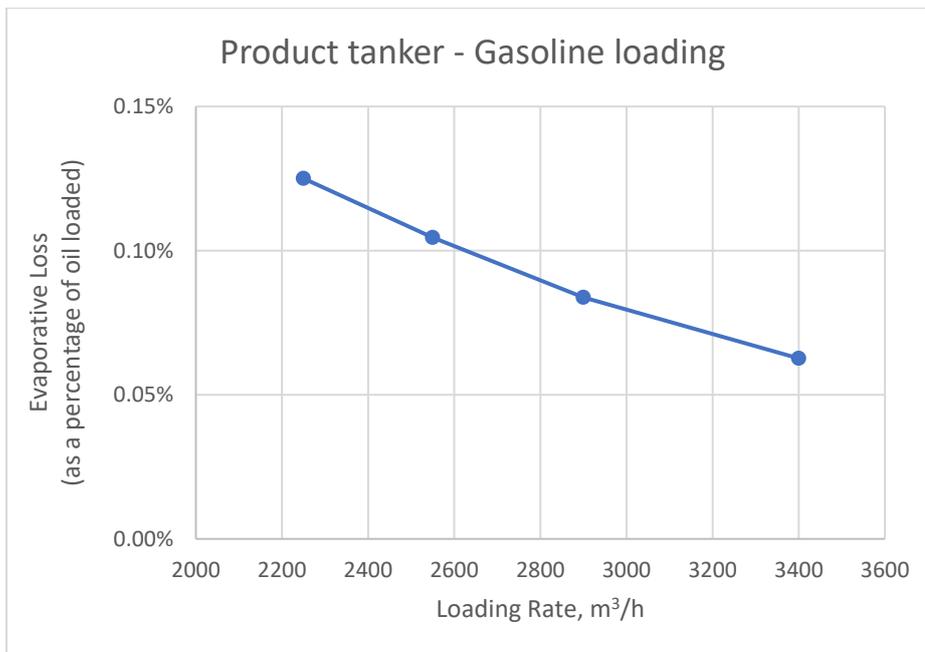
(c)

Figure 4.3 Variation in evaporative loss with Loading rate (a) for Aframax tanker for crude oil, (b) for a ULCC for crude oil, and (c) for a Product tanker, for Gasoline, for oil temperature 25℃ and tank pressure 108 kPa.

Simulation is carried out to understand the effect of Loading rate (flow rate) for all the three cases for same conditions of oil temperature and tank pressure. The results are shown in Figure 4.3, which shows a general trend of lower loading rate having higher evaporative loss. A higher loading rate increases the tank vapour pressure more rapidly than the lower loading rate due to the higher amount of low boiling point components in the tank. When the loading rate increases, higher vapour pressure built up in the tank increases the SVP of the volatile components and hence lowers the evaporation rate (MEPC47/INF.6, 2001; MEPC.1/Circ.680, 2009; Elliott and Lira, 2012; Clark, 2023). The list of lower boiling point components in crude oil and gasoline is shown in Table 4.6 below.

Crude oil component	Mole fraction	Boiling point ℃
Ethane	0.0009	-89
Propane	0.0103	-42
i-Butane	0.0285	-12
n-Butane	0.065	-1
i-Pentane	0.0297	36
n-Pentane	0.0418	36
Cyclopentane	0.0459	49
Gasoline component	Mole fraction	Boiling point ℃
n-Pentane	0.1837	36
Cyclopentane	0.0714	49

Table 4.6 Mole fraction and boiling point for various components in crude oil and gasoline (Toolbox, 2023)

Based on Table 4.6, almost 16% of the components in crude oil have boiling points below 40 to 50 ℃ which are more prone to evaporate based on surrounding conditions of temperature and pressure in the tank and the pipelines, as compared to the components in gasoline (Sutton *et al.*, 2006; Elliott and Lira, 2012; Speight, 2017). Thus, in general, crude oil shows higher evaporation loss than gasoline.

4.3 Validation of the results

The current literature review lacks details on calculating evaporative loss from tanker loading operations. However, some studies show the effect of temperature on vapour emission in tanker loading operations, and some have calculated VOC emissions. The results obtained by the simulation are compared with these studies further.

In a study conducted in an oil tanker loading terminal, Tamaddoni *et al.* collected data collected during tanker loading operations. The observations and analysis showed an increase in vapour emission (the liquid that turns into vapour) with an increase in temperature (Figure 4.4 (a)) and a decrease in evaporation of liquid fraction with an increase in tank pressure (Figure 4.5 (a)) (Tamaddoni *et al.*, 2014). The results obtained by simulation with the current assumed composition of crude oil showed a

similar trend as shown in Figure 4.4 (b) and Figure 4.5 (b). The simulation results from the current oil model also show a similar trend, i.e., rate of evaporation increases with the rise in crude oil temperature, and the evaporation rate drops with the increase in tank pressure. However, the magnitude of evaporation is different. This is mainly due to different crude oil compositions and temperatures, although the loading rate and oil temperature will also affect the evaporation. There are no details of crude oil composition reported by Tamaddoni *et al.*
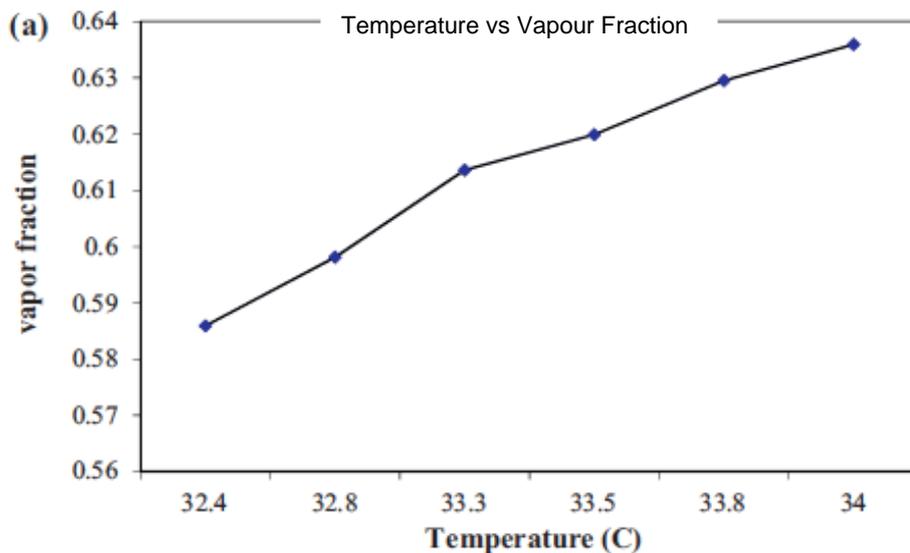
(a) (Tamaddoni *et al.*, 2014)
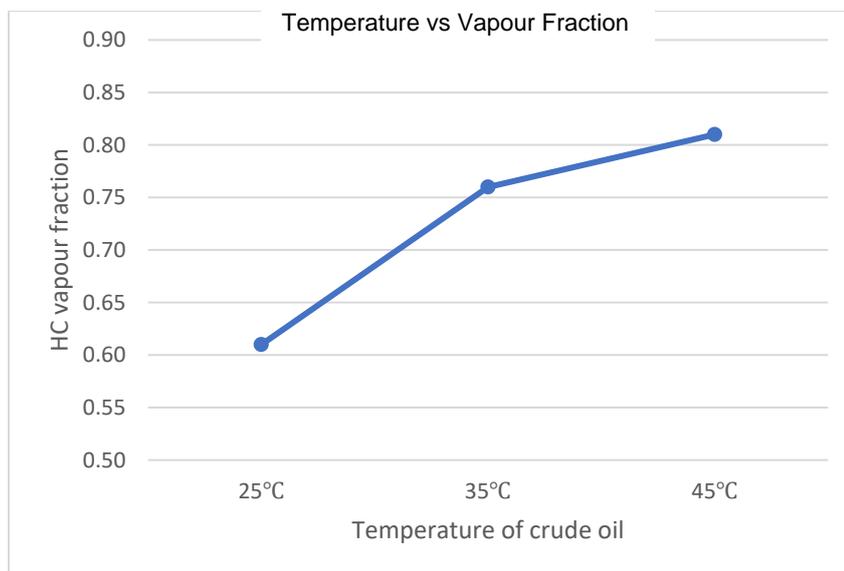
(b)

Figure 4.4 Effect of crude oil temperature on vapour emission (a) Tamaddoni *et al.* (b) HYSYS modelling of crude oil sample for Aframax tanker
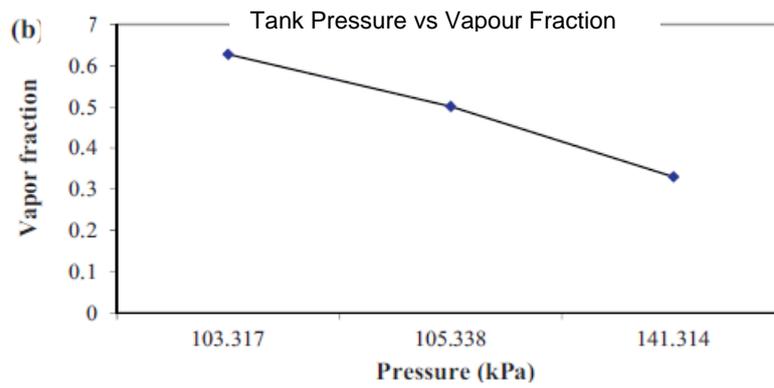
(a) (Tamaddoni *et al.*, 2014)
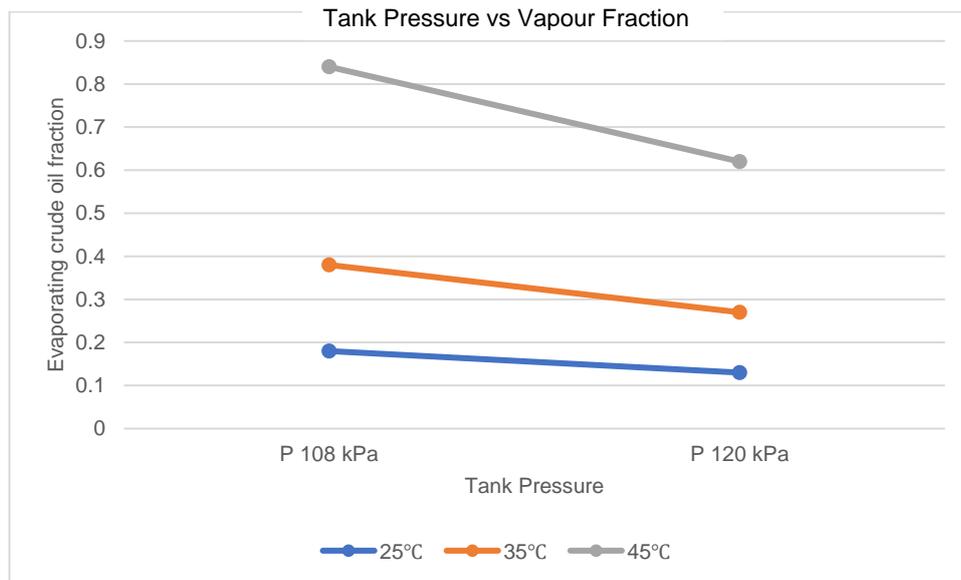
(b)

Figure 4.5 Effect of tank pressure on evaporation of crude oil fraction (a) Tamaddoni *et al.* (b) HYSYS modelling of crude oil sample for Aframax tanker

Todd *et al.* estimated that a volume of 2000 barrels of crude oil could be a potential recovery during a loading operation onboard for a two million-barrel shipment (Todd, 2016), which is approximately 0.1% of the loaded volume of crude oil. The simulation results for a ULCC loading 2 million barrels agreed with this data, showing the evaporative loss falling between 0.09% to 0.63%, for tank pressure at 108 kPa, as shown in Table 4.2.

Hansen *et al.* analysed offshore tanker loading operations to reduce VOC emissions in tanker loading operations. It was calculated that 0.2% of loaded crude oil in an Aframax tanker loading was attributed to total VOC emission. This study also analysed the effect of increased tank pressure on VOC emission. An increase in tank pressure

reduced VOC emission from the tanks, which was reported as a decrease in VOC emission by 33% when tank pressure was increased from 1.03 bar$_a$ (103 kPa) to 1.20 bar$_a$ (120 kPa). In the current simulation, this data is very close to the results obtained in Table 4.5, a 23% to 26% reduction when tank pressure is increased from 108 kPa to 120 kPa for an Aframax tanker.

Martens *et al.* measured the vapour flow from the tank during tanker loading operations. The results shown by their measurements are compared with the crude oil sample data in Figure 4.6. The trend for an increase in the volume fraction of HC gas with an increase in tank level, shown in Figure 4.6 (a), (highlighted in red) is very similar to the results shown for the current simulation in Figure 4.6 (b). As the loading operation progresses, the volume of HC in the vapour emission increases, which is attributed to the continual evaporation of lower boiling point components in the crude oil.
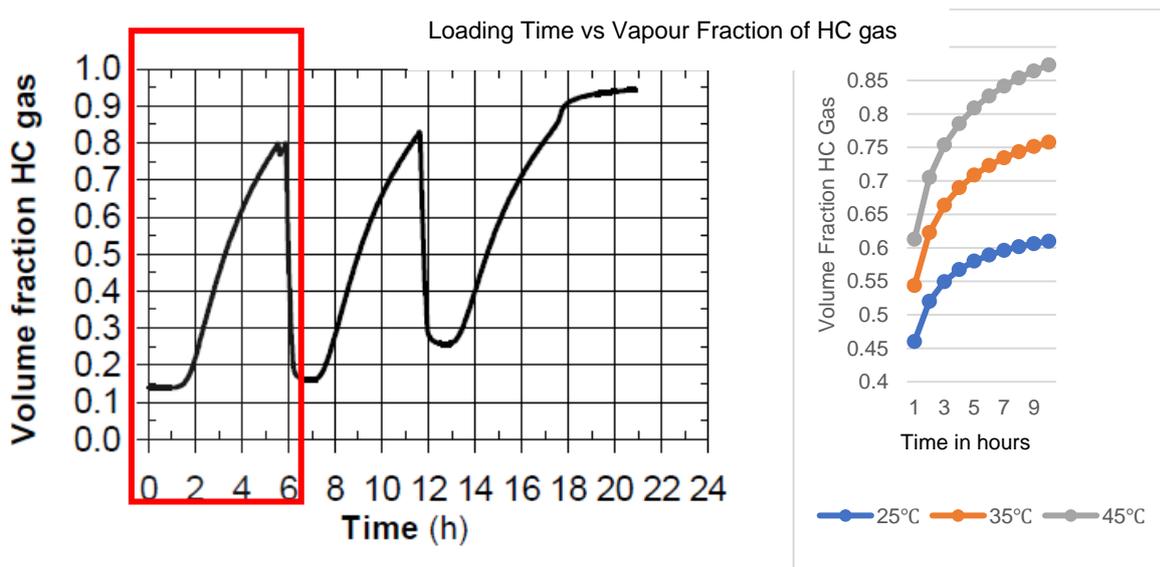
Figure 4.6 Volume fraction of HC Gas in vapour emission for crude oil loading operation (a) Results in study by Martens *et al.* (Martens *et al.*, 2001)(b) Results by Aspen HYSYS modelling of crude oil sample for Aframax tanker

The detailed information on crude oil loading rates and their exact composition for the operations are not detailed by Martens *et al.* and Tamaddoni *et al.* to make an accurate comparison. To make a precise comparison, the OVE data is compared for crude oil temperature 35℃ and 108 kPa pressure, at 30% of tank filling level, which is available in the study conducted by Martens *et al.*, Tamaddoni *et al.*, and Virdi *et al.*, as shown in Figure 4.7 C. Furthermore, individual components, C$_1$ to C$_5$, in OVE were also

measured. It is seen that there is a variation in individual concentration for C_1 to nC_4 components, whereas C_5 component concentration is somewhat closer. The variation in the results is most likely due to slightly different temperatures of crude oil, loading rates and the differing percentage of paraffinic, naphthenic and aromatic ratios in the crude oil sample used in each study.
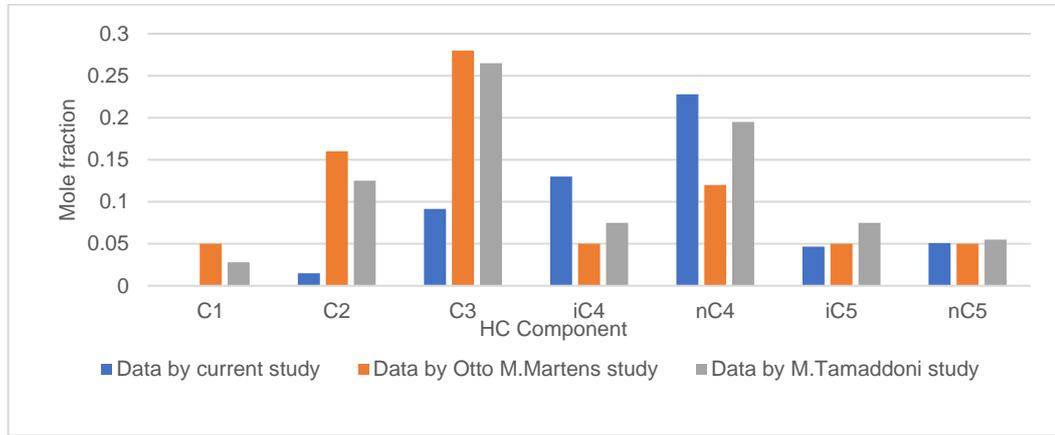
(a)
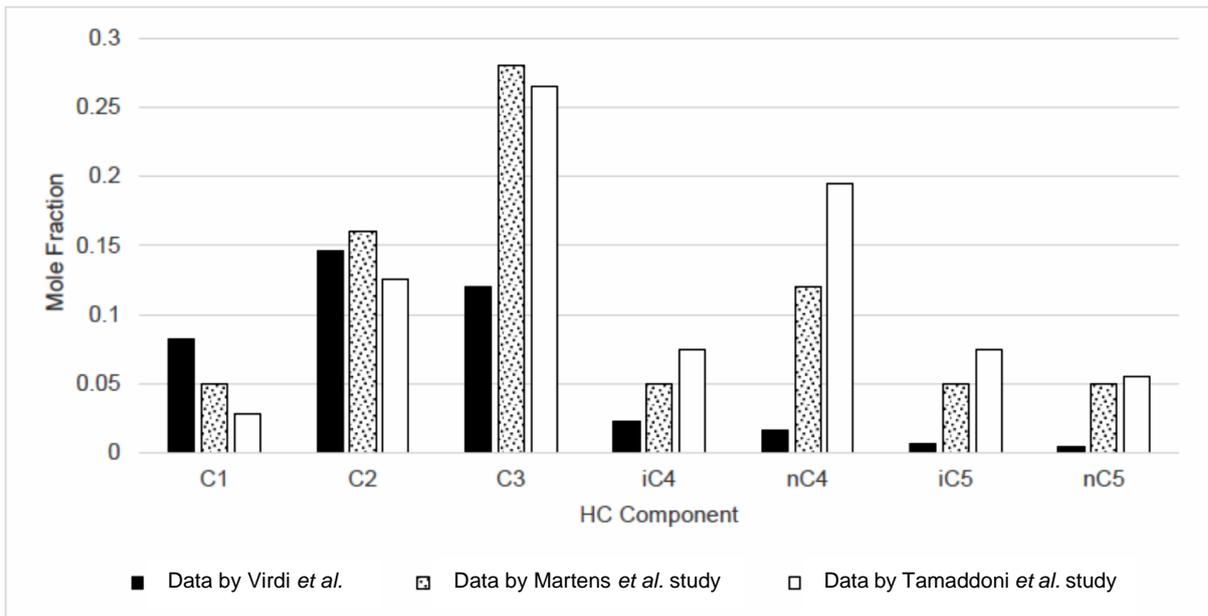
(b)

Figure 4.7 Composition of individual components in vapour emission for crude oil loading operations, (a) comparing the results from the current study and the study conducted by Martens *et al.* and Tamaddoni *et al.*, (b) comparing the current study by Virdi *et al.*

As Emission Factors (EF) have been widely used in various countries by environmental agencies, a comparison analysis is conducted with the EF obtained in the current study by the proposed crude oil sample and gasoline, shown in Table 4.6 and Table 4.7. The table also lists the limitations of each reference.

The current simulation methodology can provide EF values based on the following parameters:

a) Composition of oil
b) Loading rate
c) The temperature of the crude oil
d) The pressure of the tank in the tanker

The EF result obtained from the proposed methodology for crude oil loading operations is shown in Table 4.6 for the Aframax tanker, a ULCC tanker and a product tanker. An EF value for crude oil loading operation is 0.71 kg/tonne for an Aframax tanker and 0.41 kg/tonne for a ULCC, as per the current simulation results. This value lies within the range of EF quoted in EPA USA documents and the study conducted in the EU (0.1 kg/tonne (EPA USA) and 1 kg/tonne (UK AEAT study).

The EF result obtained from the proposed methodology for gasoline loading operations onboard product tanker are shown in Table 4.7. An EF value for gasoline loading operation is 0.37 kg/tonne for gasoline temperature at 25℃. This value lies close to the range of EF quoted in EPA USA documents and the research study conducted by other parties (0.24 kg/tonne (EPA USA), and (EU), and 0.32 kg/tonne (DeLuchi) (DeLuchi, 1993; EEA, 2019; EPA, 2020b).

EF values quoted in various studies and used by multiple environmental agencies in the EU and USA are very generic as they do not provide sufficient parameters such as the composition of the oil, loading rate, temperature of the crude oil, and pressure in the tank onboard tankers. As these parameters significantly influence the vapour emission, it can be concluded that EF values from these sources are unsuitable for validating the results. A more realistic comparison with actual observation for a specific oil sample, with known parameters, is needed to validate the results accurately.

Petroleum commodity	EF data by the current proposed sample	EF data by other agencies	Limitation / Remarks
Crude Oil	0.71 kg/tonne @ 25℃, 1.44 kg/tonne @ 35℃, 2.92 kg/tonne @ 45℃, for the Aframax tanker, Loading rate 10,500 m³/hr (66,500 bbls/hr) 0.41 kg/tonne @ 25℃, 0.94 kg/tonne @ 35℃, 2.26 kg/tonne @ 45℃, for a ULCC, Loading rate 22,800 m³/hr (143,000 bbls/hr) Density 0.83 tonne/m³, Tank pressure 108 kPa, Paraffinic component 63.2%, Naphthenic component 15.3%, and Aromatic component 21.5%	73 mg/L (0.10 kg/tonne, based on crude oil density of 0.83 tonnes/m3) (Officers, 2020)	EPA USA, and EI Hydrocarbon Management HM65. Excludes emission of methane and ethane, generic value is quoted, but no details of crude oil temperature, flow rate, tank pressure and composition of crude oil
		No details, as crude oil is primarily imported into the EU.	EEA EU
		0.12 kg/kL (0.14 kg/tonne, based on crude oil density of 0.83 tonnes/m³)	Matsumara Report, only vapour temperature is mentioned as 30℃. Generic value is quoted, but no details of crude oil temperature, flow rate, tank pressure and composition of crude oil
		292 mg/L for Alaskan crude (0.35 kg/tonne) 73 mg/L for Lower 48 crude oil (0.10 kg/tonne) based on Crude Oil Density of 0.83 tonne/m³	De Luchi Excludes Methane and Ethane in OVE. Generic value is quoted, but no details of crude oil temperature, flow rate, tank pressure and composition of crude oil
		1 kg(emitted)/tonne (loaded)	EU AEAT Report, 2001 Generic value is quoted, but no details of crude oil temperature, flow rate, tank pressure and composition of crude oil
		Arabian Heavy Crude oil 0.07 kg/ tonne loaded @ 40℃	Deligiannis et al., 2016

		Loading rate 1052 m³/h per tank	The detailed composition of each type of crude oil is not described.
		Arabian Medium Crude oil	
		0.24 kg/ tonne loaded@ 29℃	Specific details are available for loading rate and crude oil temperature.
		Loading rate 1543 m³/h per tank	
		Arabian Super light Crude oil	
		0.32 kg/ tonne loaded@ 42℃	
		Loading rate 1241 m³/h per tank	

Table 4.6 Comparison of Emission Factors for crude oil loading operations

Petroleum commodity	EF data by the current proposed sample	EF data by another agency	Remarks
Gasoline	0.37 kg/tonne @ 25℃, 0.64 kg/tonne @ 35℃, 1.17 kg/tonne @ 45℃, for a 39000 dwt product tanker Loading rate 3,400 m³/hr (21,400 bbls/hr)	180 mg/L (0.24 kg/tonne, based on gasoline density of 0.76 tonnes/m³)(Officers, 2020)	EPA USA and EI Hydrocarbon Management HM65. Excludes emission of methane and ethane, generic value is quoted, but no details of gasoline temperature, flow rate, tank pressure and composition of gasoline.
		4 g/m³ throughput / kPa TVP (0.24 kg/tonne, based on gasoline density of 0.76 tonnes/m³)	EEA EU Excludes Methane and Ethane in OVE

	Density 0.76 tonne/m^3, Tank pressure 108 kPa Paraffinic component 48%, Naphthenic component 12%, and Aromatic component 40%	0.19 kg/kL (0.25 kg/tonne, based on Gasoline density of 0.76 tonne/m^3)	Matsumara Report, only vapour temperature mentioned as 30℃ No gasoline temperature, flow rate, tank pressure, and composition details.
		240 mg/L (0.32 kg/tonne, based on Gasoline density of 0.76 tonne/m^3)	De Luchi Report Excludes Methane and Ethane in OVE No gasoline temperature, flow rate, tank pressure, and composition details.
		0.24 kg(emitted)/tonne (loaded)	EU AEAT Report The temperature ranges from 3℃ to 25℃, and RVP ranges from 50 to 90 kPa. The molecular weight of vapours is 62 to 68. The detailed composition of gasoline oil is not described.
		Condensate 0.76 kg/ tonne loaded @ 30℃ Loading rate 485 m^3/hr per tank	The detailed composition of condensate is not described. Specific details are available for loading rate, tank pressure, and condensate temperature. (Note: API of condensate is similar to gasoline, so it is used for reference only)

Table 4.7 Comparison of Emission Factors for Gasoline loading operations

4.4 Proposed amendments to tanker design and work practices to minimise monetary loss

Aspen HYSYS Simulator methodology can calculate specific values of evaporative loss, VOC emission, and EF values. This methodology considers the composition of crude oil, temperature, loading rate and tank pressure, which are the main factors affecting OVE. Specific values can be obtained, which can be a very effective tool than the current practice of using generalised Emission Factors to estimate the environmental impact of OVE associated with tanker loading operations. This section describes the proposed amendments to tanker design and work practices to minimise the monetary loss due to evaporation.

4.4.1 Modification in tanker design

OVE occurs due to oil evaporation when the pressure in the surrounding environment, such as pipelines or cargo tanks, is lower than or equal to the SVP of the oil at that temperature. As long as the tank pressure is maintained above the SVP of the cargo, equilibrium is obtained between the liquid and vapour phases of the cargo, and no further VOC will evolve from the cargo (MEPC.1/Circ.680, 2009). It is proposed that the tanker design be modified, so that tank pressure is maintained higher than the SVP of the oil being loaded.

The usual setting of current P-V valves fitted onboard oil tankers fall in the range of 98 kPa in vacuum and 114 kPa in pressure. As maximum SVP of various types of crude oil is reported to be up to 115 kPa, it is proposed that operating tank pressure be amended above this pressure (PujadÛ and Jones, 2006; Sutton *et al.*, 2006; Speight, 2017). The maximum design pressure of the current cargo tanks on oil tankers is at least 125 kPa, so increasing this operating setting by P-V valves to 120 kPa, should not require additional strengthening (MEPC.1/Circ.680, 2009). However, following factors should be considered when adopting practice of maintaining higher pressure:

a) Ensure that the tank structure is well maintained during all statutory structural surveys

b) Periodic examination of cargo and ballast tanks

c) Calibration of P-V Valves and cargo tank pressure sensors at regular intervals

d) Integrity checks to ensure correct synchronisation of remote pressure monitoring system with local reading

e) Automatic pressure monitoring of cargo tanks via control system and hydraulic control valve

f)   Effective watch keeping during cargo operations

The following methods, as recommended by IMO MEPC sub-committee, can achieve it:

a) Install P-V valves with higher settings
b) Install and use the VOCON valve during a loading operation
c) Install KVOC system
d) Install CVOC system

The details of each design are provided below.

a) Install P-V valve with higher settings

Monetary loss due to the evaporation of crude oil and gasoline during tanker loading operations is proposed to be reduced by modification in tank operating pressure. It is suggested that all cargo tanks onboard oil tankers should be fitted with P-V valve setting of at least 120 kPa, which is higher than the SVP of most of the crude oils. This high pressure in the tank will result in either negligible or very reduced need to vent any excess OVE. The estimates in Table 4.8 are based on a crude oil price of $70 per barrel and gasoline data at $2 per barrel, both being the lowest price from 2021 to 2022 (Price, 2022).

Tanker		Temp. °C	Evaporative Loss	Evaporative Volume, m³ @ 15°C	Bbls	Basis	Monetary Loss, US $	
							For one loading	Annual Loss
Aframax	Crude Oil	25	0.18%	226	1423	$70 per barrel	$ 99,615	$ 1,195,374
		35	0.38%	478	3004		$ 210,297	$ 2,523,568
		45	0.84%	1056	6641		$ 64,868	$ 5,578,413
ULCC	Crude Oil	25	0.09%	305	1919		$ 134,321	$ 1,611,849
		35	0.23%	780	4904		$ 343,264	$ 4,119,170
		45	0.63%	2136	13432		$ 940,245	$ 11,282,945
Product Tanker	Gasoline	25	0.06%	24	152	$2.00 per barrel	$ 304	$ 3,647
		35	0.14%	56	355		$ 709	$ 8,509
		45	0.27%	109	684		$ 1,368	$ 16,411

Table 4.8 Monetary loss due to evaporation during the loading operation

Evaporative loss reduces when higher tank pressure is maintained in the cargo tank, as shown in Table 4.4. As overall, the evaporative loss has the potential to be reduced

by 26% to 35% for crude oil loading and 21% to 34% for gasoline loading when tank pressure is maintained at 120 kPa during loading operations. Additional savings will be realised when there is no need to do any venting during the transit to the discharge port.

For existing tankers to modify, an additional cost will be incurred for replacing existing P-V valves for 12 tanks configurations. An additional $100,000 may be accounted for replacing P-V Breaker and additional safety survey costs. The details are shown in Table 4.9; it could be estimated as one time cost of approximately $700,000 for an Aframax tanker to about $ 1 million for a ULCC. This additional cost can be recovered in one to two years by additional cargo outturn for existing tankers, as shown in Table 4.10. This extra cost may be nominal for new tankers as the tanker will be designed with higher specifications of P-V valves.

S.No	Item to replace	Quantity	Unit Cost	Total Cost
1	P-V Valve with higher settings	12	$ 50,000	$ 600,000
2	P-V Breaker	1	$ 80,000	$ 80,000
3	Additional Survey / Steel renewal	1	$20,000	$20,000
	Total Cost			$700,000

Table 4.9 Details of the cost of retrofitting existing oil tankers

The monetary gain calculation is shown in Table 4.10. The maximum designed cargo tank pressure for all tankers is at least 2500 mm WG (125.8 kPa), and as such, increasing the setting should not require any additional strengthening in the cargo tanks. It will also need replacing or modifying P-V Breaker and other pressure safety alarms (MEPC.1/Circ.680, 2009).

Tanker	Oil Temperature	Evaporative Loss			Annual Monetary Gain by higher cargo outturn
		108 kPa	120 kPa	Decrease	
Aframax, Crude oil	25℃	0.18%	0.13%	28%	$ 332,048.38
	35℃	0.38%	0.27%	29%	$ 730,506.43
	45℃	0.84%	0.62%	26%	$ 1,461,012.87
ULCC, Crude Oil	25℃	0.09%	0.06%	33%	$ 537,283.09
	35℃	0.23%	0.15%	35%	$ 1,432,754.91
	45℃	0.63%	0.43%	32%	$ 3,581,887.29
Product, Gasoline	25℃	0.06%	0.04%	34%	$ 1,215.61
	35℃	0.14%	0.11%	24%	$ 1,823.42
	45℃	0.27%	0.22%	21%	$ 3,039.03

Table 4.10 Monetary gain by increased tank operating pressure to 120 kPa

b) Vapour pressure release control valve (VOCON valve)

The Vapour Pressure Release Control valve controls the release of oil vapours to the atmosphere via Mast Riser in crude oil tankers. The valve is operated from the cargo control room and / or ship's Bridge via a hydraulic system to be used during loading and transit (MEPC.1/Circ.680, 2009). When cargo tanks are modified to have higher pressure setting of 120 kPa, VOCON valve can assist to minimise vapour emission during the tanker loading operation. The valve allows for maintaining higher pressure during the loading operations to limit the extent of vapour evolution from the crude oil once SVP is achieved within the tank vapour system.

c) Cargo pipeline partial pressure control valve (KVOC)

The purpose of the cargo pipeline partial pressure control system (KVOC) is to prevent the formation of VOC during loading and transit, thereby minimising the release into the atmosphere. The plan was developed by Norwegian Tanker owners (Hansen *et al.*, 2008) and included in the technical information issued by IMO MEPC for operational procedures related to VOC Management Plan (MARPOL, 2020) (MEPC.1/Circ.680, 2009). Marten *et al.* estimate a 60% to 70% reduction in VOC emission during tanker loading operations using the KVOC system.

KVOC system requires a new drop pipeline column to be designed and fitted for each tanker for the expected loading rate. The new drop pipeline column has an increased diameter compared to an ordinarily fitted drop pipeline, as shown in Figure 4.8 . The increased drop pipeline diameter reduces the velocity of the oil inside the column during crude oil loading operations, ensuring that the pressure adjusts itself to approximately the boiling point of the oil independent of the loading rate. The pressure inside the column adjusts itself to the SVP of the oil so that there is a balance between the pressure inside the column and the oil SVP. When the pressure has been obtained in the column, the oil loads without any additional VOC generation. This means that KVOC column prevents under pressure to occur in the loading system during loading. A high pressure, from about 800 to 1000 mm WG, will reduce possible boiling and diffusion of VOC in the crude oil cargo tanks (MEPC.1/Circ.680, 2009), although some VOCs might be generated during the initial phase of the loading process.
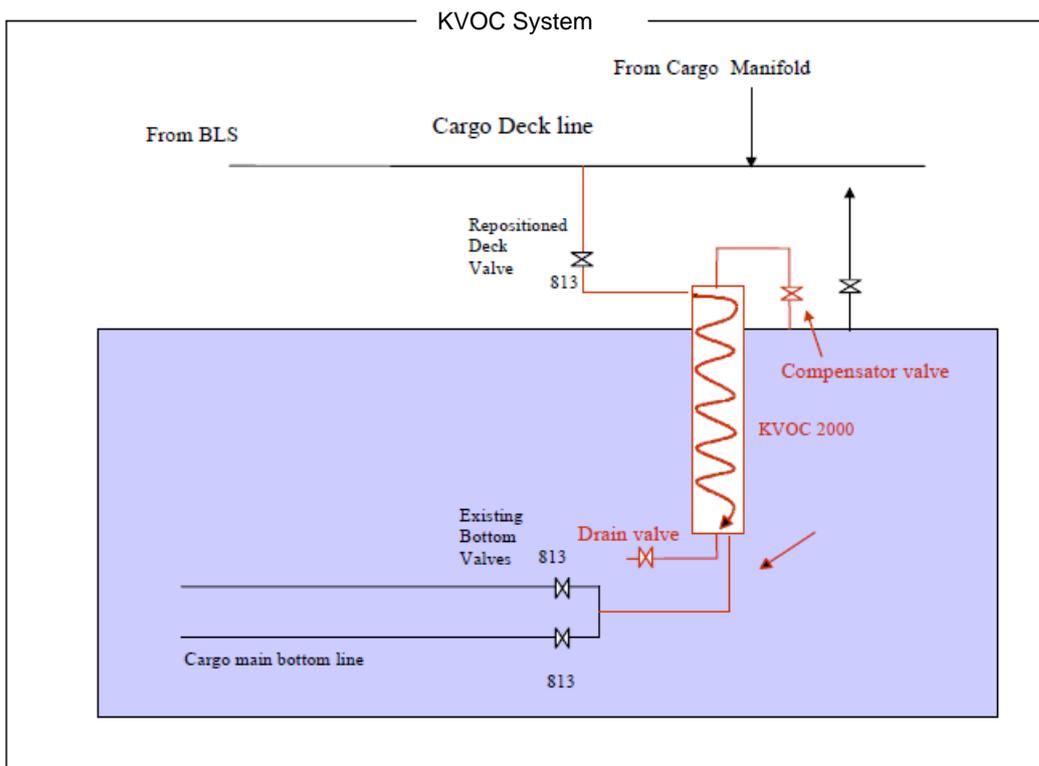
Figure 4.8 Pipeline flow plan for the KVOC system (MEPC.1/Circ.680, 2009)

d) Direct absorption of VOC in the crude oil (CVOC System)

The CVOC System has been designed to utilize hydrostatic pressure in the cargo tanks to re-absorb emitted VOC back into the Crude Oil. This process allows tank pressure

to be reduced without venting to the atmosphere, thus eliminating all cargo emissions during transit – including H_2S. The CVOC system also reduces VOC emissions from the cargo during loading and cargo transfer operations(MEPC.1/Circ.719, 2010).

The CVOC system, as described in IMO MEPC circular, is based on the direct absorption of VOC in crude oil. The Swirl Absorber, a combined ejector and mixing unit, uses crude oil from one of the cargo tanks to create a low-pressure area where vapour from the main inert gas line can be mixed with crude oil, as shown in Figure 4.9 D. The mix of VOC, inert gas and crude oil is then led back into the same cargo tank from which the crude oil was initially taken. VOC is absorbed in the crude oil due to increased pressure in the bottom of the cargo tank, while inert gas rises to the surface without being absorbed.

Oil circulation is obtained using a standard centrifugal pump driven by an electrical motor. System operation is controlled by a simple PLC located in the engine room and several pressure and temperature sensors. Operation and monitoring are done on two"10" LCD touchscreen panels in the Cargo Control Room and on the Bridge.

The CVOC System is a stand-alone installation without interfering with existing safety features or operational procedures. Automatic system operation is controlled by a dedicated pressure sensor installed in the main inert gas line and is based on pre-set pressure levels determined by the crew. The CVOC system can also be operated manually as long as the cargo tank pressure is sufficient.
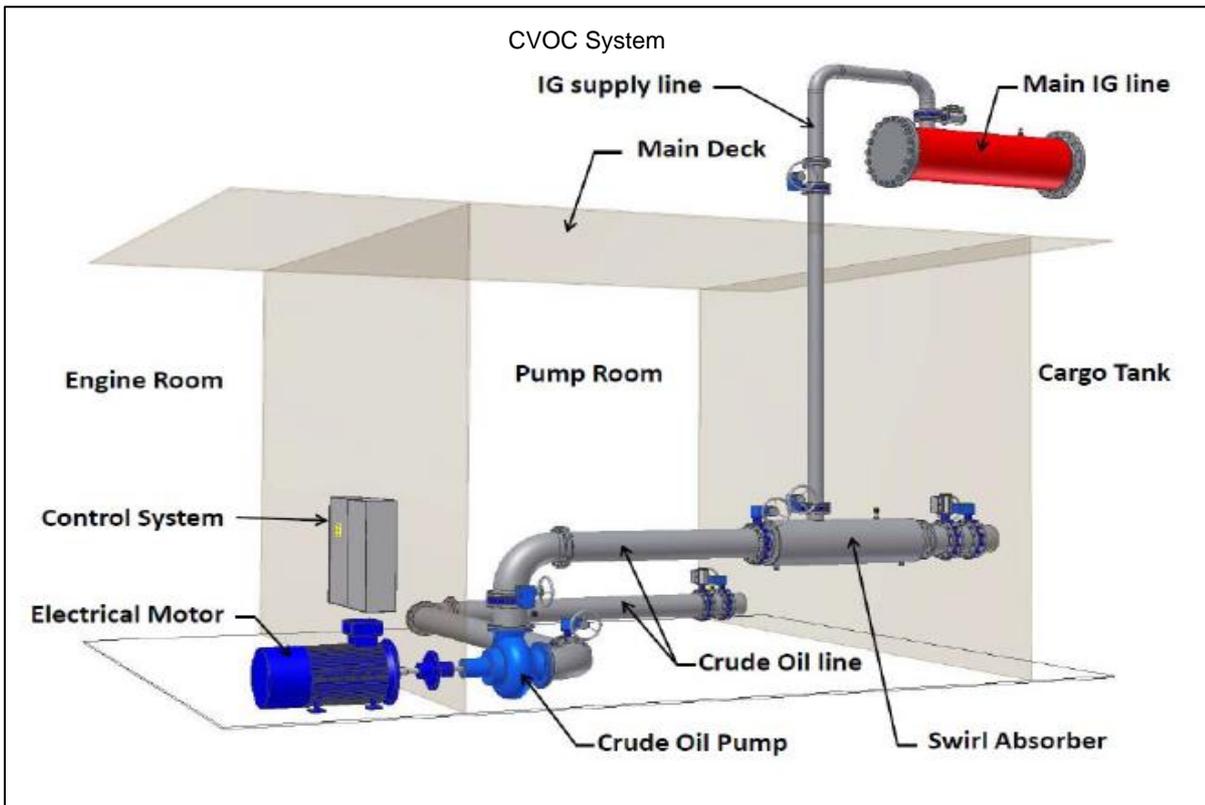
Figure 4.9 Direct absorption of VOC in crude oil – CVOC System(MEPC.1/Circ.719, 2010)

The above mentioned measures are recommended to be adopted by IMO MEPC sub-committee for their ability to control VOC formation and emission (MEPC.1/Circ.680, 2009).

4.4.2 Modification in tanker loading procedure

a) Crude oil loading procedures

Evaporative loss is increased with higher crude oil temperature and higher flow rate for the same type of tanker. Oil terminals should provide crude oil at the lowest temperature, which can be accomplished by suitable tank insulation. The rate of loading should be kept optimum to minimise the vapour generation. In the current tanker loading practice, crude oil loading rates are not evaluated for the potential of vapour generation but only follow guidelines to minimise the generation of sparks by static charge accumulation caused by oil flow in a pipeline.

Sustainable tanker loading operations require close cooperation between oil terminals, charterers and shippers. Crude oil loading operations are accomplished either by controlled venting of generated oil vapours to the atmosphere via Mast Riser or by the

connection of vapour return line to shore tank using 'Vapour Emission Control System' (VECS) (MSC/Circ.585, 1992; VOCMP, 2010; VOCMP, 2015; MARPOL, 2020). Based on the information submitted to IMO, it is seen that only very few oil terminals operating in the Netherlands and South Korea have a VECS system(MEPC.509, 2006; GISIS, 2020). Most of the crude oil loading operations are carried out by the controlled or free venting of the vapours generated during the loading operation to the surrounding atmosphere. It is proposed that the practice of free venting of oil vapours should be stopped entirely by the mandatory provision of vapour return lines at all oil exporting terminals. Tanker loading terminals must provide this facility to prevent any vapour emission, and tank pressure during the crude oil loading should be maintained to the highest possible safe value based on the tanker design. Elevated P-V valve setting, as per section 4.4.1, can assist in reducing the evaporative loss for a sustainable loading operation.

b) Gasoline loading procedures

Current Gasoline loading operations allow controlled venting of vapours at a high-pressure setting of individual P-V Valves fitted in each cargo tank. There is no requirement under SOLAS and MARPOL Convention to stop this emission during gasoline loading operations. It is proposed that P-V valves with elevated pressure side setting of 120 kPa be fitted, which is estimated to potentially reduce evaporative loss, ranging from 21% to 34%, as per current simulation analysis, and details are shown in table 4.10.

At the same time, all gasoline exporting terminals must provide Vapour Emission Control System (VECS) so that shore-based infrastructure can recover gasoline from the vapour return line for sustainable operations.

Oil exporting terminals require a commitment to provide vapor recovery line, which has not made any progress since IMO provided this guidance in 1990.

4.5 Conclusion

a) The simulation data is able to show the exact loss, which provides a basis for adopting solutions related to amendment in tanker design and working practices. The analysis is conducted for an Aframax tanker and a ULCC tanker for crude oil loading operation, as well as gasoline loading operation onboard a product tanker. The data shows annual monetary loss of $1.2 to 5.5 million for an Aframax tanker loading crude oil between the temperature range of 25℃ to 45℃, whereas the same

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loss for a ULCC is in the range of $1.6 to 11.2 million for the same temperature range.

b) In addition to this loss, the evaporative loss is related to carbon emission which will be analysed in Chapter 5. It can be concluded that evaporative loss occurring during tanker loading operations leads to direct monetary loss, as well as VOC and hence carbon emission.

c) Solutions are proposed to modify the current tanker design to operate with a higher setting of P-V valves fitted on cargo tanks. This can reduce the monetary loss by 26% to 35% for Aframax and a ULCC. Similarly, gasoline loading losses can be minimised by 21% to 34%.

d) Additionally, these measures are also able to reduce VOC emission during tanker loading operations. VOC emission is reduced from 23% to 29% for Aframax and ULCC crude oil loading operation and 15% to 18% for a product tanker gasoline loading operation.

e) Adopting additional measures such as fixing VOCON valves, CVOC system, KVOC system can further reduce monetary and carbon loss to the environment.

f) It is recommended that 'Vapour Return Line' be made mandatory at all oil exporting terminals, as per the provisions under VECS as applicable to oil tankers.

Chapter 5. Quantitative analysis of VOC emission

Oil tanker loading and ship bunkering operations release a large amount of oil vapours in the surrounding environment. This chapter provides details on the volume of OVE being released during these operations.

5.1 Total vapour emission

Current research conducted a detailed simulation of crude oil and gasoline loading operations. Crude oil loading operation is simulated for an Aframax tanker and a ULCC, whereas gasoline loading operation is simulated for a clean petroleum product tanker. The basis of selection is described in Chapter 3 (Section 3.3). The details of the loading operations are summarised in Table 5.1.

Type of Tanker	Ddwt. (tonnes)	The total volume of crude oil at the ambient temperature (m^3)	Number of cargo tanks, excluding slop tanks	Loading duration (in hours)	Loading rate In one tank (m^3/hour)	Overall loading rate (m^3/hour)	Overall loading rate (bbls/hour)
Aframax	113,458	126,772	12	12	880	10,564	66,448
ULCC	308,492	341,879	15	15	1520	22,792	143,457
Product Tanker (Gasoline)	37,900	40,778	12	12	283	3,398	21,374

Table 5.1 Details of the tanker loading simulation

Simulation is conducted for oil loading operations at 25℃,35℃ and 45℃, covering various geographical oil exporting locations. The tank pressure selected for simulation is 108 kPa and 120 kPa, as per the description in Chapter 3.

The simulation output can show the rate of OVE with a change in tank level for the respective oil temperature during loading, cargo tank pressure maintained onboard, and the flow rate (loading rate). The details are shown in figures 5.1 to 5.3 for crude oil and gasoline loading operations.

The following conclusions can be drawn from the Figure 5.1, Figure 5.2, and Figure 5.3, as below:

a) The rate of oil vapour emission is highest when the tank is empty, for crude oil loading at temperature of 25°C (Figure 5.1 (a) & Figure 5.2 (a)), and for gasoline at all loading temperatures (Figure 5.3 (a)) under the pressure of 108 kPa and 120 kPa. In contrast, the rate of OVE for crude oil temperature at 35°C, and 45°C, rises initially and then falls steadily with the rise in tank filling level, as shown in Figure 5.1 (a) and Figure 5.2 (a) at both loading pressures. This trend may be attributed due to the tank pressure being lower than the SVP of the oil at that temperature and the available free space in the empty cargo tank. For crude oil temperatures at 35°C and 45°C, HC components having a lower boiling point in crude oil evaporate more at the start of the loading operation, thereby showing an increase in the rate of OVE in the initial loading stage. The maximum rate of OVE can be predicted from the trend to estimate the optimum time to operate VOC recovery equipment.

b) Total OVE is summed up and the trend is shown in Figure 5.1 (b), Figure 5.2 (b) and Figure 5.3 (b). It is observed that the total volume of vapours does not increase in steady manner. This is expected due to higher rate of evaporation in the initial stage of loading since larger available free space in the tank would increase the evaporation rate of lower boiling point components. The trend on total OVE is helpful for understanding and the calculation of environmental impact of each loading operation. Similar simulation results can be obtained for different loading rates to get a real impact on air quality.

c) Maintaining higher tank pressure reduces the rate of vapour emission and total OVE. This is due to higher tank pressure leading to a higher SVP of the crude oil components in the total OVE.

d) The higher the oil temperature, the higher the vapour emission rate and the overall OVE. This could be due to the evaporation of lower BP components in the crude oil for the respective loading temperature.
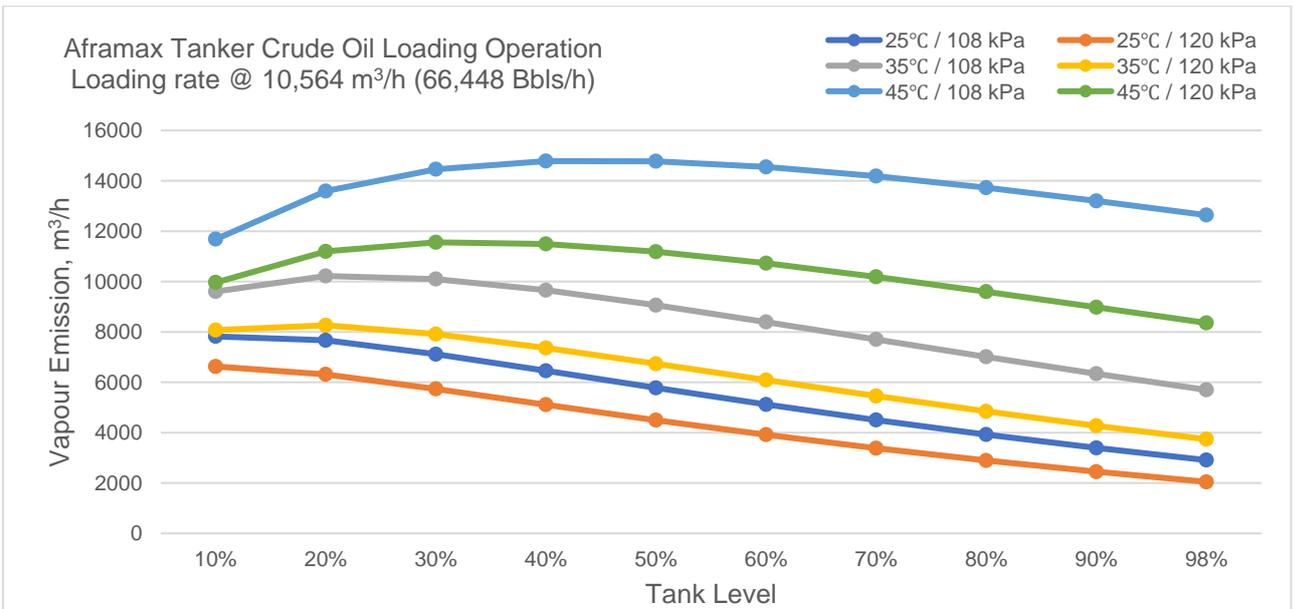
(a)
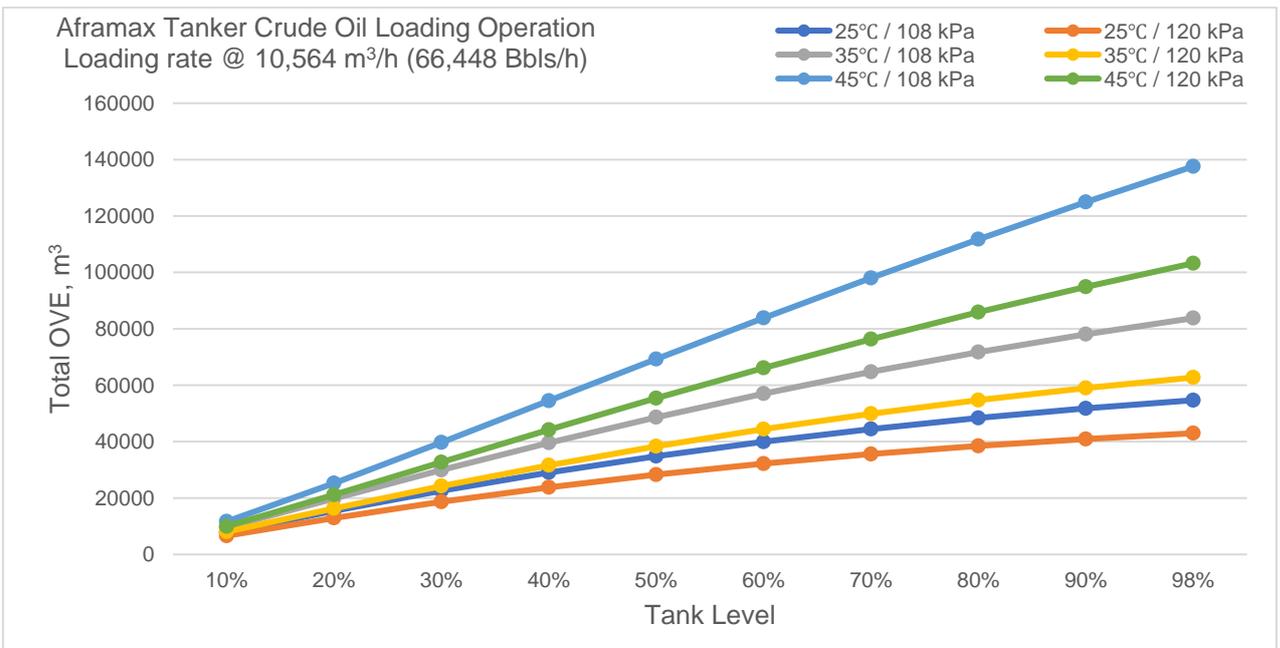
(b)

Figure 5.1 Vapour emission details for an Aframax tanker crude oil loading operations, showing (a) Vapour emission rate, and (b) Total OVE, with tank filling level
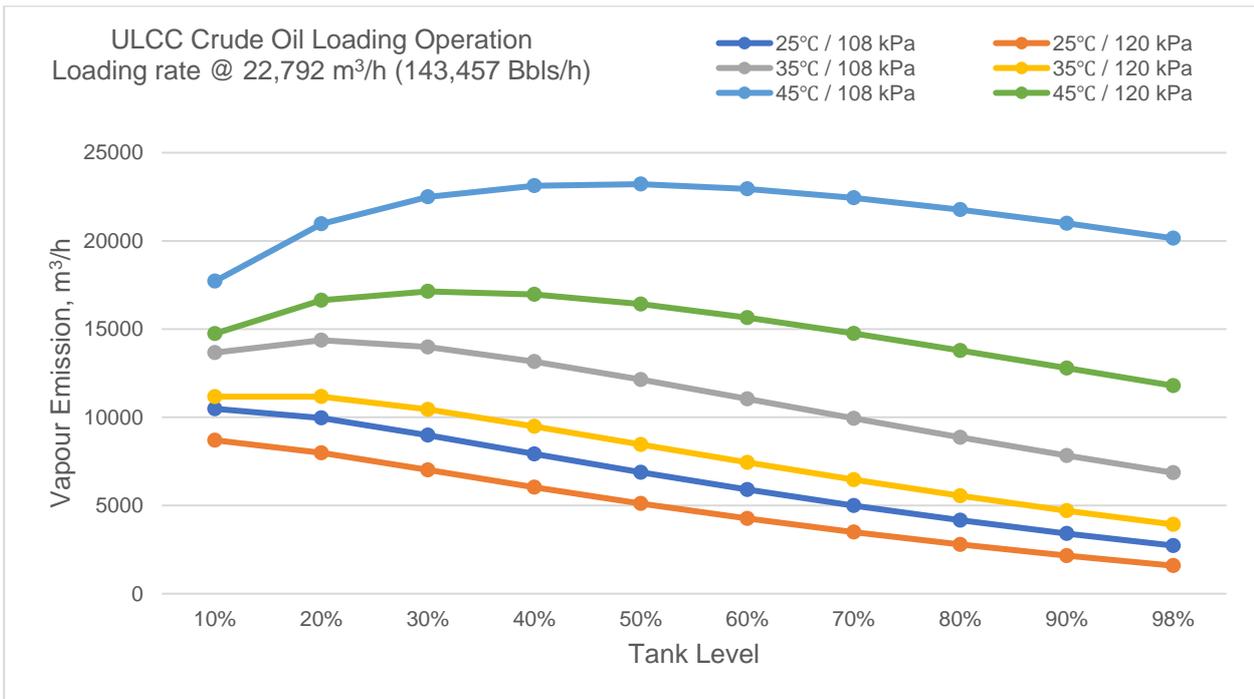
(a)
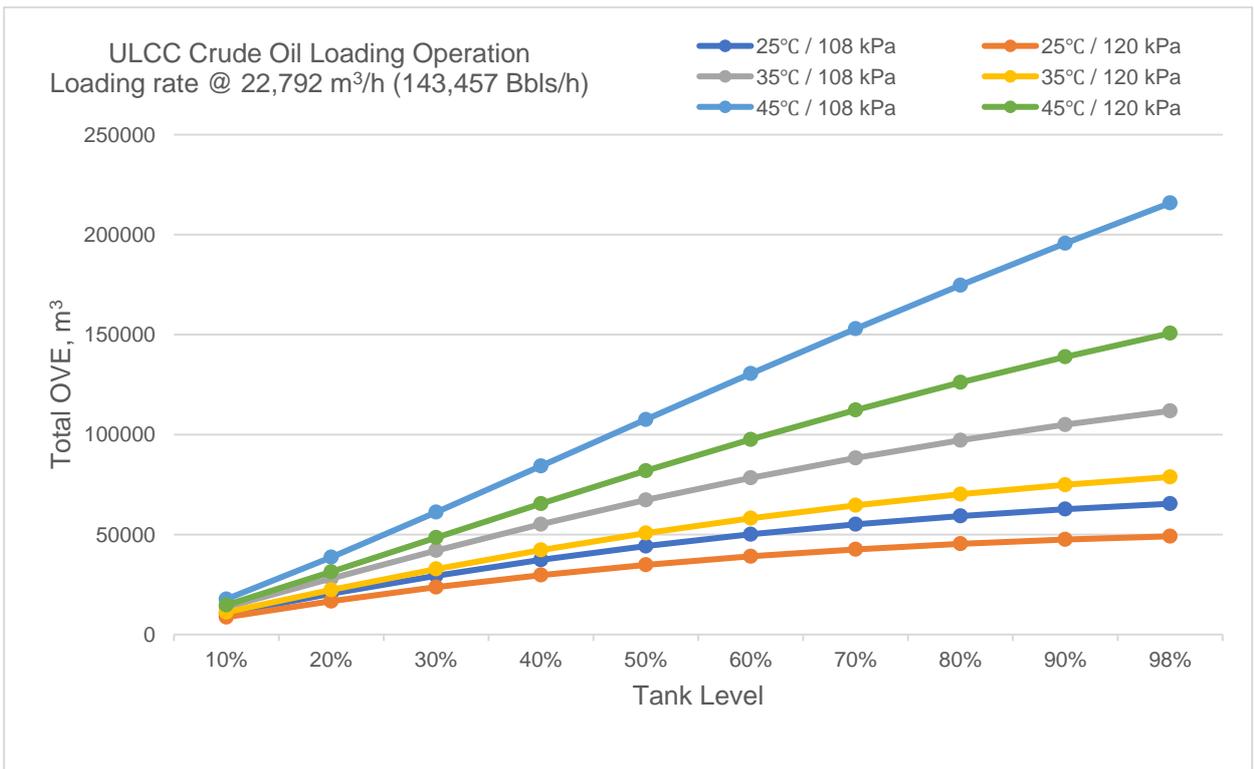
(b)

Figure 5.2 Vapour emission details for a ULCC, crude oil loading operations, showing (a) Vapour emission rate, and (b) Total OVE, with tank filling level
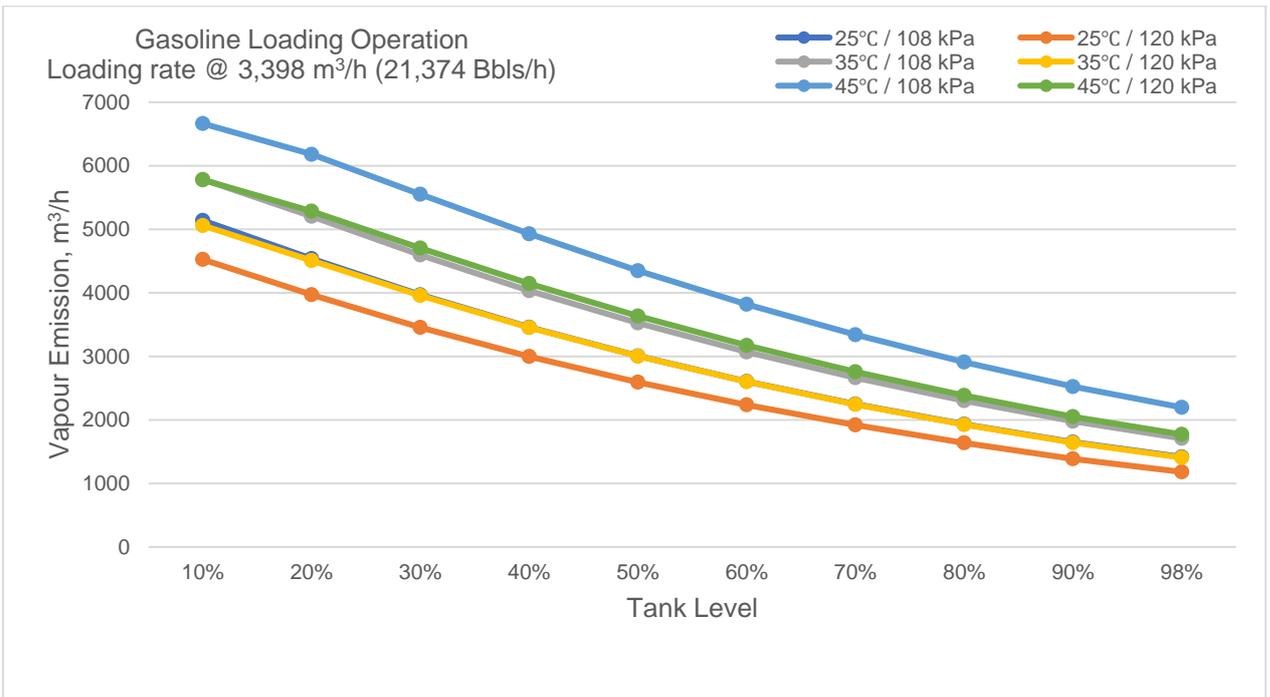
(a)
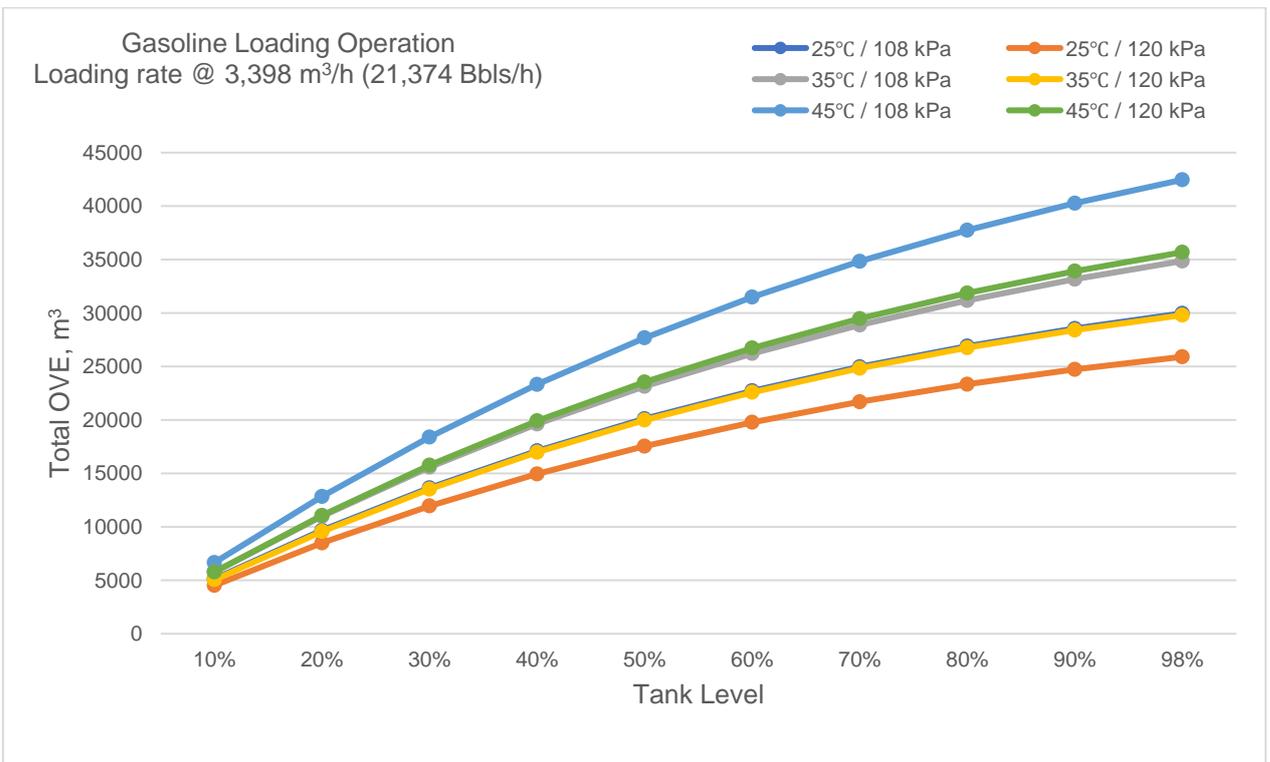
(b)

Figure 5.3 Vapour emission details for a product tanker loading gasoline, showing (a) Vapour emission rate, and (b) Total OVE, with tank filling level

Information from Figure 5.1 to Figure 5.3 is also summarised in Table 5.2.

Tanker and Loading Rate	Oil Temperature	Total OVE (m³)		Reduction in OVE due to higher tank pressure
		108 kPa	120 kPa	
Aframax 10,564 m³/h	25℃	54685	42974	21%
	35℃	83785	62751	25%
	45℃	137592	103247	25%
ULCC 22,792m³/h	25℃	65435	49135	25%
	35℃	111845	78812	30%
	45℃	215838	150679	30%
Gasoline 3,398m³/h	25℃	29967	25904	14%
	35℃	34866	29804	15%
	45℃	42463	35683	16%

Table 5.2 Total OVE on completion of loading and its reduction at 120 kPa tank pressure, compared to 108 kPa

According to data presented in Table 5.2, the vapour emission rate during crude oil loading operation in an Aframax tanker is reduced by 21% to 25% and 25% to 30% for ULCC by maintaining higher tank pressure in the cargo tanks. Similarly, a 14% to 16% reduction is noted for a gasoline loading operation in a product tanker. For an oil temperature of 25℃, at 120 kPa cargo tank pressure, the ULCC loading rate is almost twice the loading rate of an Aframax tanker, but the resulting increase in OVE is only 14% (49,135 m³ for a ULCC and 42,974 m³ for an Aframax tanker).

This showed that the OVE is significantly less in a ULCC loading operation than in an Aframax tanker and hence, selecting a giant tanker for an oil shipment can help reduce overall OVE and has less impact on air quality in loading ports.

The total amount of OVE is higher in an ULCC than an Aframax tanker as ULCC handles almost three times volume of crude oil, even though percentage evaporative loss is higher in an Aframax tanker as shown in Table 4.4. Overall higher volume loaded in a ULCC increases the overall OVE volume.

5.2 Hydrocarbon (HC) emission

For oil tanker loading operations, OVE from the oil consists of inert gas, which is also present in the tank before the commencement of loading. The total evaporated components of the oil during loading operations are known as hydrocarbon emissions.

Figure 5.4 (a), Figure 5.4 (b) and Figure 5.4 (c) show the rate of variation of hydrocarbon fraction present in the OVE for crude oil and gasoline loading operations for three tanker models at different operating conditions. For an Aframax tanker loading crude oil at 25℃, HC fraction in OVE varies from 0.46 at 10% tank level to 0.61 when the tank is 98% full, whereas the fraction varies from 0.54 to 0.76 at crude oil temperature of 35℃, and the fraction varies from 0.61 to 0.87 at crude oil temperature of 45℃. The increased fraction at higher temperatures is due to more evaporation of individual components with an increase in temperature. The same trend is observed in ULCC and gasoline loading operations.

Generally, the hydrocarbon fraction in gasoline loading (Figure 5.4 (c)) is much lower than that observed in crude oil loading operations. This may be explained by higher number of low boiling point HC components present in the crude oil, whereas gasoline has already been refined to contain only few HC components.

The results also indicate that maintaining higher tank pressure during loading operations could reduce HC emission. This is due to the higher SVP of oil vapours at the elevated tank pressure.
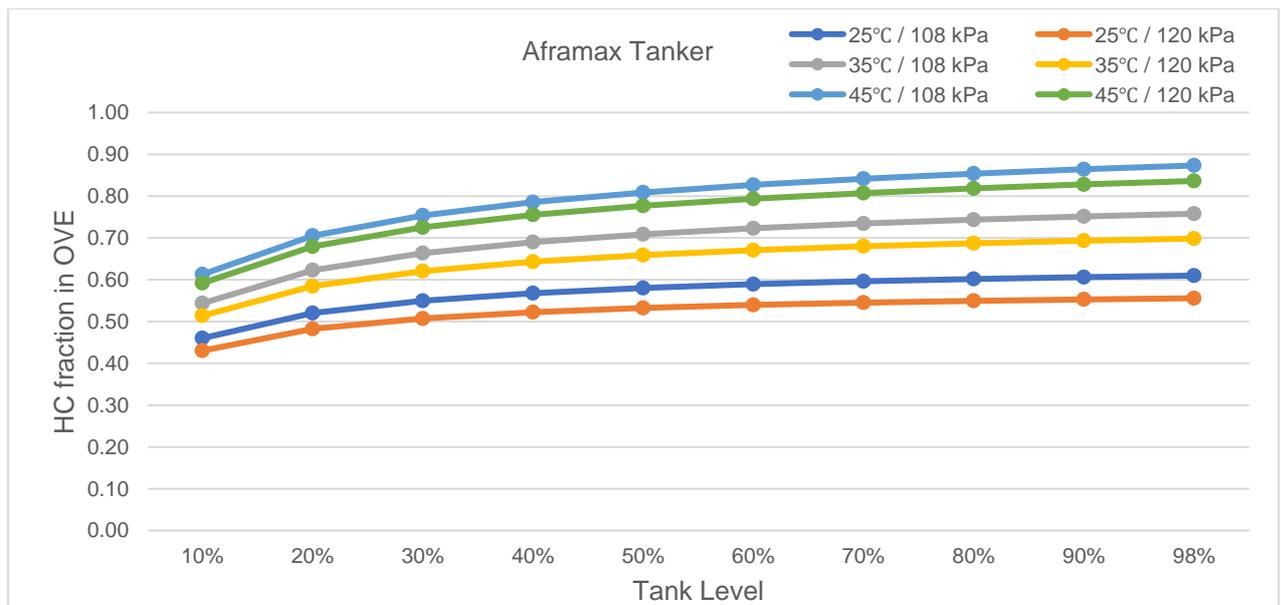
(a)
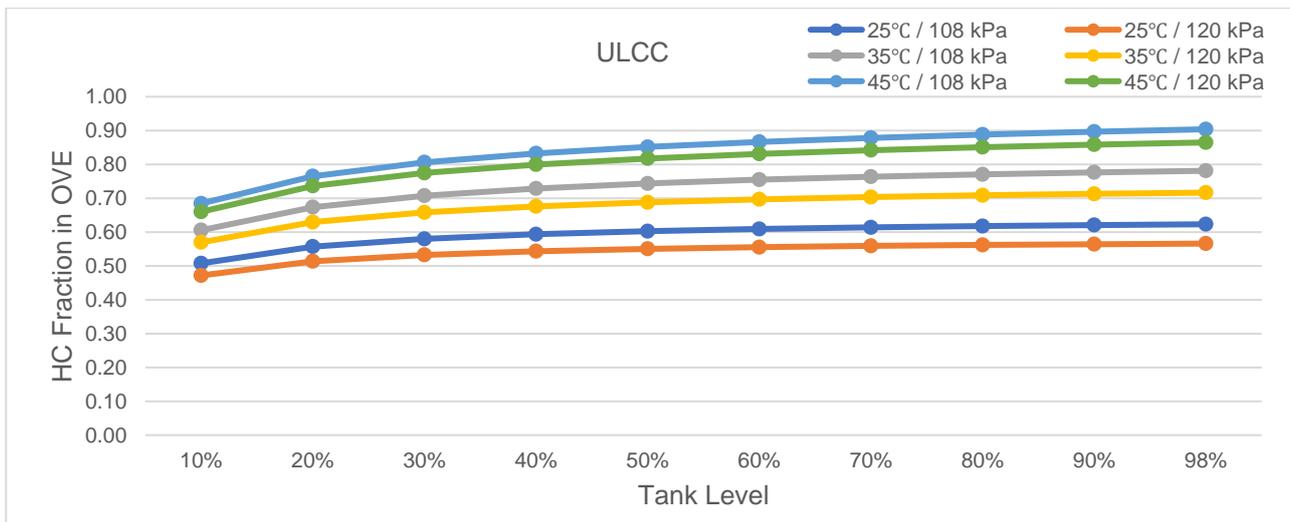
(b)
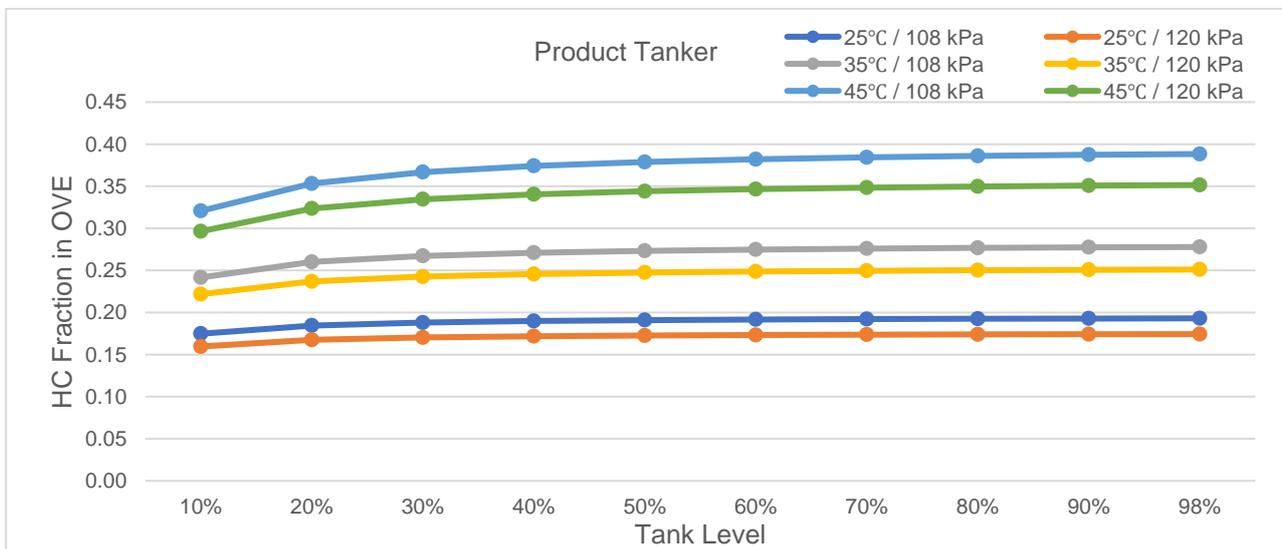
(c)

Figure 5.4 Variation in HC Fraction in total OVE for (a) an Aframax tanker loading crude oil, (b) a ULCC loading crude oil, and (c) a product tanker loading gasoline

The proportion of hydrocarbon vapours (including methane and ethane) in the total OVE can be determined via simulation, which is declared in this research as the total VOC emission (USA, 2023).

Table 5.3 and Table 5.4 summarized the data in Figure 5.4. The following observations are noted when a tank pressure of 120 kPa is used during the loading operation, the base case being maintaining a tank pressure of 108 kPa, based on the current tanker loading practice:

a) The volume of HC emitted ranges from 33,353 m^3 for crude oil at 25℃ to 120,156 m^3 at 45℃ for an Aframax tanker loading at 10,564 m3/h. For a ULCC crude oil loading rate of 22,792 m^3/h, the HC emitted ranges from 40,774 m^3 for crude oil at 25℃ to 195,085 m^3 for crude oil at 45℃, as shown in Table 5.3.

b) When the crude oil loading temperature increased from 25℃ to 35℃, HC emission increased by 114% for ULCC, whereas HC emission only increased by 40% in an Aframax tanker. In contrast, for Aframax crude oil loading operation, there is a phenomenal increase of 158% when the temperature increases from 35℃ to 45℃. whereas an increase of 123% was determined for ULCC oil loading operation under the same temperature increment. This is possibly due to a greater number of individual HC components boiling off due to elevated temperature.

c) HC fraction in total OVE is reduced by 4% to 9% for crude oil loading operation in an Aframax tanker and onboard a ULCC when loading operation is conducted at tank pressure 120 kPa, instead of 108 KPa. This is due to the higher SVP of the vapours when an elevated tank pressure of 120 kPa is maintained.

d) For a product tanker loading gasoline, the volume of HC emitted ranges from 5,786 m^3 for gasoline at 25℃ to 16,490 m^3 for gasoline at 45℃, at loading rate of 3,398 m^3/h

e) HC emission increased by 70% when the gasoline loading temperature increased from 25℃ to 35℃, whereas there was an increase of 67% when the gasoline loading temperature increased from 35℃ to 45℃, similar to the crude oil loading. This is also due to more individual HC components boiling off due to elevated temperature.

f) For a gasoline loading operation onboard a product tanker, HC fraction in total OVE is reduced by 9% to 10% for an increase in tank pressure from 108 kPa to 120 kPa.

Tanker	Oil Temperature	HC Volume emission (m³) 108 kPa	HC Fraction at 98% tank level		Reduction in HC content (%)
			108 kPa	120 kPa	
Aframax	25℃	33353 ↘ +40%	0.61	0.56	9%
	35℃	46564	0.76	0.70	8%
	45℃	120156 +158%	0.87	0.84	4%
ULCC	25℃	40774 ↘ +114%	0.62	0.57	9%
	35℃	87363	0.78	0.72	8%
	45℃	195085 +123%	0.90	0.86	4%
Gasoline	25℃	5786 +70%	0.19	0.17	10%
	35℃	9687	0.28	0.25	10%
	45℃	16490 +67%	0.39	0.35	9%

Table 5.3 HC content in total OVE on completion of loading and its reduction at 120 kPa, with respect to maintaining 108 kPa tank pressure.

The total hydrocarbon components in OVE consist of evaporated components which are paraffins, naphthenes and aromatic components, as identified from the simulation results(Lake *et al.*, 2006). The average VOC emission, described as Emission Factor (EF) in the literature, is calculated for Aframax, ULCC and product tanker loading operations. The data is presented in Table 5.4, and the results are described below:

a) For the simulation analysis, VOC emission for Aframax tanker loading operation is calculated as 0.73, 1.46, and 2.90 kg/tonne for crude oil temperature of 25℃, 35℃, and 45℃ for a tank pressure of 108 kPa. VOC emission reduces by 22 to 25% when an elevated tank pressure of 120 kPa is kept during loading. Similarly, for the simulation analysis, VOC emission for ULCC loading operation is calculated as 0.43, 0.97, and 2.29 kg/tonne for crude oil temperature of 25℃, 35℃, and 45℃ for a tank pressure of 108 kPa. VOC emission reduces by 28 to 31% when an elevated tank pressure of 120 kPa is kept during loading.

b) For gasoline loading operation in a product tanker, VOC emission for the simulation analysis is calculated as 0.37, 0.66, 1.20 kg/tonne for gasoline temperature of 25℃, 35℃, and 45℃, for a tank pressure of 108 kPa. VOC emission reduces by 15 to 18% when an elevated tank pressure of 120 kPa is kept during loading.

c) VOC emission is lower when a ULCC is used as compared to loading onboard an Aframax tanker. E.g., for an oil temperature of 25℃, at 120 kPa cargo tank pressure, the ULCC loading rate is around twice the loading rate of an Aframax tanker, but the resulting VOC emission is lower by 80% (0.31 kg/tonne for a ULCC and 0.56 kg/tonne for an Aframax tanker). Similar decrease of VOC emission by 78% and 39 % is observed for crude oil temperature at 35℃ and 45℃, respectively.

d) VOC emission increases with increase in oil temperature, e.g., VOC emission (1.46 kg/tonne) for an Aframax tanker loading crude oil at 35℃ temperature is double of the VOC emission(0.73 kg/tonne), for oil temperature at 25℃. Similar increase is also observed for other tankers. It is thus recommended that shore storage tanks should strive to keep oil temperature as low as possible. Likewise, ship's tanks should also be cooled down to minimise VOC emission.

Tanker	Oil Temperature	Average VOC emission (kg/tonne of oil loaded)		
		108 kPa	120 kPa	Reduction in VOC emission (%)
Aframax	25℃	0.73 [+100%]	0.56	22%
	35℃	1.46	1.09	25%
	45℃	2.90	2.26	22%
ULCC	25℃	0.43	0.31	28%
	35℃	0.97	0.61	31%
	45℃	2.29	1.63	29%
Gasoline	25℃	0.37	0.32	15%
	35℃	0.66	0.55	16%
	45℃	1.20	0.98	18%

Table 5.4 Average VOC emission during loading operations, and its reduction at 120 kPa, with respect to maintaining 108 kPa tank pressure.

The above analysis of the observations in Section 5.1 and Section 5.2 conclude that the following methods can minimise OVE and VOC emission:

a) Loading temperature should be as low as possible.

b) Cargo tanks onboard tankers should maintain the highest safe operating pressure as per the design during loading.

c) Choose the largest possible tanker for oil shipments.

   a)

5.3 Data validation for HC emission

The EF data are tabulated for the tanker loading operations in different countries, as per the available literature in Table 5.5 and Table 5.6, respectively (Matsumura, 1974; DeLuchi, 1993; AEAT, 2001; Deligiannis *et al.*, 2016; EEA, 2019; EPA, 2020a).

The EF values in the current study range from 0.73 to 2.90 kg/tonne for an Aframax tanker for oil temperature range from 25℃ to 45℃. EF in the available literature ranges from 0.1 kg/tonne (US EPA) to 1 kg/tonne (AEAT,UK). The EFs calculated for the ULCC case cannot be compared with any existing study as they exclude such loading rates in their information (EPA, 2020a). The EF values for the gasoline loading operation in the current study range from 0.37 kg/tonne at 25℃, 0.66 kg/tonne at 35℃, and 1.20 kg/tonne at 45℃ in a product tanker. The value in the available literature lies between 0.24 to 0.32 kg/tonne, as shown in Table 5.6.

Currently, cumulative OVE in various countries, such as the EU and USA, is estimated using generalised EF, which neither considers the nature of crude oil nor its temperature, loading rate and tank pressure. Similarly, other available data in the current literature does not provide similar details necessary to calculate the exact impact on air quality. Results obtained in the current research need further validation when data from other sources are available, or further field observations are required to validate these results.

Hansen investigated VOC emission for a crude oil loading operation on an Aframax tanker; the mass of emitted VOC was calculated as 0.20% of the loaded mass(Hansen *et al.*, 2008). However, the study does not describe the temperature of crude oil and its detailed composition. The analysis of the current simulation results for an Aframax tanker shows the amount of emitted VOCs as 0.07%, 0.15% and 0.29% for crude oil temperatures of 25℃, 35℃, and 45℃, respectively, of the loaded mass. The values obtained in the current research for the mass of emitted VOCs are in close agreement with the above study.

Otto Martens analysed loading operation in a shuttle tanker for a volatile crude oil at a temperature of 33℃, yielding HC volume fraction in the OVE between 0.15 to 0.8 (Martens *et al.*, 2001). The current simulation results for a similar temperature of 35℃ yield the HC fraction in OVE between 0.51 and 0.70 (Figure 5.4). Another study by Deligiannis *et al.* provides the HC fraction in OVE between 0.3 to 0.5 (Deligiannis *et al.*, 2016). The variation in the results is attributed to the different chemical compositions of the crude oil, which is not provided in this paper.

Tamaddoni *et al.* analysed the effect of temperature and pressure on OVE in a tanker loading operation(Tamaddoni *et al.*, 2014). Their observation and simulation data of the current study show that the higher temperature of crude oil has higher OVE, and maintaining higher tank pressure reduces the OVE, as shown in table results in Figure 5.1 to Figure 5.3, and Table 5.2.

Above analysis of related work concludes that the results obtained by the simulation methodology used in this research are in close agreement with their experimental or field observations. The variations in the results are mainly attributed to lack of sufficient data which could have helped to do better validation of the results. It is suggested that actual chemical composition analysis of a particular oil, together with the field observations of the loading operation of the same oil, be conducted further to validate the methodology.

Petroleum commodity	Reference	EF value / VOC emission				Remarks
Crude Oil	Current simulation on the crude oil					EF is based on the following data:
		EF (kg/tonne)				The chemical composition is described in Chapter 3, Section 3.3, table 3.7.
		Tanker	Oil Temp.	Tank Pressure (kPa)		Crude Oil Density 830.3 kg/m^3
				108	120	Gasoline density = 752.7kg/m^3
		Aframax	25℃	0.73	0.56	Loading rate for Aframax tanker = 10,564 m^3/h
			35℃	1.46	1.09	Loading rate for ULCC = 22,792 m^3/h
			45℃	2.90	2.26	Loading rate for gasoline = 3,398 m^3/h
		ULCC	25℃	0.43	0.31	The temperature of oil and cargo tank pressure, as mentioned
			35℃	0.97	0.61	
			45℃	2.29	1.63	
		Gasoline	25℃	0.37	0.32	
			35℃	0.66	0.55	EF includes Methane.
			45℃	1.20	0.98	
	EEA	No data quoted				Due to limited loading operations in the EU.
	EPA USA	73 mg/L (0.10 kg/tonne)				Basis Crude Oil Density 0.83 tonne/m^3, 73 mg/L = 0.10 kg/tonne
						Excludes Methane and Ethane in OVE.
						It does not account for the nature of oil, loading rate and tank pressure.

EI Hydrocarbon Management HM65	73 mg/L (0.10 kg/tonne)	Basis Crude Oil Density 0.83 tonne/m^3, 73 mg/L = 0.10 kg/tonne Excludes Methane and Ethane in OVE. It does not account for the nature of oil, loading rate and tank pressure.
Matsumara report	0.12 kg/kL (0.14 kg/tonne)	Vapour temperature 30℃ Basis Crude Oil Density 0.83 tonne/m^3, 0.12 kg/kL = 0.14 kg/tonne It does not account for the nature of oil, loading rate and tank pressure.
DeLuchi	292 mg/L for Alaskan crude (0.35 kg/tonne) 73 mg/L for Lower 48 crude oil (0.10 kg/tonne)	Basis Crude Oil Density 0.83 tonne/m^3, 292 mg/L = 0.35 kg/tonne, 73 mg/L = 0.10 kg/tonne Excludes Methane and Ethane in OVE It does not account for the nature of oil, loading rate and tank pressure.

	EU AEAT report	1 kg(emitted)/tonne (loaded)	It does not account for the nature of oil, loading rate and tank pressure.
	Deligiannis report	Arabian Heavy Crude oil 0.07 kg/tonne loaded @ 40℃ Arabian Medium Crude oil 0.24 kg/tonne loaded@ 29℃ Arabian Super light Crude oil 0.32 kg/tonne loaded@ 42℃	Data is for different crude oil at different temperatures. The detailed composition of crude oil is not described.
Gasoline	EEA	4 g/m^3 throughput/kPa TVP (0.24 kg/tonne)	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne It does not account for the nature of oil, loading rate and tank pressure.
	EPA USA	180 mg/L (0.24 kg/tonne)	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne

			It does not account for the nature of oil, loading rate and tank pressure.
	EI Hydrocarbon Management HM65	180 mg/L (0.24 kg/tonne)	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 180 mg/L = 0.24 kg/tonne It does not account for the nature of oil, loading rate and tank pressure.
	Matsumara report	0.19 kg/kL ().25 kg/tonne)	Vapour temperature 30℃ Basis Gasoline density 0.76 tonne/m^3 0.19 kg/kL = 0.25 kg/tonne It does not account for the nature of oil, loading rate and tank pressure.
	DeLuchi	240 mg/L ().32 kg/tonne)	Excludes Methane and Ethane in OVE Basis Gasoline density 0.76 tonne/m^3 240 mg/L = 0.32 kg/tonne

			It does not account for the nature of oil, loading rate and tank pressure.
	EU AEAT report	0.24 kg(emitted)/tonne (loaded)	The temperature range used varies from 3℃ to 25℃ RVP ranges from 50 to 90 kPa The molecular weight of vapours is 62 to 68 It does not account for the nature of oil, loading rate and tank pressure.
	Deligiannis report	Condensate EF 0.76 kg/tonne loaded@ 30℃	Data is for condensate, which has a similar API as Gasoline. It does not account for the nature of oil, loading rate and tank pressure.

Table 5.5 EF Values from the current study and other available literature for crude oil and gasoline loading

Source	EF values (kg/tonne)		Remarks
	Crude Oil	Gasoline	
Current Research	Aframax Tanker: 0.73 to 2.90 ULCC: 0.43 to 2.29	0.37 to 1.20	Data is for temperature of oil between 25℃ to 45℃, for tank pressure maintained between 108 kPa to 120 kPa, and specific flow rate, for a specific composition of oil.
US EPA	0.10	0.24	Exclude Methane emission
EEA EU	Nil	0.24	
EI (EU)	0.10	0.24	
Matsumara research, Japan	0.14	0.25	Crude oil temperature 30℃
DeLuchi USA	0.35 and 0.10 for two types of crude oil	0.32	
EU AEAT Report	1	0.24	
Deliggianis Research	0.07, 0.24, 0.32 for three different crude oils		

Table 5.6 Summary of EF Values from the current study and other available literature for gasoline loading

5.4 Proposed amendments to ship design and working practices to minimise or stop VOC emission to preserve air quality

The oil tanker design and working procedures to load oil tankers need modifications compared to the current situation to achieve the common purpose of maintaining air quality in tanker loading ports. This section will describe the proposed amendments to tanker design and loading practices to minimise or stop OVE and hence VOC emission.

5.4.1 Amendments to tanker design to minimise or stop OVE/VOC emission

a) As OVE emission tends to be lower when higher tank pressure is maintained, it is proposed to operate all oil tankers with elevated tank pressure of 120 kPa. This can be achieved in the current tanker designs without incurring any additional strengthening of cargo tanks, as the maximum design pressure of a cargo tank is at least 2500 mm WG (125 kPa)(MEPC.1/Circ.680, 2009). Some oil tankers use a VOCON valve to keep tank pressure as high as possible during tanker loading operation, which reduces OVE but is insufficient to stop OVE.

b) All oil tankers should be mandated to be fitted with either KVOC or CVOC system to minimise VOC emission during tanker loading operations, as described in Chapter 4, Sub-section 4.4.1.

c) OVE increases with an increase in oil temperature. The current designs fully expose the tank top to direct sunlight, potentially increasing the tank temperature and OVE and VOC emissions. Cargo tanks onboard oil tankers should be constructed with double top sides to reduce the heat convection rate from the sun. Alternatively, the tanks should either be painted with light shade colour to reduce the absorption of heat or fitted with a seawater spray system to keep the deck temperature least during the loading operation.

d) Each tanker loading terminal must provide a vapour return line as a mandatory requirement, per VECS guidelines (MSC/Circ.585, 1992). This will capture all the OVE, which the higher tank pressure and radiation effect of sunlight could not control.

e) Oil tankers shall be fitted with VOC Recovery Equipment as mandatory under the SOLAS convention. VOC Recovery Equipment operating on condensation and absorption systems has been fitted on certain crude oil tankers to enhance operation efficiency and preserve air quality (Martens *et al.*, 2001; MEPC.1/Circ.680, 2009).

f) All oil tankers should be fitted with an in-line sampling system where it is possible to collect oil samples as per charter party clauses, on completion of loading, without needing to de-pressurise tanks by venting oil vapours to the atmosphere.

g) Oil tankers should be fitted with an independently verified remote tank gauging system to record tank ullage and temperature as per the charter party. The Custody Transfer and Measurement System (CTMS), as used in Liquefied Gas Tankers, may be referred to for such purpose.

h) The oil shipment should be carried out by employing as large a tanker as possible, as the average VOC emission for a ULCC is observed to be lower than that of an Aframax tanker (Table 5.4).

5.4.2 Amendments to tanker loading practices to minimise or stop OVE/VOC emission

a) Oil tanker loading terminals should supply oil shipments at as low a temperature as possible. Oil tanks at tanker terminals should be painted with the most negligible heat-absorbing properties to maintain the lowest oil temperature.

b) The oil tanker loading rate should be analysed in detail to propose the optimum loading rate for the least rate of OVE. It will require a detailed tanker terminal pipeline layout analysis and process simulation software to calculate the optimum loading rate in case VECS system is not provided.

c) In the current practice, oil tanks must be brought to the lowest pressure to facilitate local ullage measurement and oil sampling. It is proposed to stop this practice as this involves releasing a large amount of oil vapours into the atmosphere on completion of loading. Oil samples should be collected via an in-line sampling system, as oil tankers shall maintain as high a tank pressure as possible, proposed to be 120 kPa.

d) Before and after loading operations, tank gauging should be verified by a remote ullaging system, which should be acceptable by all concerned parties, such as the shipper, consignee, or any other party, as this practice will stop any OVE during tank inspection by local portable ullage and temperature measuring devices.

5.5 Conclusion

Simulation data can show that OVE increases as the temperature of oil increases and decreases when higher cargo tank pressure is maintained during tanker loading operations. OVE can be reduced by adopting a working practice of maintaining

elevated tank pressure of 120 kPa instead of the current practice of 108 kPa. This practice will safeguard the marine personnel from the local air pollution due to this OVE from loading operations.

Process Safety Simulation software can quantify total OVE for consecutive loading operations in a tanker loading port with multiple loading berths. Cumulative OVE for the port can be considered as a concentrated point source of emission affecting regional air quality.

HC emission is reduced by 4% to 9% for crude oil loading operations and 9% to 10% for a gasoline loading operation when the oil temperature is between 25℃ to 45℃ by operating at higher cargo tank pressure of 120 kPa.

The Emission Factor (EF) values obtained in this research have been used in Aspen HYSYS software to determine the exact composition of OVE for crude oil and gasoline loading, by using specific loading rate, oil temperature and tank pressure, of specific crude oil and gasoline sample. This method is expected to be more accurate than other methods for calculating VOC emissions, and it is not constrained by API gravity (Environment, 2006). However, the current practice of using generalised EFs by various agencies worldwide has the inherent limitation such as not considering the chemical composition of the oil, tank pressure and oil temperature. Hence it may not be suitable to use for estimating the exact impact of OVE on air quality.

In terms of effectiveness to minimise or stop OVE and hence VOC emission, the following are recommended to be adopted:

a) A vapour return line is to be provided at each tanker loading terminal, as per VECS guidelines, which is the most effective way to minimise or stop OVE and VOC emissions.

b) SOLAS regulations for the design of oil tankers are to be amended to minimise VOC emission, as per below:

    i.   Provide a 'Vapour recovery system' as mandatory equipment for each oil tanker that must be used if oil terminals do not offer a vapour return line. The systems should have acceptable VOC emission reduction targets of 80 to 100% as per realistic industry practice.

    ii.   Provide a KVOC or a CVOC system to reduce VOC emission during oil tanker loading.

iii. Provide each cargo tank with P-V valves of at least 120 kPa pressure relief setting.

iv. Provide a remote tank gauging system onboard oil tanker, capable of being used for commercial purposes to enable accurate readings.

v. Provide an In-line oil sampling system for oil sampling.

In addition, oil shipment should be done in tankers with higher loading rates, such as ULCCs due to their lower VOC emission during crude oil loading operations.

Chapter 6. Qualitative analysis of VOC emission

Tanker loading operations release a large amount of oil vapours, which contain a large proportion of hydrocarbon components. These hydrocarbon components, known as Volatile Organic Compounds (VOCs), harm human health and air quality. This chapter provides details on the toxic components present in this VOC emission.

6.1 Analysis of the composition of OVE

Chapter 5 provided the details on OVE and HC volume in this emission for crude oil loading in an Aframax tanker and a ULCC and gasoline loading in a product tanker. The results are obtained from the simulation of the crude oil and gasoline loading operation using Aspen HYSYS chemical process simulator as shown in Table 6.1.

Tanker and Loading Rate	Oil Temperature	HC Fraction at 98% tank level @ tank pressure:		Reduction in HC content (%)
		108 kPa	120 kPa	
Aframax 10,564 m^3/h	25℃	0.61	0.56	9%
	35℃	0.76	0.70	8%
	45℃	0.87	0.84	4%
ULCC 22,792m^3/h	25℃	0.62	0.57	9%
	35℃	0.78	0.72	8%
	45℃	0.90	0.86	4%
Gasoline 3,398m^3/h	25℃	0.19	0.17	10%
	35℃	0.28	0.25	9%
	45℃	0.39	0.35	9%

Table 6.1 HC content in total OVE on completion of loading and its reduction at 120 kPa, with respect to maintaining 108 kPa tank pressure.

For an Aframax tanker, loading crude oil at 25℃, maintaining 108kPa cargo tank pressure, it is observed that 61% of the total OVE contains VOCs on completion of

loading. For a higher temperature of crude oil at 35℃ and 45℃, the percentage of OVE containing VOCs is 76% and 87%, respectively.

Similarly, the percentage of OVE containing VOCs for a ULCC loading is 62%, 78% and 89% for crude oil at 25℃, 35℃ and 45℃, respectively, for a tank pressure at 108 kPa.

For gasoline loading operations, the percentage of OVE containing VOCs is 19%, 28% and 39% for gasoline at 25℃, 35℃ and 45℃, respectively, for a tank pressure at 108 kPa.

The lower value for gasoline can be explained by the fact that gasoline has already been processed at the refinery, which does not contain many other volatile components as in crude oil. Nevertheless, the data indicates a significant percentage of VOCs in total OVE, which can potentially affect the air quality and health of seafarers onboard tankers.

The average value of VOC emission per tonne of crude oil and gasoline loaded is shown in Table 6.2, to elaborate on the toxicity potential of the VOC emission. (Note: The simulation results for the average value of VOC emission are also shown in Chapter 5, Table 5.4, for the impact on air quality). The same data is analysed here for assessing impact on human health. For a cargo tank pressure at 108 kPa, the VOC emission values for an Aframax tanker and a ULCC crude oil loading operation, was found to fall in the range between 0.43 kg/tonne to 2.90 kg/tonne for crude oil temperature between 25℃ to 45℃ respectively. For a gasoline loading operation at the similar tank pressure and temperature range, , the VOC emission values are range from 0.37 kg/tonne to 1.20 kg/tonne. This data shows that crude oil and gasoline loading can act as an intermittent source of VOC emission onboard tankers as well as in a tanker loading port. The VOC emission contains toxic components which have been shown to affect human health in numerous studies related to emission from petroleum refineries and tanker loading terminals(ATDSR, 1995; Sólnes, 2000; Kalabokas, 2001; Cetin *et al.*, 2003; Villasenor, 2003; Lin *et al.*, 2004; Paulauskiene *et al.*, 2009; Quality, 2012; Claxton, 2014b; Viana *et al.*, 2014; Wei *et al.*, 2014; Yin *et al.*, 2015; Li *et al.*, 2017; Milazzo *et al.*, 2017; Rajabi *et al.*, 2020; Polvara *et al.*, 2021; Virdi *et al.*, 2021). Thus, it is imperative that toxic VOC released in the environment due to tanker loading and ship bunkering operations be analysed in detail to understand their impact on air quality and human health.

Tanker and Loading Rate	Oil Temperature	Average VOC emission (kg/tonne of oil loaded) @ tank pressure:		Reduction in Average VOC emission (%)
		108 kPa	120 kPa	
Aframax 10,564 m^3/h	25℃	0.73	0.56	22%
	35℃	1.46	1.09	25%
	45℃	2.90	2.26	22%
ULCC 22,792m^3/h	25℃	0.43	0.31	28%
	35℃	0.97	0.61	31%
	45℃	2.29	1.63	29%
Gasoline 3,398m^3/h	25℃	0.37	0.32	15%
	35℃	0.66	0.55	16%
	45℃	1.20	0.98	18%

Table 6.2 Average VOC emission during loading operations, and its reduction at 120 kPa, with respect to maintaining 108 kPa tank pressure.

The VOC emission is further analysed to identify potential toxic components.

6.2 Identification of toxic VOCs

Total OVE for crude oil and gasoline loading operation, oil temperature and cargo tank pressure for specific loading rate are used in the Aspen HYSYS chemical process simulator. Simulation data can provide mole fraction of individual hydrocarbon components as shown in Figure 6.1 to Figure 6.3.

In a study conducted by Claxton (2014), it was reported that aromatic hydrocarbons makeup 25 to 35% of gasoline by volume and can provide much of a gasoline's energy content; the toxicity of this fraction is a concern. E.g., Benzene is limited to 1% or less by volume because Benzene is a known carcinogen.

In USA federal regulation, EPA regulates 'Hazardous Air Pollutants' (HAPs) through 'National Emission Standards for Hazardous Air Pollutants (NESHAP), authorized under Title III of the Clean Air Act (CAA). Many VOCs are HAPs and hence potentially subject to NESHAP. The most significant VOC emission sources in crude oil and gasoline production emit both hazardous and non-hazardous VOCs. However, since

the hazardous VOCs typically cannot be controlled separately from the non-hazardous VOCs, NESHAP which applied g to HAPs from a given source applies to all VOCs from the source (DeLuchi, 1993). As marine tanker loading operation is identified as an industrial source category evaluated in risk and technology review, there are specific regulations to monitor VOC emission from marine terminals during crude oil and gasoline loading operations, specified in US Federal Register under 40 CFR Part 63(EPA, 2020e; EPA, 2022). HAPs identified by EPA include Benzene, Toluene, Ethyl benzene, Xylene, and Hexane (EPA, 2023).

The American Petroleum Institute (API) crude oil category assessment report describes occupational exposure. The individual constituents of crude oil volatilize by their unique physical-chemical properties. One of the two primary inhalations is from the VOCs similar to gasoline which can readily volatilize from crude oil, the other being from hydrogen sulphide. There are enforceable OSHA Permissible Exposure Limits (PEL) and recommended ACGIH Threshold Limit Values (TLV) occupational exposure standards for numerous volatile constituents typically found in crude oil (API, 2011). This is clear evidence that personnel working near areas where crude oil is being handled and the resulting OVE needs to be monitored for safe exposure, which is currently lacking for marine personnel. Examples of the PEL and TLV as per OSHA and ACGIH are shown in Table 6.3.

Component in crude oil		OSHA PEL (ppm)	ACGIH TLV (ppm)
C_4			1000
			1000
C_5	Pentane	500	600
C_6	Benzene	1	1
	Hexane	500	50
	Cyclohexane	300	100
C_7	Toluene	200	20
C_8	Ethyl Benzene	100	100
	Xylenes	100	100
C_9	Cumene	50	50
	Trimethyl Benzene		25
Others	Hydrogen Sulphide	2 mg/m^3	1
	Methyl mercaptan		0.5
	Gasoline		300

Table 6.3 OSHA and ACGIH Occupational Exposure Standards

Based on the literature review related to VOCs affecting air quality and human health, the research focuses on the following VOCs (Kalabokas, 2001; Cetin *et al.*, 2003; Lin *et al.*, 2004; Liu *et al.*, 2008; Claxton, 2014b; Milazzo *et al.*, 2017; Rajabi *et al.*, 2020):

a) Paraffin: Lighter hydrocarbons from Methane C_1 up to Heptane (C_7), Components from Octane (C_8) and above are not considered as their share in overall emission is found to be very negligible, possibly due to their high boiling point.

b) Naphthene: Cyclo-pentane, Cyclo-hexane, Methyl-cyclopentane

c) Aromatic: Benzene, Toluene, Ethyl benzene, and Xylene

The Aspen HYSYS data for OVE provides detailed composition of all the individual compounds in this emission. The inert gas components are removed to find the mole fraction of all the HC components, which are further analysed to identify VOCs. The compounds containing toxic VOCs, identified as per the above literature review, are analysed, and the results are shown in Figures 6.1 to 6.3.

Aframax Tanker, Loading Rate 10,564 m^3/h, Crude oil temperature @ 25°C
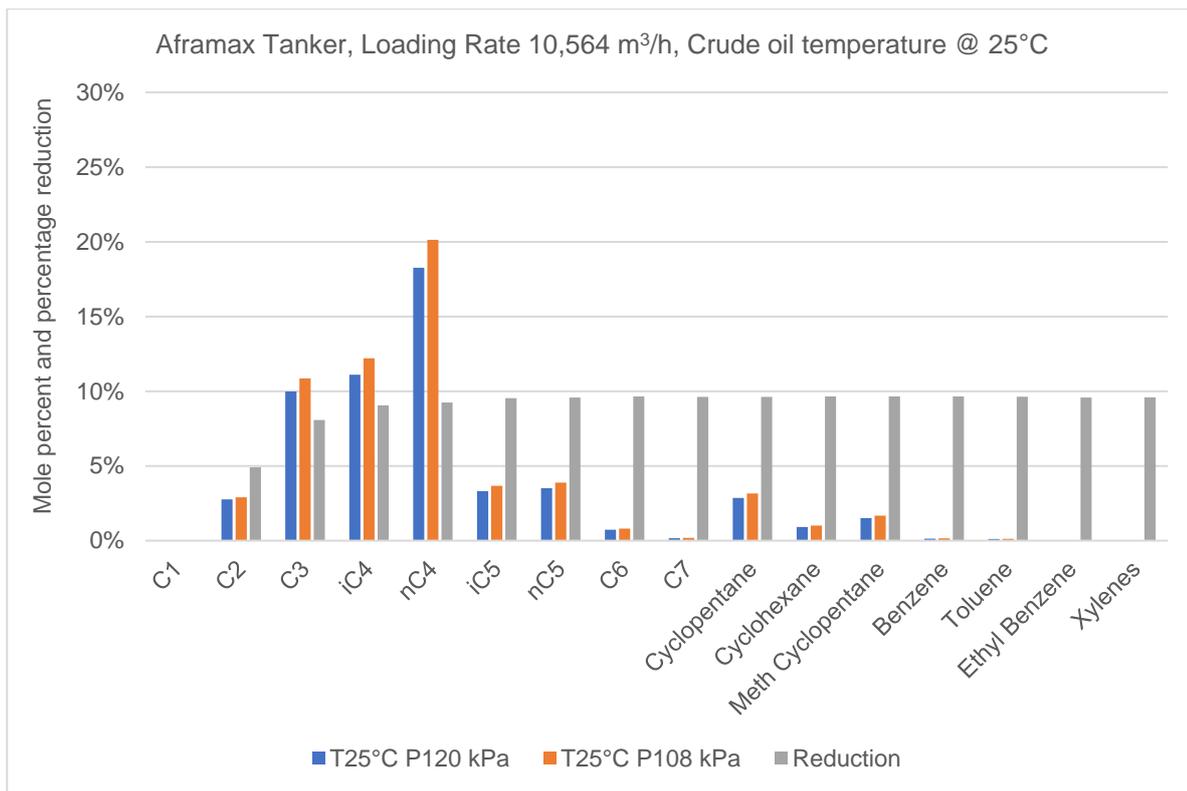
(a)
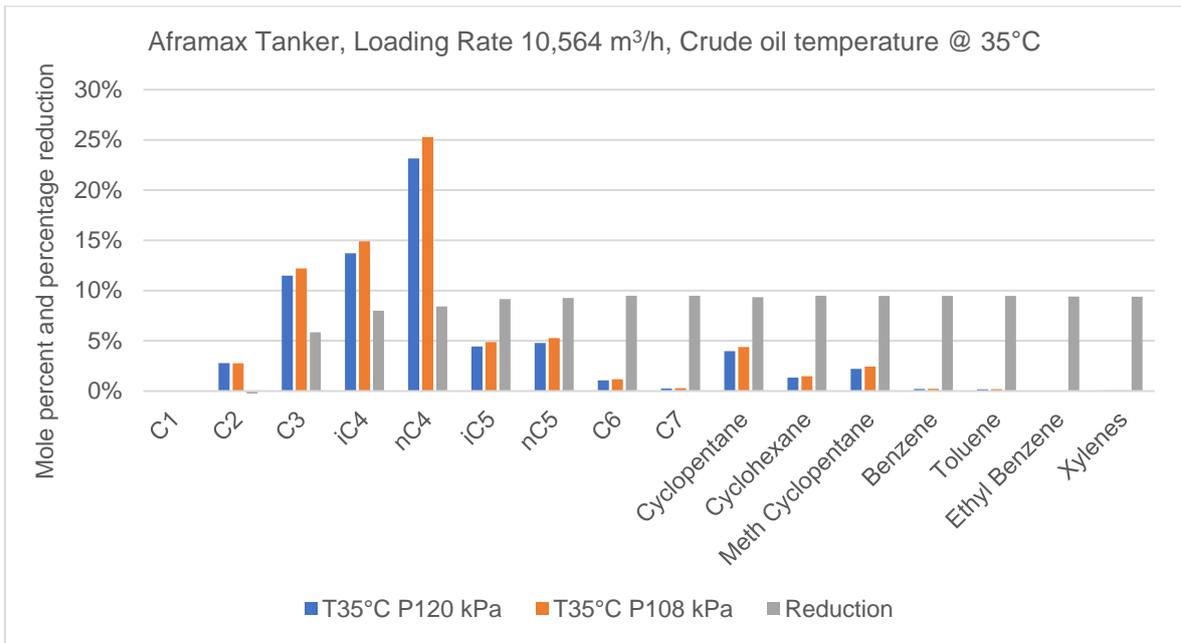
(b)
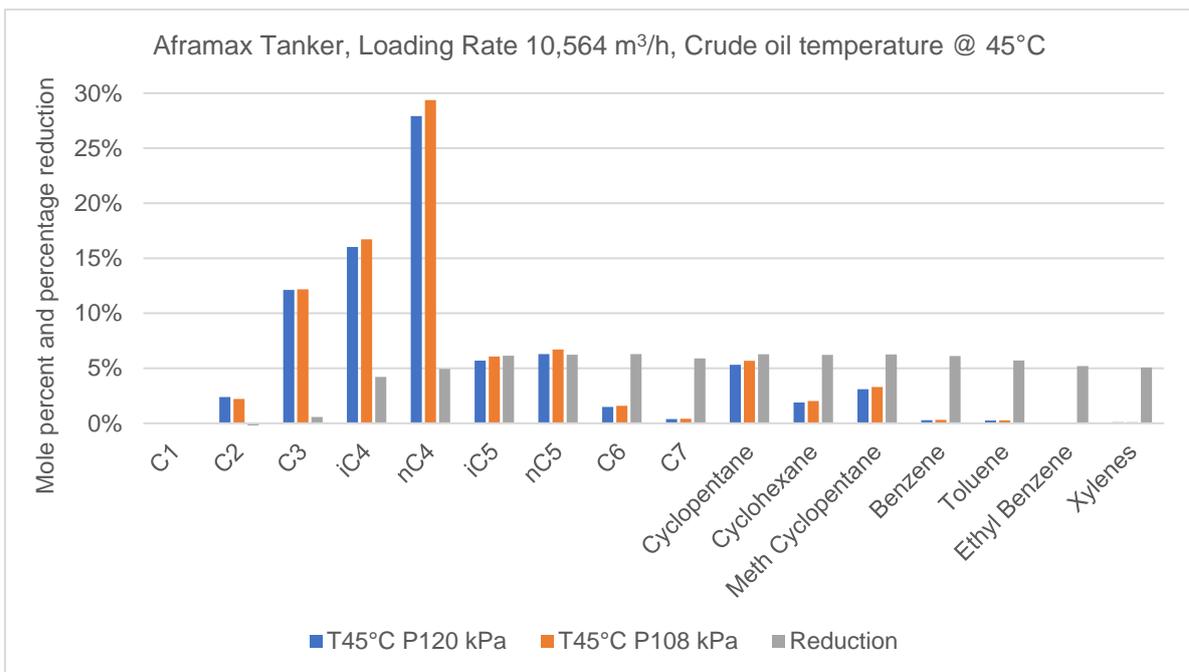
(c)

Figure 6.1 Mole percentage of individual VOCs in OVE, and corresponding reduction due to higher pressure, on completion of crude oil loading in an Aframax tanker, for crude oil temperature at (a) 25°C (b) 35°C, and (c) 45°C
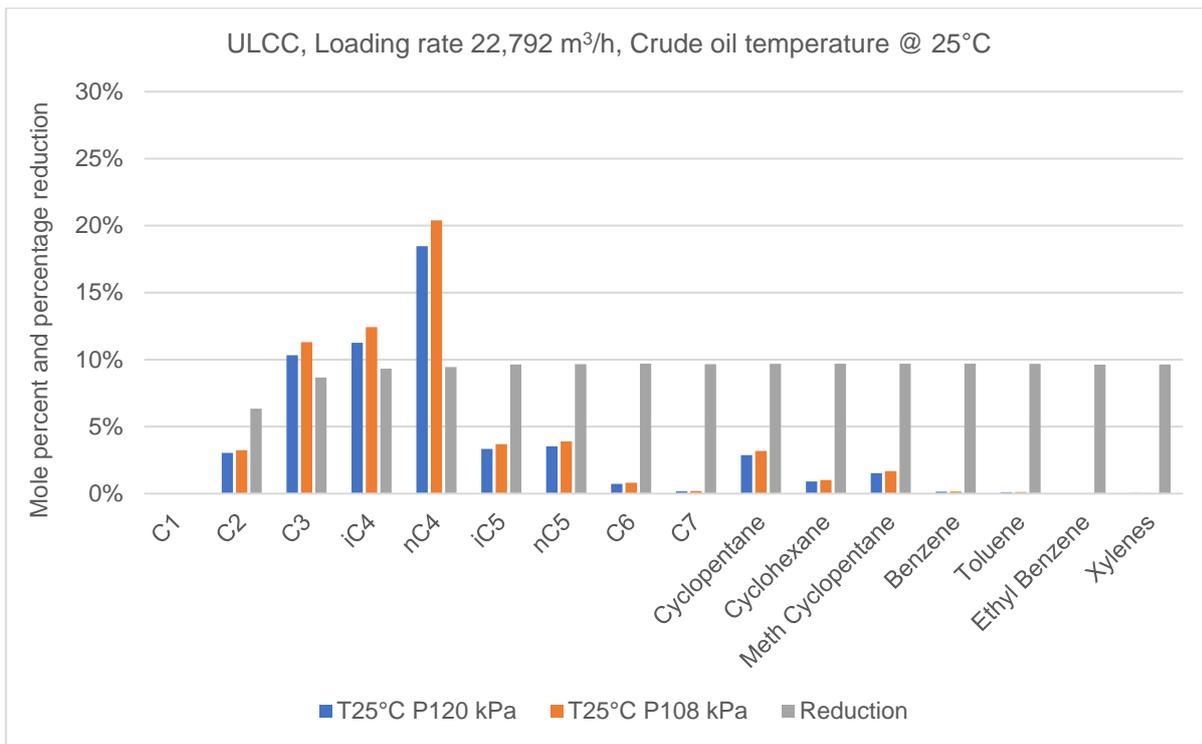
(a)
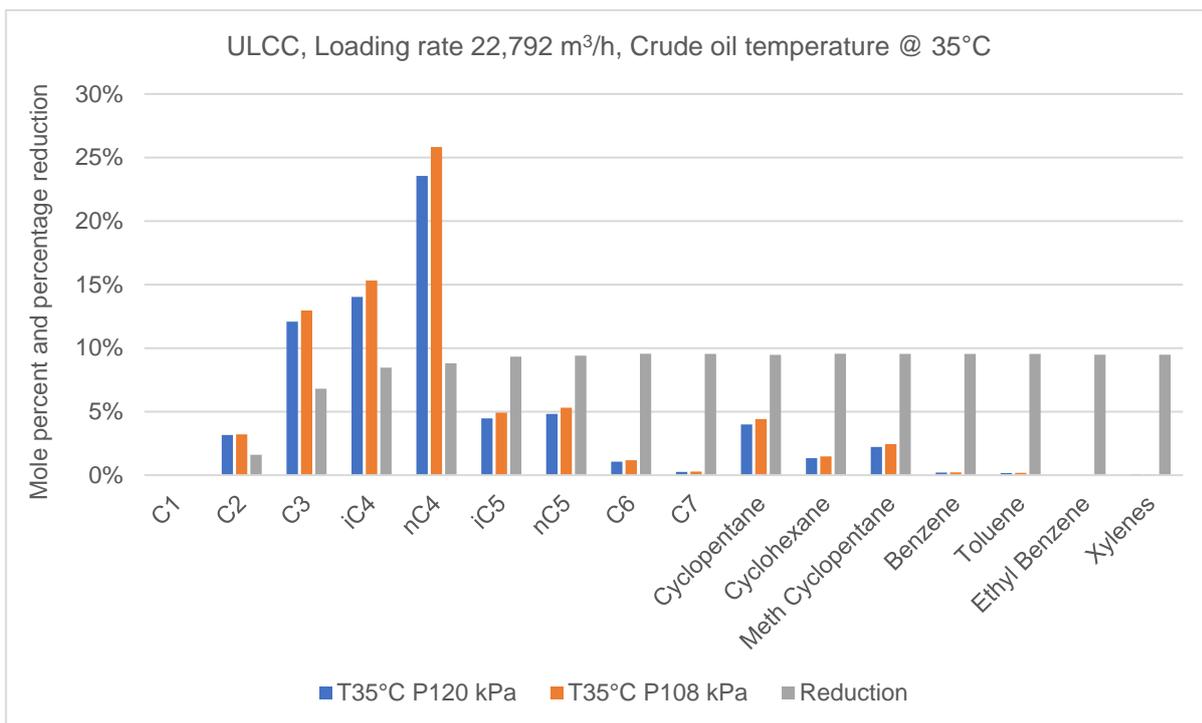
(b)
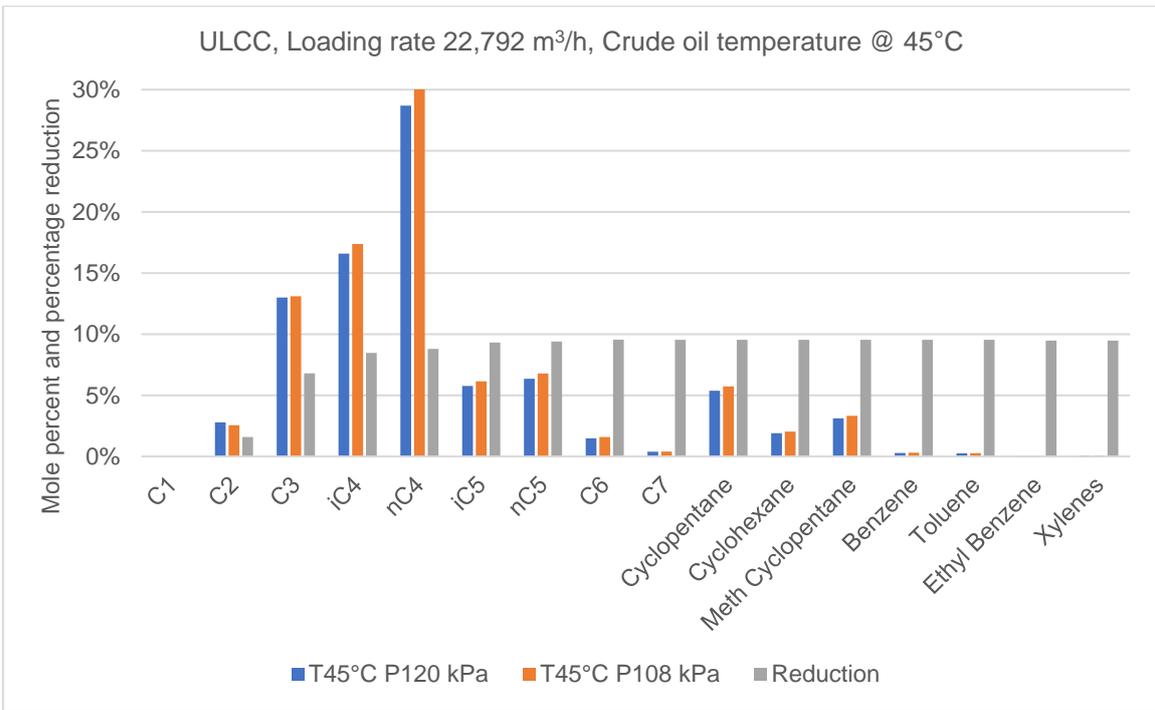
(c)

Figure 6.2 Mole percentage of individual VOCs in OVE, and corresponding reduction due to higher pressure, on completion of crude oil loading in a ULCC, for crude oil temperature at (a) 25°C (b) 35°C, and (c) 45°C

(a)

Product tanker, Loading rate 3,398 m³/h, Gasoline temperature @ 35°C

(b)

Product tanker, Loading rate 3,398 m³/h, Gasoline temperature @ 45°C
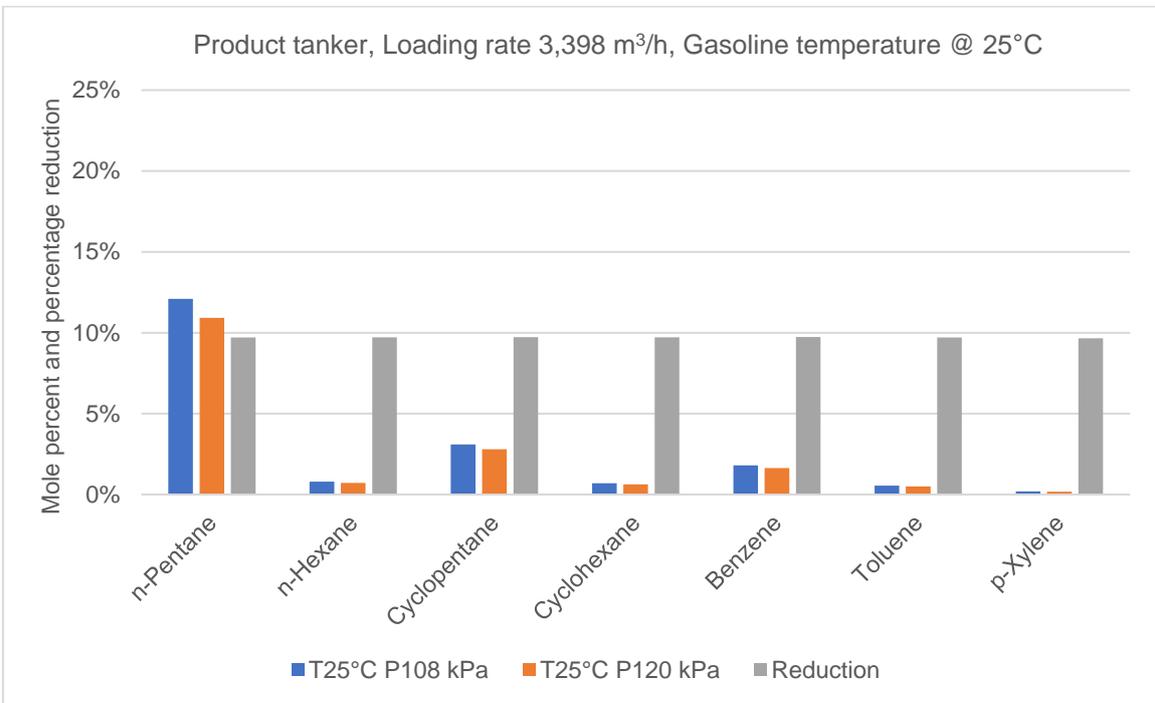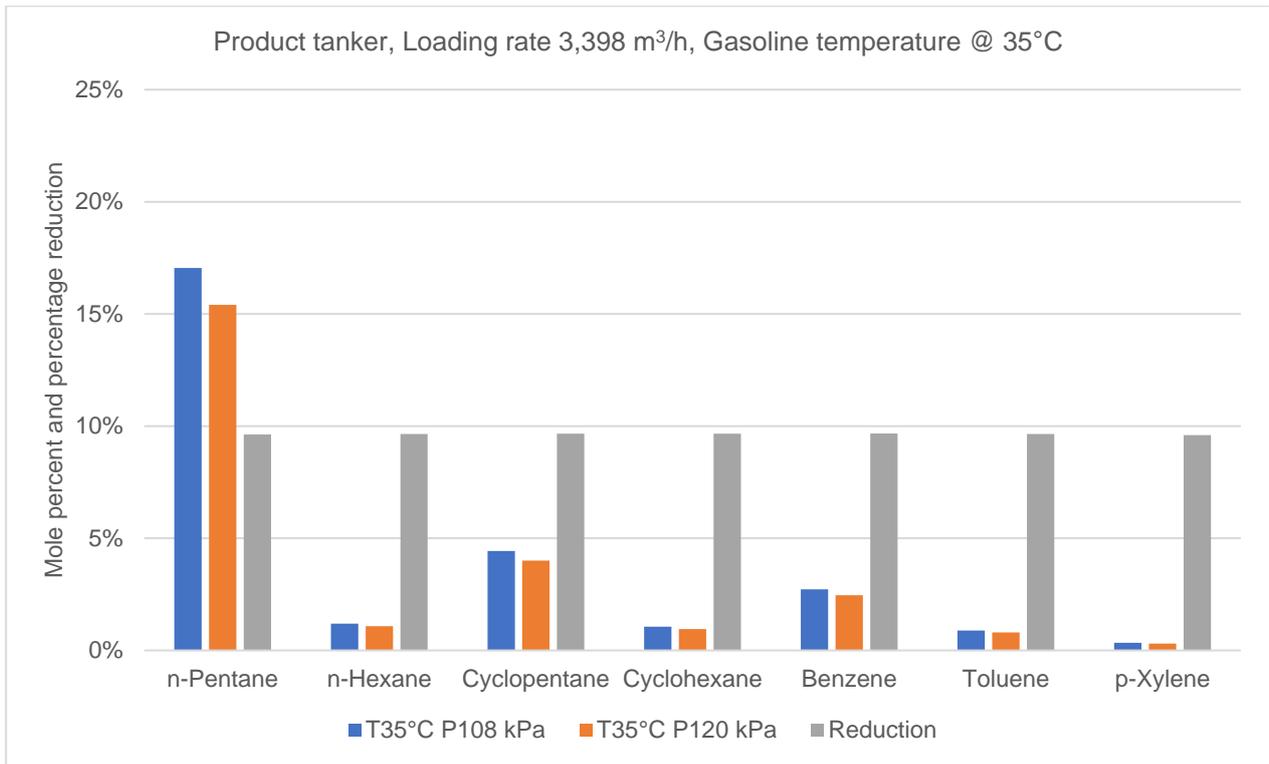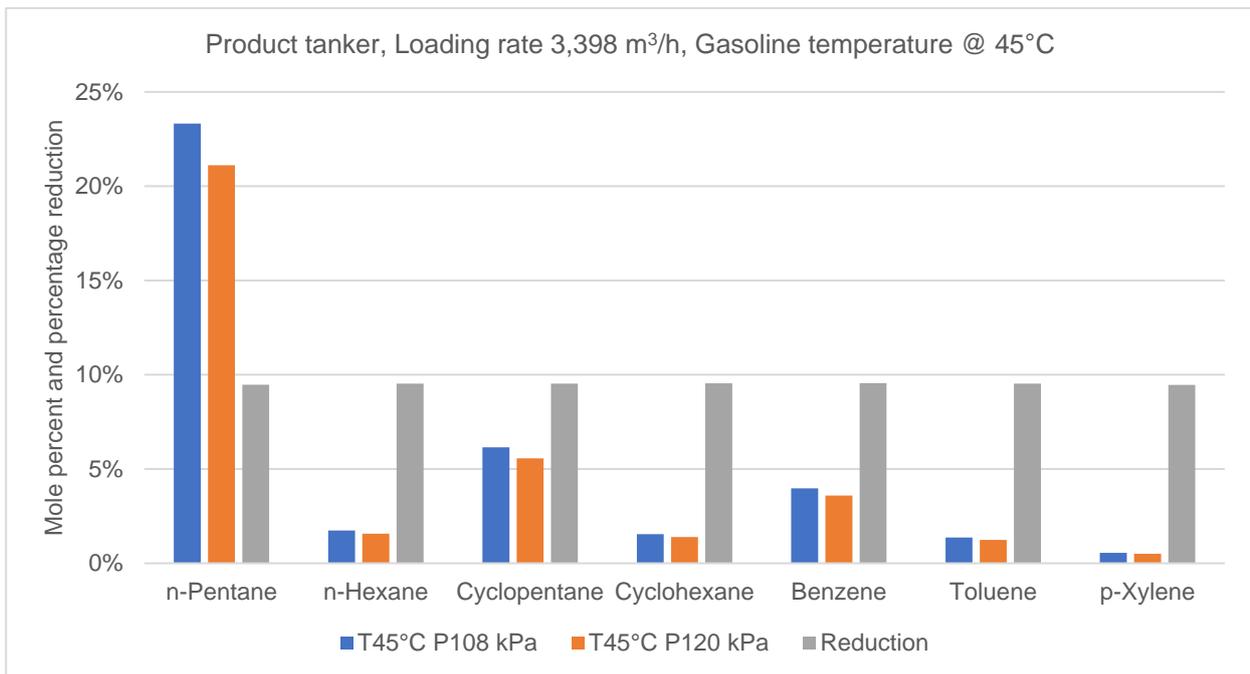
(c)

Figure 6.3 Mole percentage of individual VOCs in OVE, and corresponding reduction due to higher pressure, on completion of gasoline loading in a product tanker, for gasoline temperature at (a) 25°C (b) 35°C, and (c) 45°C

The following observations are drawn from Figure 6.1, Figure 6.2, and Figure 6.3:

a) The largest share of VOCs present in the OVE is from low boiling point paraffinic components, identified as ethane, propane, butane and pentane. Naphthenic and aromatic components are lower in terms of their percentage mole fraction.

b) Butane is the most prominent component for crude oil loading, whereas Pentane is the most significant component in gasoline loading operations. This is possible because these components are the largest in crude oil and gasoline, and their boiling point lies lower than other components.

c) The higher cargo tank pressure can reduce the VOC emission of all individual components by approximately 10%. This is due to the reduced pressure difference between the SVP of the oil and the cargo tank pressure, leading to lower VOC emission.

6.3 Data validation for toxic VOCs

The data obtained from the current simulation is compared with similar results in the available literature. Currently, there is no paper published to analyse OVE related to oil tanker loading operations. OVE analysis conducted for petroleum oil refineries and oil exporting terminals is used to compare with the results obtained in the current research, as various studies reveal that oil refineries are a potential source of hydrocarbons.

Lin *et al.* (2004) conducted an air quality assessment around the refinery area from 26 sampling sites. Gas chromatography and Ultra-Violet Differential Optical Absorption Spectroscopy (UV-DOAS) were employed to analyse the samples. The most abundant VOC detected were Benzene and Toluene. Two different methods, Gas chromatography and Ultra-violet differential optical absorption spectroscopy, verified measured concentrations, and the correlation of the results helped to validate the merits of individual techniques applied for VOC analysis.

Kalabokas *et al.* (2004) analysed the ambient air concentration of several sites around an oil refinery near the city of Corinth in Greece in 1997 to detect hydrocarbons. The total aromatic hydrocarbons (Benzene, toluene, ethylbenzene, xylenes and trimethyl benzene) were higher than the total saturated hydrocarbons (hexane, heptane, and octane). The most abundant aromatic and saturated hydrocarbons were hexane and toluene, respectively.

Ras *et al.* (2009) analysed VOC levels in the ambient air zone with numerous chemicals and petrochemical industrial plants in the south of Europe. The methods employed included dynamic sampling in sorbent tubes, thermal desorption, and gas-chromatography-mass spectrometry. Ambient air profiles of different areas provided information on the component vapours of VOCs contributing to photochemical ozone creation potential (POCP). Predominant compounds from all sampling sites were toluene, benzene, ethylbenzene, m,p-xylene, i-pentane, and isoprene.

Rajabi *et al.* (2020) analysed the overall scale of global emission of VOCs from all stages of oil processing, identifying the type, average concentration, and detection frequency of the most prevalent VOCs. Their research identified toluene, benzene, hexane, heptane, cyclohexane and pentane as high-detected and high-concentrated compounds among all VOCs emitted from crude oil (Rajabi *et al.*, 2020).

As per US Environmental Protection Agency (EPA), HAP, also known as toxic air pollutants, is known, or suspected to cause cancer or other serious health effects, such as reproductive effects, birth defects, or adverse environmental effects. Hazardous Air Pollutants (HAP), such as Benzene, Toluene, Ethyl benzene, Xylene, and Hexane, have been identified as present in the VOC emission resulting from crude oil and gasoline loading operations(EPA, 2023).

Based on the analysis of the results from the different studies related to the identification of toxic VOCs, it can be concluded that the major VOC components identified in the simulation results match with the above studies (Kalabokas, 2001; Lin *et al.*, 2004; Ras *et al.*, 2009; Rajabi *et al.*, 2020; EPA, 2023). The simulation results can provide mole fraction of the toxic VOCs in the OVE, such as hexane, benzene, toluene, ethyl benzene, and xylene, as presented in figures 6.1 to 6.3.

The toxic effect of VOCs for oil tanker loading and bunkering operations has not been recognised and analysed so far. Further analysis of their impact during loading and bunkering operations onboard ships and in the port area is required, such as using CFD software, or by actual field observations, to understand their specific effect. The methodology validated in this research can provide a specific mole fraction of toxic VOCs at the vent outlet.

6.4 Proposed amendments to ship design and working practices to minimise exposure to toxic VOCs

Seafarers working onboard oil tankers are regularly exposed to toxic VOCs. It is observed that crude oil and gasoline loading operations onboard oil tankers introduce toxic VOCs to the surrounding environment, affecting local air quality and detrimental to human health. Currently, no systematic risk assessment is being done to evaluate this exposure risk to seafarers during the design of tankers.

SOLAS convention rules related to oil tanker design are solely based on the prevention of fire due to its flammability potential. It is proposed that a systematic 'VOC Toxic Hazard Assessment' must be conducted to assess its impact on health of seafarers as well as its effect on air quality, as part of standard design requirements. Venting of oil vapours being carried through mast risers or P-V valves needs to be analysed for VOC toxic exposure risks. Siting of P-V valves and Mast Riser needs to be analysed based on this analysis and may require manual tank inspection points to be re-located. This should be included as a mandatory goal-based approach in the SOLAS convention.

Also, ship staff, especially engineers, are regularly exposed to OVE emission from the air pipe of the ship's fuel tanks. The current height of bunker tank air pipes is solely based on Loadline regulations, typically only 760 mm in height, well below the average height of a human being. Hence, ship staff is fully exposed to this OVE during oil bunkering operations. VOC toxic exposure risk should include the analysis of OVE from new fuel oils that are being adopted, such as low sulphur fuel, HVO, FAME, or bio-fuel blends. Currently, fuel tank air pipes are situated around the accommodation areas and their choice of siting at the design stage does not include any toxic exposure assessment based on the OVE escaped during bunkering operations.

Based on the above description, the following are proposed:

6.4.1 Amendments to ship and oil tanker design to minimise or stop VOC emission

The amendments proposed for ships and oil tankers designs are similar to those proposed for minimising or stopping OVE, as reducing or stopping OVE would proportionally reduce toxic VOC emission.

All oil tankers and ships must be fitted with one of the following options to minimise or stop VOC emission, in order of priority:

1. The tanker loading terminal must provide a vapour return line to ensure zero oil vapour emission (MSC/Circ.585, 1992).
2. If the above is unavailable, all oil tankers must use VOC Recovery Equipment, which should be mandatory as part of regulations under the SOLAS convention(MEPC.1/Circ.680, 2009).
3. Oil tankers must also be fitted with VOC emission reduction technologies such as CVOC and KVOC systems (MEPC.1/Circ.719, 2010).
4. Oil tankers must be fitted with P-V Valves' highest possible safe pressure setting, such as at 120 kPa and above, to minimise VOC emission during loading and transit.
5. In-line sampling and the remote gauging system must be mandated as standard equipment for all cargo and bunker tanks to minimise or stop VOC exposure to ship staff due to oil sampling and gauging activities.
6. Bunker tank air pipes are to be situated away from the accommodation, and the height of air pipes should be decided based on VOC toxic exposure assessment.

6.4.2 Amendments to current working practices to minimise or stop VOC emission

A proposed amendment to working practices is as follows:

1. CII Rules under the MARPOL convention must include VOC emission from tanker loading and ship bunkering operations.
2. Use all available technology provided onboard to minimise or stop VOC emissions. This should be recorded and reported in the logbook related to SEEMP and CII records.
3. Working practice should mandate provision and use of fixed and personal VOC emission monitoring equipment during loading and bunkering operations.
   b)

6.5 Conclusion

a) Ship staff are routinely exposed to toxic VOCs in OVE resulting from tanker loading and ship bunkering operations. Currently, the risk is not being assessed systematically. An objective assessment using the latest simulation and field studies must be conducted to analyse if the current ship and tanker design rules and working practices are adequate to address this risk.

b) Simulation methodology is able to identify various components of hydrocarbons present in the OVE from crude oil and gasoline loading operations. Identification

of hydrocarbons reveals that the major share of the hydrocarbons are VOCs, which has been identified as toxic VOCs, as reported by research studies and agencies around the world. Toxic VOCs identified by the current research methodology include hexane, benzene, toluene, ethyl benzene, and xylene, which are also in accordance with other studies (Kalabokas, 2001; Lin *et al.*, 2004; Ras *et al.*, 2009; Rajabi *et al.*, 2020; EPA, 2023).

c) Oil exporting and ship bunkering organisations must work together with shipowners to achieve a common goal of minimising or stopping VOC emissions. Modifications to tanker design and working procedures which are proposed to minimise or stop VOC emissions are similar to those proposed for minimising or stopping OVE as both OVE and VOC are directly proportional to each other in terms of amount / concentration.

d) The proposed modifications related to design include mandatory provision of vapour return line at oil exporting terminals, VOC recovery equipment, or VOC reduction technologies such as KVOC, CVOC, P-V valves with higher pressure setting of 120 kPa, in-line oil sampling, remote oil level gauging equipment and specifying appropriate height and siting of bunker tank vent pipes.

e) The proposed modifications related to working practices include VOC emission from oil tanker loading and ship bunkering operations in SEEMP reporting and CII rules, incorporating equipment listed in (d) in working practice, and use of fixed and personal VOC emission monitoring equipment.

Chapter 7. Proposed amendments to the international conventions and local rules to minimise or stop VOC emission

Literature review and the data provided in the previous chapters indicate that OVE from the oil tanker loading and ship bunkering operations leads to an economic loss. In addition, the presence of toxic VOCs in the emission also causes local air pollution which consequently affect the health of marine personnel onboard and in port areas.

Various guidance and regulations on VOC emission from loading operations in oil tankers can be classified as international, national, and tanker industry-specific practices. The international regulations about tankers are covered under 'International Maritime Organization' (IMO) conventions such as 'Safety of Life at Sea' (SOLAS) and 'Prevention of Marine Pollution from the ships' (MARPOL). The regional and national regulations related to tankers can be regional and local conventions and acts such as the 'Long-Range Transboundary Air Pollution' (LRTAP) convention under 'United Nations Economic Commission for Europe' (UNECE), and the 'Clean Air Act' in the USA. The tanker industry-specific practices are related mainly due to commercial considerations to seek tanker business, such as 'Oil Companies International Marine Forum' (OCIMF) led 'Ship Inspection Report Programme' (SIRE) inspections and the oil tanker industry best practices under 'International Safety Guide for Oil Tankers and Terminals' (ISGOTT).

A current review of the various studies on the effect of VOC emissions on human health indicates that there should be specific regulations in international conventions to minimise or stop t VOC emissions to safeguard the health of seafarers onboard and in port areas. Though IMO has provided specific guidelines since 1992, these are not mandatory to follow, limiting the efficacy of such measures(MSC.731; MSC/Circ.585, 1992; MEPC.1/Circ.680, 2009; MEPC.1/Circ.719, 2010; MARPOL, 2020; SOLAS, 2023).

This chapter provides details on the proposed new regulations, the amendments to the existing regulations in SOLAS and MARPOL conventions, and unique regional or local regulations to minimise or stop VOC emission from the oil tanker loading and ship bunkering operations.

No regulation under SOLAS and MARPOL conventions references the VOC emission from oil venting operations. The toxic effect of VOC emission from venting operations during tanker loading operations and ship bunkering operations has been neither analysed nor mentioned directly in any of these conventions. The literature review in Chapter 2, Sub-sections 2.4.1 and 2.4.2 concludes that there are no regulations in SOLAS and MARPOL convention, which require:

a) to provide any specific fixed or portable equipment to monitor exposure risks due to VOC emission,
b) to install any equipment in ship design to limit or stop VOC emission,
c) to have a minimum safe distance between air vents and sounding pipes for oil tanks, based on the VOC vapour cloud propagation for exposure risk assessment,
d) ships to monitor VOC emission for exposure risks during tanker loading and ship bunkering operations,
e) tankers to have any target for the reduction of VOC emission during loading operations,
f) tankers transporting clean petroleum products such as gasoline and naphtha to have any VOC Management Plan, and
g) ships/tankers to include VOC emission during loading and bunkering operations to calculate direct CO_2 emission from ship operations under SEEMP or CII rules.

The local and regional regulations are stricter than SOLAS and MARPOL under local air quality laws such as in the U.S.A., E.U., and Norway. The local laws in E.U., U.S.A., and Norway declare clear VOC reduction goals and specify standards and technological solutions to regulate the VOC emission from tanker loading operations.

SIRE programme under OCIMF and standard operating guidelines from ISGOTT guide provide details on the operational procedures to manage the oil vapour exposure risks for the ship staff onboard.

VOC Toxicity from tanker loading and ship bunkering operations is not addressed in any international convention. As per the report prepared for the EU Commission, for every tonne of crude oil loaded in a tanker, there is 1 kg emission of VOCs if no control measures are adopted (AEAT, 2001). 1886 million tonnes of crude oil was loaded in 2018, thereby implying 1886 thousand tonnes of VOC emission from tanker loading operations at the global level (UNCTAD, 2020). The concentrated VOC emission from the oil-exporting ports at a local level is a significant cause of concern. Bunkering ports

such as Rotterdam, Singapore, Houston, and Fujairah handle a few thousand ship bunkering operations annually, contributing to toxic VOC emissions in the local area.

The impact of VOC emission needs to be highlighted and accounted for during the ship design process. This is proposed to be handled by issuing a separate Risk Assessment advisory by an additional code, proposed to be named as VOC Toxicity Hazard Assessment (VOCTHA) Code. The code would provide guidance to tanker designers to design tank venting and ullage pockets keeping in mind the dispersion of toxic VOCs during tanker loading operations from the designated P-V Valves. This will address the exposure risk of the ship's crew during tanker loading operations, which is not being accounted for currently.

The importance of regulating this VOC emission is evidenced from the list of a few oil tanker terminals in various countries, where local air quality rules have enforced no VOC emission during tanker loading operations, as shown in Table 7.1.

S.No	Port	Description	Remarks
	As per Regulation 15(b): A party regulating tankers for VOC emission shall submit a notification to the Organization.(MARPOL, 2023).		
1	Netherlands	VOC emission is regulated and reported to IMO, under Regulation 15 Annex VI of MARPOL convention (GISIS, 2020).	Reported to IMO as below: In 2011, for the port of Amsterdam, Vlissingen, Terneuzen, and Moerdijk, In 2012, for the port of Gronningen, and In 2014: for port of Rotterdam.
2	South Korea	VOC emission is regulated and reported to IMO, under Regulation 15 Annex VI of MARPOL convention (GISIS, 2020)	Reported to IMO as per below: In 2009, for the port of Busan, Incheon, Pyongtaek, Ulsan, Yeosu, and Kwangyang, In 2015, for the port of Taesan.
	As per local rules		
3	Gothenburg, Sweden	Local air quality rule to regulate VOC emission from tanker loading operations, under Gothenburg Energy Port Regulations (EEA, 2019; Gothenburg, 2020)	Enforced as a local initiative to control air quality in the port.
4	The U.S.A.	Under 'The Clean Air Act' rule, oil exporting terminal to adopt either MACT or RACT options to regulate	National initiative to control air pollution from tanker loading terminals.

		VOC emission, based on the quantum of oil handled, as required under 40 CFR Part 63 of EPA regulations. (EPA, 2020e)	
5	Norway	Vapour Recovery Unit is fitted at the oil exporting terminals to receive full OVE back to the oil terminal (Martens *et al.*, 2001; Energy, 2008a)	Local initiative to control emission in the port areas. Started in 1996, in the port of Sture, and in 2008, in the port of Mongstad.

Table 7.1 List of ports regulating VOC emission during tanker loading operations

Various guidelines issued by IMO and the related developments in the maritime industry to minimise or stop VOC emission are proposed to be included as new or amended regulations in SOLAS and MARPOL conventions, as listed below:

a) Provision of 'Vapour Return Line' at all oil exporting terminals to operate VECS systems onboard tankers, and provision of VECS system on all oil tankers (MSC/Circ.585, 1992)

b) Increased setting of P-V Valves onboard oil tankers to at least 120 kPa(MEPC.1/Circ.680, 2009).

c) Provision of VOCON valve for oil tanker loading operations (MEPC.1/Circ.680, 2009).

d) Provision of KVOC system onboard oil tankers (MEPC.1/Circ.680, 2009).

e) Provision of CVOC system onboard oil tankers (MEPC.1/Circ.719, 2010).

f) Provision of Vapour Recovery Systems onboard oil tankers (MEPC.1/Circ.680, 2009).

g) Use of recovered VOCs, from Vapour Recovery Systems, as fuel, onboard oil tankers (DNV, 2010; AET, 2020).

h) Inclusion of activities related to oil tanker loading and ship bunkering operations in enhancement of efficiency of operations as per SEEMP Regulation 22 in Annex VI of MARPOL convention (MARPOL, 2023)

i) Inclusion of activities related to oil tanker loading and ship bunkering operations as a potential carbon emission activity, calculate operational carbon intensity under Carbon Intensity Indicator (CII) rules, as per Regulation 28 in Annex VI of MARPOL convention(MARPOL, 2023).

j) Review Regulation 15 Annex VI of MARPOL convention, to include product tankers to have mandatory 'VOC Management Plan', to minimise or stop VOC emission during loading operations (MARPOL, 2023)

The following section provides specific details on the proposed amendments.

7.1 Proposed amendments for ship design in the SOALS convention

Current information from oil and gas industry practices and local air quality rules in various countries justifies amendments to existing SOLAS and MARPOL regulations to regulate VOC emission at the local level.

The basis of the proposed amendments in the SOLAS convention is to carry out a detailed risk assessment for VOC toxicity in any shipboard operations involving OVE, such as oil tanker loading and ship bunkering operations. The following mandatory task is proposed to be included in the SOLAS and MARPOL convention for all ships:

a) To conduct 'VOC Toxicity Hazard Assessment' (VOCTHA) for the location of venting points and manual sounding ports for cargo oil and bunker tanks (for cargo tanks as shown in Figure 7.1 and for bunker tanks as shown in Figure 7.2). It is proposed to be included in the SOLAS convention.

b) To conduct VOCTHA also for the tanker loading ports, where multiple loading operations are performed, and for the bunkering ports, to make a regional basis of strict compliance to stop VOC emission, as shown in Figure 7.3). This is proposed to be included in the MARPOL convention.
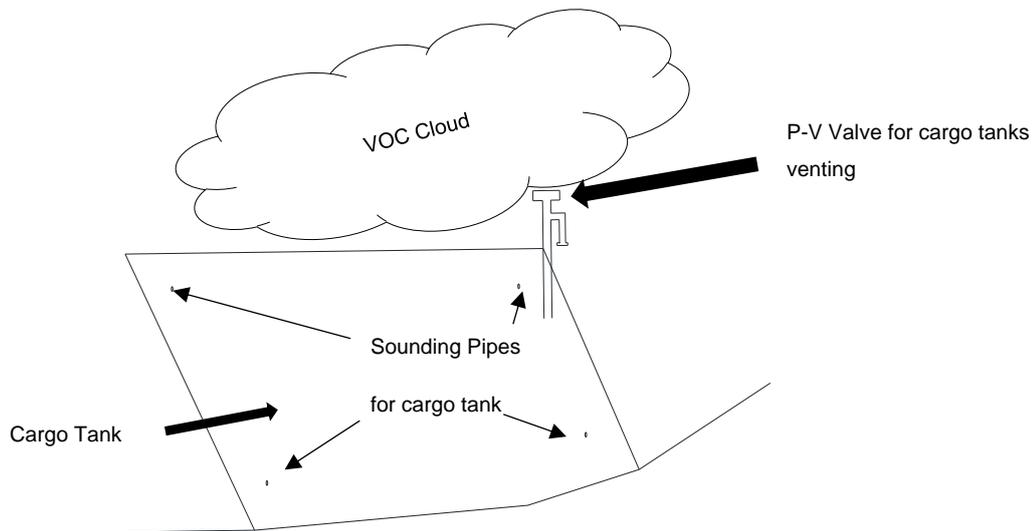
Figure 7.1 P-V Valve arrangement and location of sounding points for a cargo tank, showing the probabilistic extent of VOC cloud for venting during the loading operation

Figure 7.2 Proximity of the bunker tank air vent and the sounding ports to the accommodation entrance
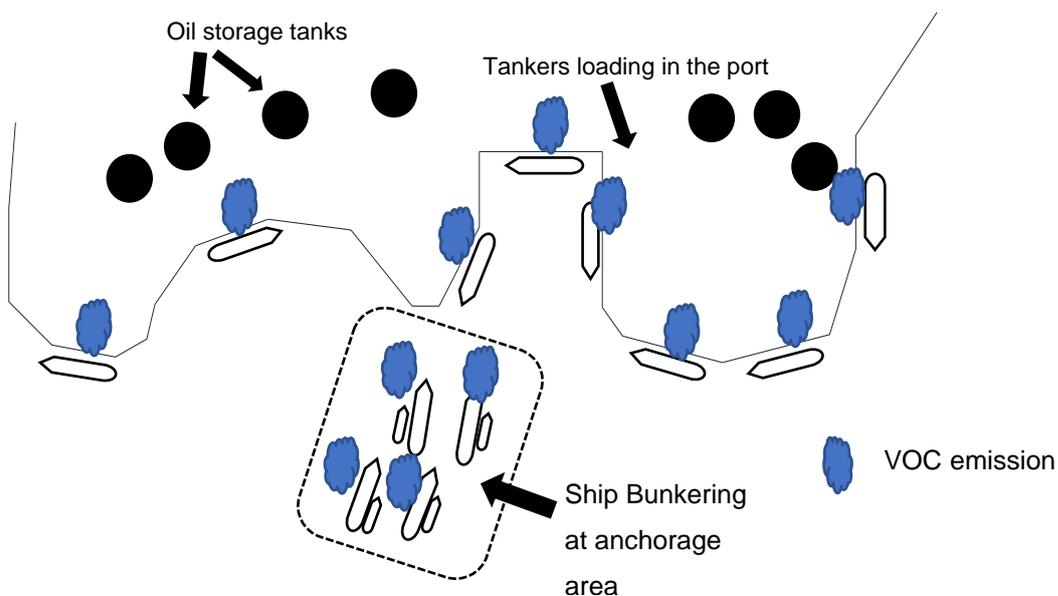
Figure 7.3 Overview of VOC emission from a tanker loading port and ship bunkering operations at the anchorage

7.1.1 Introduction of a new Chapter XI-3 titled 'Special measures to enhance maritime health'

a) No explicit and clear-cut acknowledgement and management of toxicity of VOC emission from oil vapour venting, affecting human health, exist in any IMO convention. It is proposed to include VOC Toxicity issues in the SOLAS convention under a new Chapter XI-3 titled 'Special measures to enhance maritime health', on similar lines as per the existing Chapter XI-1 'Special measures to enhance maritime safety' and Chapter XI-2, 'Special measures to enhance maritime security'.

This chapter should provide guidance to include 'VOC Toxicity Hazard Assessment' (VOCTHA) as part of the current 'Risk Assessment' under Chapter IX 'ISM'. This code should provide detailed guidance for conducting exposure risk assessment due to VOC emissions from various oil tank vents, such as cargo oil tanks onboard tankers and fuel tanks onboard all ships. The code should guide the recommended spacing between air vents and sounding pipes, the height of the vent pipe and the safe distance of bunker tank air vents from the accommodation area and entrances for safe exposure to toxic VOCs in OVE. The code should provide the methodology for assessing VOC exposure

risk with simulation tools such as CFD software within the ship's vicinity and software such as MARPLOT for dispersion analysis within a port.

b) The proposed new Chapter XI-3 should regulate the shipboard crew's mandatory carriage of 'Personal VOC Monitors' during oil vapour venting during tanker loading and ship bunkering operations. The safe alarm limits should be specified to assist the crew in timely evacuation to a safe area. Alternatively, the ship may also be required to have a fixed 'VOC Emission Monitoring System' on deck to provide centralised information in the control room to guide the crew for safe evacuation.

c) It is proposed to issue a new Code, under the SOLAS convention, titled 'VOC Toxicity Hazard Assessment (VOCTHA) Code, on similar lines to 'Fire Safety and Systems' (FSS) Code, to support the proposed new Chapter XI-3, as per above.

d) The position of vapour vents for all oil tanks should be finalised based on exposure risk assessment, as per the VOCTHA code, to ensure minimum exposure to VOCs for seafarers working on deck. The requirement for the safe height of the vapour vent should also apply to bunker tanks.

7.1.2 Amendments to SOLAS Chapter VI Regulation 3 'Oxygen Analysis and Gas Detection Equipment'

SOLAS Chapter VI Regulation 3 'Oxygen Analysis and Gas Detection Equipment' should be amended to include its compliance for tankers transporting oil and all ships using oil as fuel. The mandated equipment to include a personal 'VOC Monitor' (PGM) for ship staff working on deck.

7.1.3 Amendment to SOLAS Chapter VI Regulation 5-1 'Material Safety Data Sheets'

SOLAS Chapter VI Regulation 5-1 'Material Safety Data Sheets' should be expanded to declare the toxicity of VOC emission from oil vapour venting, like Regulation 3, in the same chapter, which explicitly states the reasons for precautions for solid bulk cargo liable to emit toxic or flammable gas.

7.1.4 Introduction of a new Part D, 'Special Provisions for Carriage of oil' in SOLAS Chapter VI

It is proposed to introduce a new part, Part D, 'Special Provisions for Carriage of oil' in SOLAS Chapter VI, like the existing 'Part B' and 'Part C', which address particular issues related to the carriage of Solid Bulk Cargo and Grain respectively. This chapter should include the possible options to regulate VOC emission based on the available technological or design options, such as 'VOC Recovery Systems' and using captured VOCs as fuel. Other mandated ship equipment includes remote oil gauging and in-line oil sampling systems. It should be mandatory to have such equipment to maintain air quality and protect the health of seafarers due to toxic VOC emissions from oil tanks.

7.1.5 Summary of equipment for oil tankers based on the proposed amendment to regulations under the SOLAS convention

It is proposed to apply a tiered design requirement based on the cargo-carrying capacity of an oil tanker to minimise or stop VOC emissions. This is proposed to be achieved by the available equipment and technologies as per various IMO guidelines, as suggested below, according to the ship's deadweight, as per Table 7.2.

.Tanker Size Applicable to all Oil Tankers	Design Requirement for regulating VOC emission (loading, in-transit, or any other venting operations from cargo tanks) (Proposed under new SOLAS Ch VI Part D, and new Chapter XI-3)	Safety requirement for assessment of VOC Toxicity Hazard onboard tankers (Proposed under SOLAS Ch VI, Reg 3 to amend, and new chapter SOLAS XI-3)
DWT < 100,000 tonnes	Oil vapour vents, ullage port and sampling port location to be designed as per VOCTHA code, Remote gauging and in-line sampling system are mandatory. Use P-V Valves with pressure setting of 2100 mm WG, Vapour Recovery Unit, and any one of the following options to be installed: VOCON valve, or KVOC system, or CVOC system	Provide Personal VOC Monitor Or Fixed VOC Emission Monitoring System covering potential emission areas onboard.
DWT between 100,000 tonnes to 150,000 tonnes	Oil vapour vents, ullage port and sampling port location to be designed as per VOCTHA code,	Provide Personal VOC Monitor And

	Remote gauging and in-line sampling system are mandatory. Use P-V Valves with pressure setting of 2100 mm WG, Vapour Recovery Unit, VOCON valve, and either KVOC or CVOC to be installed.	Fixed VOC Emission Monitoring System covering potential emission areas onboard.
DWT 150,000 tonnes and above	Oil vapour vents, ullage port and sampling port location to be designed as per VOCTHA code, Remote gauging and in-line sampling system are mandatory. Use P-V Valves setting to 2100 mm WG, Vapour Recovery Unit, VOCON valve, KVOC, and CVOC systems to be installed.	Provide Personal VOC Monitor And Fixed VOC Emission Monitoring System covering potential emission areas onboard.

Table 7.2 Proposed summary of amendments in SOLAS convention for design of oil tankers

7.1.6 Summary of equipment for oil bunker tanks onboard all ships based on the proposed amendment to regulations under the SOLAS convention

Similarly, for ship bunkering operations, a tiered design requirement based on the ship's deadweight is proposed to minimise or stop VOC emission, as shown in Table 7.3.

Ships DWT	**Design Requirement for regulating VOC emission during ship bunkering operations (Proposed under new SOLAS Ch XI-3)**	**Safety requirement for assessment of VOC Toxicity Hazard under SOLAS regulations (Proposed under SOLAS Ch VI, Reg 3 to amend, and new Chapter SOLAS XI-3)**
DWT < 100,000 tonnes	Bunker tanks vapour vent height and spacing between bunker tank vapour vent and sounding pipe, to be designed as per VOCTHA code. Remote gauging and in-line sampling systems are mandatory.	Provide Personal VOC Monitor Or Fixed VOC Emission Monitoring System covering potential emission areas

DWT 100,000 tonnes and above	Bunker tanks vapour vent height and spacing between bunker tank vapour vent and sounding pipe, to be designed as per VOCTHA code. Remote gauging and in-line sampling systems are mandatory.	Provide Personal VOC Monitors And Fixed VOC Emission Monitoring System covering potential emission areas

Table 7.3 Proposed summary of amendments in SOLAS convention for all ships

7.2 Proposed amendments for ship operations in the MARPOL convention

The current MARPOL regulations in Annex VI focus mainly on preventing air pollution from exhaust gas emissions and monitoring energy efficiency through ship manoeuvring and fuel oil consumption.

Only Regulation 15, Annex VI, in MARPOL convention, mentions VOC emission from tankers. In this regulation, the decision to regulate VOC emission depends on the oil terminal, thus limiting its effectiveness. The requirement for tankers to have a 'VOC Management Plan' applies only to crude oil tankers. For tankers handling clean petroleum products, there is no mandatory requirement to control VOC emissions. There is no reference to monitoring the surrounding atmosphere from oil vapour vents for toxic VOCs in OVE, whether from oil loading or ship bunkering operations.

Monitoring of operational environmental efficiency is required as per IMO guidelines related to Regulation 26, Annex VI of MARPOL convention, under Ship Energy Efficiency Management Plan (SEEMP). Current activities mentioned in enhancing operational environmental efficiency in SEEMP does not include VOC emission from oil tanker loading and ship bunkering operations (MSC.282(70), 2016).

Operational carbon intensity reporting, as per Regulation 28, introduced in year 2022. However, the amendments in Annex VI of MARPOL convention, also does not include VOC emission from oil tanker loading and ship bunkering operations (MEPC.304(72), 2018; MEPC.328(76), 2023).

For tanker loading operations and ship bunkering operations, there are no regulations in the MARPOL convention which require:

a) ships to monitor VOC emission for exposure risks during tanker loading and ship bunkering operations,

b) tankers to have any target for the reduction of VOC emission during loading operations,

c) clean petroleum tankers transporting clean petroleum products such as gasoline and naphtha to have any VOC Management Plan,

d) ships/tankers to include VOC emission during loading and bunkering operations for the calculation of direct CO_2 emission from ship operations under SEEMP Regulation 26, and CII Regulation 28, Annex VI of MARPOL convention.

The following amendments are proposed in Annex VI of the MARPOL convention:

7.2.1 Amendments to the existing Regulation 15 MARPOL Annex VI, Volatile organic compounds

a) It should be mandatory for all tanker loading terminals to regulate VOC emission by providing a 'Vapour Return Line' to facilitate closed loading operations to preserve air quality in the port areas. To assist the tanker terminals in monitoring VOC emission in the port area, MARPOL convention should issue simplified guidance on calculating VOC emission by adopting 'Emission Factors' issued by EPA or EU regulations. Ports loading 100 million barrels of crude oil, or 10 million barrels of gasoline (same basis as per the current U.S.A. regulations) must enforce the installation of' VOC Recovery Equipment' in their oil terminals to preserve local air quality.

b) Currently Regulation 15 requires only crude oil tankers to have VOCMP. It is proposed that scope of VOCMP should be extended to also include product tankers

c) As oil loading operation will cause VOC emission, the current regulation should be expanded to also include monitoring of VOC emission from ship bunkering operations, especially when new fuels such as HVO, FAME, LSFO, and blends are being adopted to be used as new fuels. Appropriate guidance should be made available for different fuel types to record VOC emissions in VOC Management Plan (VOCMP) for bunkering. Reference should be made to VOCMP guidance provided for oil tanker loading operations.

d) Oil tanker loading operations must use a vapour return line or shipboard VOC recovery equipment. The amendment should include this as an operating requirement. Appropriate records related to the vapour return line, VOCs recovered

by the recovery equipment, CVOC and KVOC systems, as applicable, should be maintained.

e) Oil level monitoring and sampling in cargo and bunker tanks must be done by remote gauging systems and an in-line sampling system fitted as per amended SOLAS Ch XI-3.

f) It should also set specific reduction targets for VOC emission, i.e., by using VOC Recovery Systems, from oil tanker loading and ship bunkering operations, similar to those defined for NOx emission Regulation 13 in Annex VI. Detailed guidance should be included for each ship's standardised calculations by amending the current Regulation 15, Annex VI of MARPOL convention.

g) Fixed VOC emission monitoring systems or personal VOC monitor (PGM) shall be used during oil tanker loading and ship bunkering operations to safeguard the health of seafarers. The requirement to provide VOC Emission Monitoring System and personal VOC monitor (PGM) is proposed in Sub-section 7.1.1 and 7.1.2, under amendments to SOLAS convention.

7.2.2 Amendment to monitor operational environmental performance by 'Carbon Intensity Indicator' and SEEMP

VOC emission from oil tanker loading and ship bunkering operations should be included in reporting under 'Annual Operational Carbon Intensity Indicator', as per Regulation 28, Annex VI, in MARPOL convention. Similarly, the reuse of recovered VOCs as fuel to enhance fuel consumption efficiency should be included in SEEMP records (MEPC.328(76), 2023).

7.2.3 Amendments to IMO Strategic Directions

The current IMO Strategic Direction Roadmap does not include any VOC emissions to be monitored from oil tanker loading and ship bunkering operations. It is proposed that Strategic Direction 2 (SD2), 'Integrate new and advancing technologies' in the regulatory framework and Strategic Direction 3 (SD3), 'Respond to climate change', to be reviewed and amended to include this critical VOC emission (IMO, 2019).

7.2.4 Summary of amendments in MARPOL convention

The summary of amendments proposed for regulations in MARPOL convention is shown in Table 7.4.

Ship Type	Design requirement for regulating VOC emission for air quality (Annex VI, MARPOL convention)	Operational requirement for monitoring VOC emission (Annex VI, MARPOL convention)
Oil Tankers, during loading operations	Vapour Return Line to be mandated on all oil exporting terminals. (Regulation 15)	Oil tankers must use close loading operations (Vapour return line) or VOC recovery equipment, as applicable. (Regulation 15)
	The efficiency of VOC Recovery Systems should be indicated (Regulation 15).	VOC emission from tanker loading operations at oil terminals must be recorded. (Regulation 15)
	Include VOC emission in SEEMP. (Regulation 26)	Must use personal VOC detectors or / and fixed VOC Emission Monitoring System, as applicable. (Regulation 15)
	Include VOC emission in Annual operational Carbon Intensity Indicator reporting. (Regulation 28)	Oil level monitoring and oil sampling must be executed by using remote gauging systems and in-line sampling system. (Regulation 15)
		Monitor and report VOC emission during loading for product tankers by referring to VOCMP. (Regulation 15)
		Monitor and report VOC emission in SEEMP and Annual CII reporting. (Regulation 26 and 28)
All Ships, during bunkering operations	Include VOC emission in SEEMP (Regulation 26)	Use personal VOC detectors and fixed VOC Emission Monitoring System. (Regulation 15)
	Include VOC emission in Annual Operational Carbon Intensity Indicator report. (Regulation 28)	Oil level monitoring and oil sampling must be executed by using remote gauging systems and in-line sampling system. (Regulation 15)
		Ship staff to record VOC emission as per VOCMP for bunkering operation. (Regulation 15)
		Monitor and report VOC emission in SEEMP and Annual CII reporting. (Regulation 26 and 28)

Table 7.4 Proposed summary of amendments in MARPOL convention for all ships

7.3 Proposed amendments in the local regulations

Monitoring toxic VOCs in OVE from oil tanker loading and ship bunkering operations largely depends on local and regional initiatives. It is seen that few nations and regional blocks are active in regulating such emissions. The national and regional agencies include E.P.A. U.S.A., E.E.A. E.U., and N.E.A. Norway, as described in section 2.4.3, chapter 2 (UNECE, 2015; EEA, 2019; EPA, 2020c; NEA, 2020) . Industry led initiative such as SIRE programme under OCIMF and standard operating guidelines from ISGOTT provide guidance to manage the exposure risks of shipboard staff are also described in section 2.4.4 in chapter 2 (ICS, 2020). Examples include 'Clean Air Act' in the USA, 'LRTAP Convention' under 'UNECE', and the reduction in VOC emission in Norway under 'The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone' (Hansen *et al.*, 2008; EPA, 2020a; UNECE, 2020). These regulations/protocols may be adopted by other nations and regional blocks as reference to actively regulate such toxic emissions from oil tanker loading and ship bunkering operations.

7.4 Conclusion

a) The regulations in SOLAS and MARPOL conventions have not included any 'VOC Toxicity Exposure Assessment' for oil tanker loading and ship bunkering operations. The current oil tanker and ship design can expose seafarers to toxic VOCs during oil tanker loading and ship bunkering operations due to siting tank vents and sounding pipes in proximity. Due to toxic VOCs in OVE, current ship design rules do not account for exposure risk assessment.

b) A new chapter, 'Chapter XI-3', is proposed to be included in the SOLAS convention to address 'Special measure to enhance maritime health'. A new code-named 'VOC Toxicity Hazard Assessment' is proposed to be included in this new chapter to provide a methodology to conduct toxic hazard assessment from VOC emission within the ship's perimeter and the port. The code will also guide a safe distance between air vents and sounding pipes, air vents and the nearest accommodation doors and the height of air vents for bunker tanks and cargo tanks to address the toxicity hazards. VOC Emission Monitoring System is proposed to be fitted to monitor exposure risk during oil tanker loading and ship bunkering operations.

c) The shipboard environment is proposed to be monitored for VOC emission by the mandatory carriage of personal VOC monitor (PGM) or / and fixed VOC Emission Monitoring System during tanker loading and ship bunkering operations.

d) Remote monitoring devices and in-line oil sampling systems are proposed to minimise or stop VOC exposure during oil loading and bunkering operations.

e) A new part, 'Part D', is proposed to be included in SOLAS Chapter VI to specify various technological solutions to minimise VOC emission.

f) Current MARPOL Regulation 15 in Annex VI does not apply to clean petroleum tankers and oil-exporting terminals. It is proposed to be amended to apply to all oil-exporting terminals for effective regulation of VOCs at the global level. All oil loading terminals must provide a vapour return line to stop VOC emission.

g) Alternatively, all oil tankers are proposed to be fitted with VOC recovery equipment. The scope of this regulation is proposed to apply to all ships, which carry oil as cargo, or oil as fuel on similar lines as per SOPEP regulation in Annex I.

h) Lastly, it is proposed that MARPOL regulations should declare VOC emission reduction targets on the same lines as done for current NOx emission regulation in Annex VI.

The proposed amendments in SOLAS and MARPOL may reference the local rules in various countries where VOC regulation has been more proactive and from different oil industry standard operating practices. A summary of the proposed amendments is shown in Table 7.5.

Aspect under study as per the current research	Oil Vapour Emission during oil tanker loading and ship bunkering operations		
Identified issues	Flammability	Toxicity	Air pollution
Current status	Regulations exists in SOLAS Ch II-2	Not addressed in any SOLAS Regulation	Addressed partially in MARPOL Annex VI
Proposed recommendations	Nil	Amendments in SOLAS convention	Amendments in Annex VI, MARPOL convention
		a) Add a new Chapter XI-3 titled 'Special measures to enhance maritime health'. • This chapter will include VOCTHA code to be used for exposure risk assessment for designing and siting of oil vapour vents and sounding pipes. • It will also specify safe exposure level of toxic VOCs. • VOC Emission Monitoring System is proposed to be fitted to monitor exposure risk during oil tanker loading and ship bunkering operations. b) Amend Regulation 3 in Chapter VI, to include mandatory carriage of personal VOC monitors	a) Amend Regulation 15 as follows: • Mandatory for all oil-exporting terminals to provide Vapour Return Line during tanker loading operations. • To mandate VOC Management Plan for all ships (Tankers and non-tankers), like the requirement of oil pollution prevention plan, SOPEP, for all ships, which cover oil tanker loading and ship bunkering operations. • Specify VOC emission reduction targets, like NOx regulations in MARPOL convention. d)

| | | for oil tankers transporting oil and all ships using oil as fuel.

c) Include 'VOC Toxicity Hazard' in Regulation 5-1, Chapter 6, for oil cargo and ships using oil as fuel.

d) Introduce new Part D, 'Special Provisions for Carriage of oil' in SOLAS Chapter VI, as follows:
c)
•   Options to regulate VOC emission based on the available technological or design options, such as 'VOC Recovery Systems', and re-use of captured VOCs as fuel.

•   Remote oil level monitoring system and in-line oil sampling systems to be mandated for oil tankers and all ships using oil as fuel. | •   Mandatory for oil exporting terminals to reporting VOC emission from tanker loading operations.

•   Mandatory use of portable and fixed VOC Emission Monitoring System during oil tanker loading and ship bunkering operations.

•   Mandatory use of remote monitoring of tank levels and in-line sampling systems for oil sample collection during oil tanker loading and ship bunkering operations.

b) Amend Regulation 26 and Regulation 28 to include VOC emission from oil tanker loading and ship bunkering operations to be included in SEEMP and annual CII reporting. |

Table 7.5 Summary of the proposed amendment in SOLAS and MARPOL convention

Chapter 8. Conclusion

Oil tanker loading and ship bunkering operations release a large volume of oil vapours (OVE) which contain toxic VOCs. The OVE not only leads to monetary loss, but the presence of toxic VOCs in the OVE is also harmful to the environment and human health. Current ship design rules do not require any equipment to be fitted onboard to minimise or stop OVE. In addition, the presence of toxic VOCs in the surrounding environment has not been accounted for in ship design and operations under various SOLAS and MARPOL convention regulations.

As per the aims and objectives, the research findings are summarised in this chapter.

8.1 Aim and Objective 1: Quantify economic loss due to evaporation and proposing a feasible solution.

An evaporative loss occurring during tanker loading operations leads to direct monetary loss and VOC emission. The simulation data indicates the exact evaporative loss, which provides a basis for adopting solutions related to amendments in tanker design and working practices. The data shows an annual monetary loss of $1.2 to 5.5 million for an Aframax tanker loading crude oil between the temperature range of 25℃ to 45℃. In contrast, the same loss for a ULCC ranges from $1.6 to 11.2 million for the same temperature range.

8.1.1 Proposed solutions to amend tanker design

Proposed solutions include modifying the current tanker design to operate with a higher setting of P-V valves in all cargo tanks, which can reduce the monetary loss by 26% to 35% for an Aframax tanker and a ULCC. Similarly, gasoline loading losses can be minimised by 21% to 34%. Higher tank operating pressure can also reduce VOC emissions during tanker loading operations. VOC emission is reduced by 23% to 29% for an Aframax tanker and a ULCC crude oil loading operation and 15% to 18% for a product tanker loading gasoline. Adopting additional measures such as fixing VOCON valves, CVOC system, KVOC system, and provision of Vapour Return Line can further reduce the monetary loss and environmental pollution. Proper risk assessment should be conducted to ensure that the tank is able to withstand higher setting of P-V valves when this solution is adopted.

8.2 Aim and Objective 2: Quantify the volume of vapours (VOCs) emitted during tanker loading operations and propose amendments to preserve air quality.

Simulation data shows that OVE increases as the temperature of oil increases and decreases when higher cargo tank pressure is maintained during tanker loading operations. OVE can be reduced by adopting a working practice of maintaining elevated tank pressure of 120 kPa instead of the current practice of 108 kPa. This practice will safeguard marine personnel from local air pollution, as fewer oil vapours are vented.

Process Safety Simulation software can quantify total OVE for consecutive loading operations in a tanker loading port with multiple loading berths. Cumulative OVE for the port can be considered as a concentrated point source of emission affecting regional air quality.

The simulation results indicate that HC emission is reduced by 4% to 9% for crude oil loading operations and 9% to 10% for a gasoline loading operation by maintaining tank pressure as 120 KPa during loading, for the oil temperature between 25℃ to 45℃.

Emission Factor (EF) values obtained in this research have been used in Aspen HYSYS software to determine the exact composition of OVE for crude oil and gasoline loading, by using specific loading rate, oil temperature and tank pressure, of specific crude oil and gasoline sample. This method is expected to be more accurate than other methods for calculating VOC emissions. However, the current practice of using generalised EFs by various agencies worldwide has its inherent limitation. It is hence may not be suitable for estimating the exact impact of OVE on air quality.

8.2.1 Proposed solutions to amend ship design

In terms of effectiveness to stop or minimise OVE and hence VOC emission, the following are recommended to be adopted:

a) A vapour return line must be provided at each tanker loading terminal, as per VECS guidelines, which is the most effective way to minimise or stop OVE and VOC emissions.

b) SOLAS regulations for the design of oil tankers are to be amended to minimise VOC emission, as per below:

    i.   Provide a 'Vapour recovery system' as mandatory equipment for each oil tanker that must be used if oil terminals do not offer a vapour return line. The systems

should have acceptable VOC emission reduction targets of 80 to 100% as per realistic industry practice.

ii. Provide a KVOC or a CVOC system to reduce VOC emission during oil tanker loading.

iii. Provide each cargo tank with P-V valves of at least 120 kPa pressure relief setting.

iv. Provide a remote tank gauging system onboard an oil tanker, capable of being used for commercial purposes to enable accurate readings.

v. Provide an In-line oil sampling system for oil sampling.

8.3 Aim and Objective 3: Identifying and analysing the composition of vapour emissions (VOCs) for toxicity hazard assessment of tanker loading and ship bunkering practice. Propose amendments to ship design and working practice to minimise toxic VOC exposure to safeguard the health of seafarers.

Ship staff are routinely exposed to toxic VOCs in OVE resulting from tanker loading and ship bunkering operations. Currently, this risk is not being assessed systematically. An objective assessment using the latest simulation and field studies must be conducted to analyse if the current ship and tanker design rules and working practices are adequate to address this risk.

The simulation conducted for crude oil and gasoline loading operation identifies low boiling point paraffins as the largest share in terms of mole fraction in VOC. The components include ethane, propane, butane, and pentane. Naphthenic and aromatic components are in lower mole fraction. Among all, butane and pentane are identified as the highest mole fraction VOC in OVE for crude oil and gasoline loading operations respectively. It is also observed that maintaining higher tank pressure of 120 kPa, as compared to 108 kPa during the loading, reduced the VOC emission by approximately 10%.

It is proposed that regulations under SOLAS and MARPOL conventions be amended to include 'VOC Toxicity Hazard Assessment' (VOCTHA) as part of the mandatory ship and tanker design requirement. Oil exporting and ship bunkering organisations must work together with shipowners to achieve a common goal of zero emissions. Modifications to tanker design and working procedures are proposed to stop or minimise VOC emissions.

The amendments proposed for ships and oil tankers designs to minimise or stop VOC emission, are similar to those proposed for minimising or stopping OVE, as reducing or stopping OVE would proportionally reduce toxic VOC emission.

8.3.1 Proposed solutions to amend working practices
A proposed amendment to working practices is as follows:

a) CII Rules under the MARPOL convention must include VOC emission from tanker loading and ship bunkering operations.
b) Use all available technologies provided onboard to stop or minimise VOC emissions. This should be recorded and reported in the logbook related to SEEMP and CII records.
c) Working practice should mandate carriage and use of personal VOC monitoring equipment during loading and bunkering operations.

8.4 Aim and Objective 4: Critical analysis of the current international conventions (SOLAS and MARPOL) and local rules related to VOC emission from OVE due to oil tanker loading and ship bunkering operations, with reference to toxic vapour exposure to seafarers and localised air pollution. Propose amendments to minimise carbon emission from tanker loading and ship bunkering operations.

Literature review is conducted for SOLAS and MARPOL conventions, regional and national rules, and industry practices. The analysis concludes that:

a) The toxicity hazard of VOC needs to be included in the SOLAS convention to minimize or stop toxic exposure for seafarers and marine personnel.
b) MARPOL convention Annex VI Regulation 15 and Regulation 22 be amended to stop or minimise VOC emission and account for VOC emission during loading operations in oil tankers and bunkering operations on all ships.
c) Local rules in the USA, EU states, and Norway related to controlling VOC emissions from tankers should be studied in detail for their efficacy. That approach may be used to amend international conventions and national regulations.
d) Guidelines in ISGOTT may provide reference to control inhalation exposure risk of seafarers.

The following addition and amendments are proposed in SOLAS and MARPOL convention:

8.4.1 Amendments to SOLAS Convention for ship design

a) To include a new chapter to address 'Special measure to enhance maritime health' with a new code namely 'VOC Toxicity Hazard Assessment'. It is proposed to provide a methodology to conduct toxic hazard assessment from VOC emission within the ship's perimeter and the port. The code will provide guidance for a safe distance between air vents and sounding pipes, air vents and nearest accommodation doors and the height of air vents for bunker tanks and cargo tanks to address the toxicity hazards.

b) Provide mandatory portable and fixed VOC Emission Monitoring System to monitor surrounding atmosphere during tanker loading and ship bunkering operations.

c) Provide mandatory remote tank level monitoring devices and in-line oil sampling systems.

d) Include a new part, 'Part D', in Chapter VI to specify various technological solutions for regulating VOC emission.

8.4.2 Amendments to MARPOL Convention for design and operations

a) VOC regulations should be made applicable to clean petroleum tankers and ship bunkering operations.

b) All oil loading terminals to provide a mandatory vapour return line under VOC regulation.

c) All oil tankers must install and use VOC recovery equipment during tanker loading operations, fitted as per regulations in SOLAS convention.

d) Targets to reduce VOC emission shall be added in VOC regulation. specifically.

e) Oil level monitoring and oil sampling must be executed using remote level gauges and in-line sampling systems, respectively.

f) VOC emitted from oil tanker loading and ship bunkering operations should be included in the records related to energy efficiency and carbon emission.

The proposed amendments in SOLAS and MARPOL may reference the local rules in various countries where VOC regulation has been more proactive and from different oil industry standard operating practices.

In conclusion, oil tanker loading and ship bunkering operations have great potential to improve their efficiency of operations, protect the environment, and health of seafarers. It can be achieved by improving ship design and their related operational practices. It requires adopting a close loop oil tanker loading operations by a mandatory provision

of vapour line by shore terminals. Design rules and operational practices are recommended to be adopted by suitable amendments in various regulations in SOLAS and MARPOL conventions. National rules in certain countries are highlighted which may be adopted in international conventions to minimise or stop VOC emission from oil tanker loading and ship bunkering operations.

Chapter 9. Future works and risk analysis

The work done in the current research has potential to be continued further.

9.1 Modelling for oil sample

Current research has assumed crude oil and gasoline chemical composition based on various petroleum engineering handbooks and available literature. There are various types of bunker oil being adopted in the maritime industry. The accuracy of the simulation results can be improved by if results from the actual chemical analysis of individual oil is used.

9.2 Field observations

The novel methodology used in the current research should be validated further with field observations. Alternatively, a scaled cargo and bunker tank model with an actual ship's replica can be used. Various VOC detectors placed at suitable locations may be used to gather accurate data on the rate of concentration variation in a horizontal and vertical direction. As stricter GHG emission regulations are expected to be adopted under various IMO conventions, further work in understanding the emissions from oil tanker loading and ship bunkering operations using simulation methodology could be helpful in the assessment of different scenarios.

9.3 Guidebook on quantity and quality of VOC emission

Crude oil can be classified based on its paraffinic, naphthenic, and aromatic compounds. Simulation of crude oil samples at various loading rates and oil temperatures, should be used to compile a guidebook on the quantity and quality of OVE and the toxic VOCs released at different loading conditions. This international guidebook can help to formulate policies and regulations to regulate air quality and understand their potential impact on human health. The data is also helpful in ship design and operations to ensure OVE from loading operations does not cause monetary loss and can control carbon emissions as per the international goals.

9.4 Modelling for VOC toxic exposure

The detailed analysis of OVE from the vents may further be carried out by Computational Fluid Dynamic (CFD) simulation software to know the exposure concentration of toxic VOCs that seafarers working on deck could inhale. Realistic wind and weather parameters should be considered to understand toxic VOC exposure during such modelling.

9.5 Amendments to IMO GHG strategy and international conventions

The annual quantum of oil exported by oil tankers and oil fuel consumption rises steadily from year to year. However, the impact assessment on the environment due to carbon emission during oil tanker loading and ship bunkering operations has not been included so far. Similarly, the guidance for the calculations of EEDI, EEOI, or data under SEEMP and CII records kept under the MARPOL convention does not include the environmental and carbon emission impact of OVE from oil tanker loading and ship bunkering operations. Hence, it is recommended to highlight to IMO that GHG strategy and strategic directions must account for such OVE due to the activities mentioned earlier so that improvements can be made by adopting proposed amendments to the regulations in SOLAS and MARPOL conventions.

9.6 Recommendation to conduct Risk Analysis for proposed measure

Risk Assessment must be carried out as per industry practice before any measures recommended in the current work are adopted in tanker loading operations. Though the recommendations to operate at higher tank pressure are below the tank design pressure, additional safety considerations, such as deterioration of ship structure due to poor maintenance or substandard workmanship, may necessitate difficulty in adopting the recommendations. Each case must be analysed carefully so as not to compromise the safety of personnel onboard.

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Appendix A: Simulation results from DWSIM and HYSYS

Simulation results from DWSIM Simulation and Ansys HYSYS
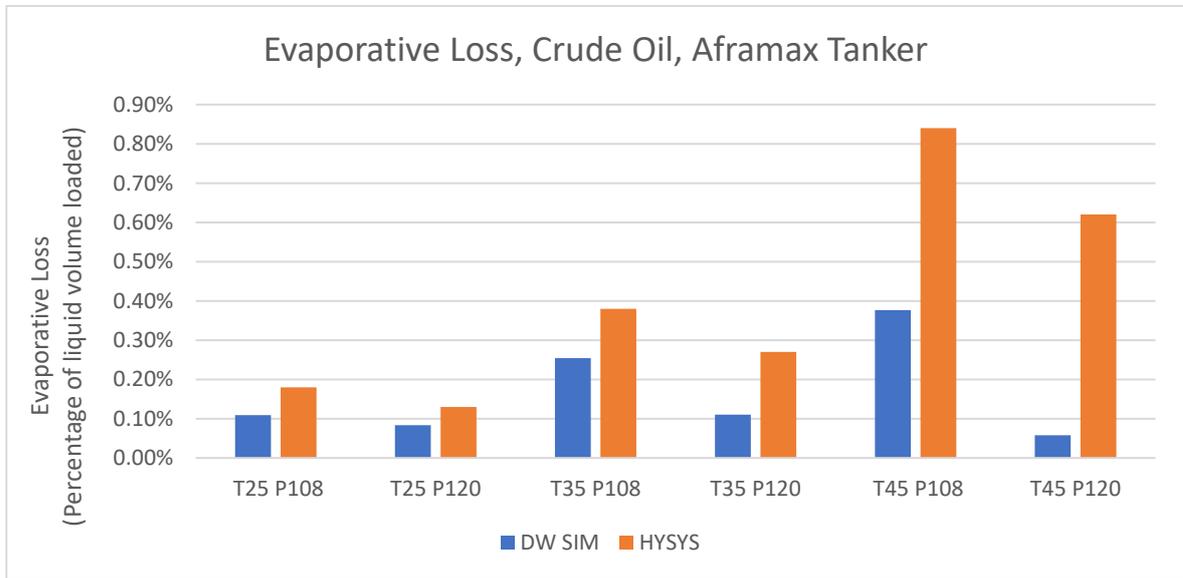

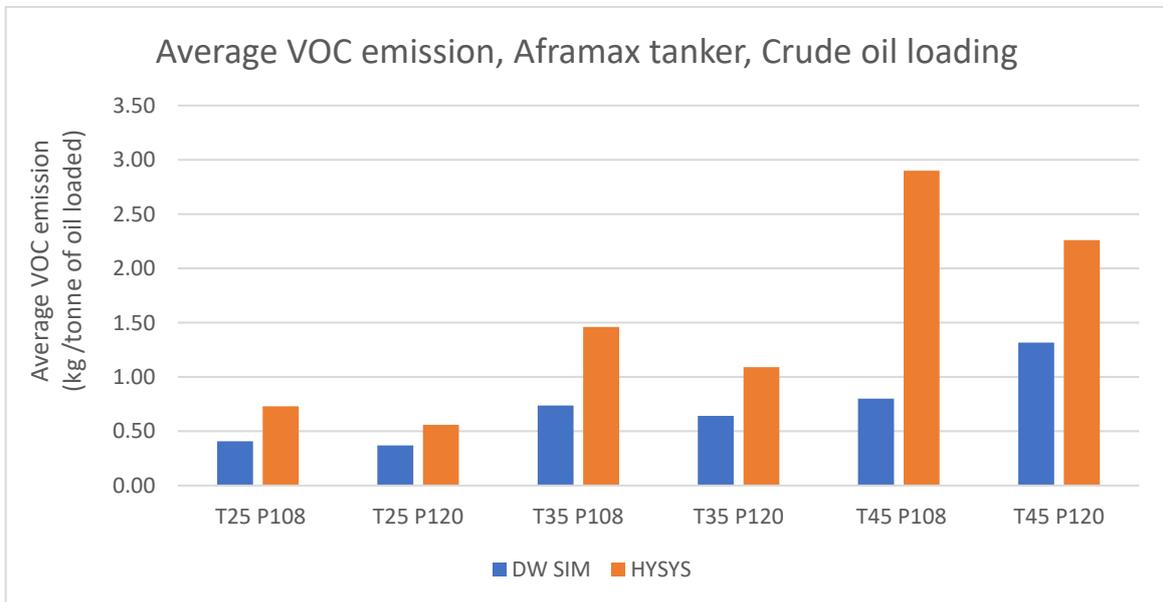Figure A.1 Evaporative loss for crude oil loading operation in an Aframax tanker

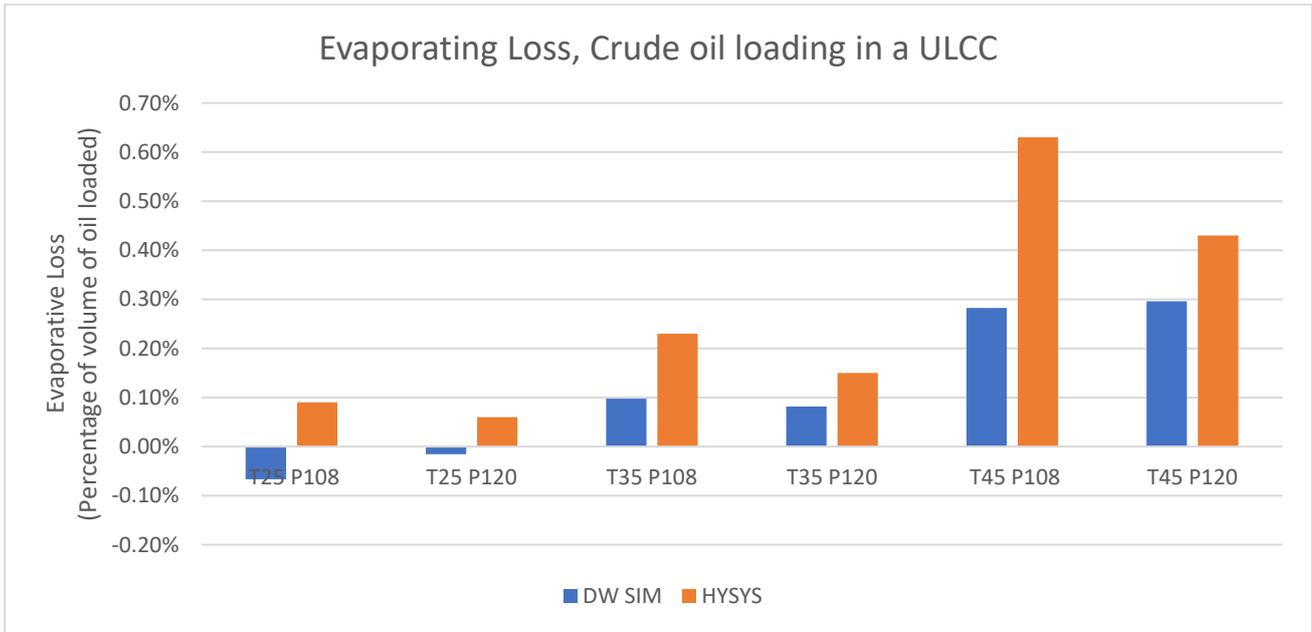Figure A.2 Average VOC emission for crude oil loading operation in an Aframax tanker

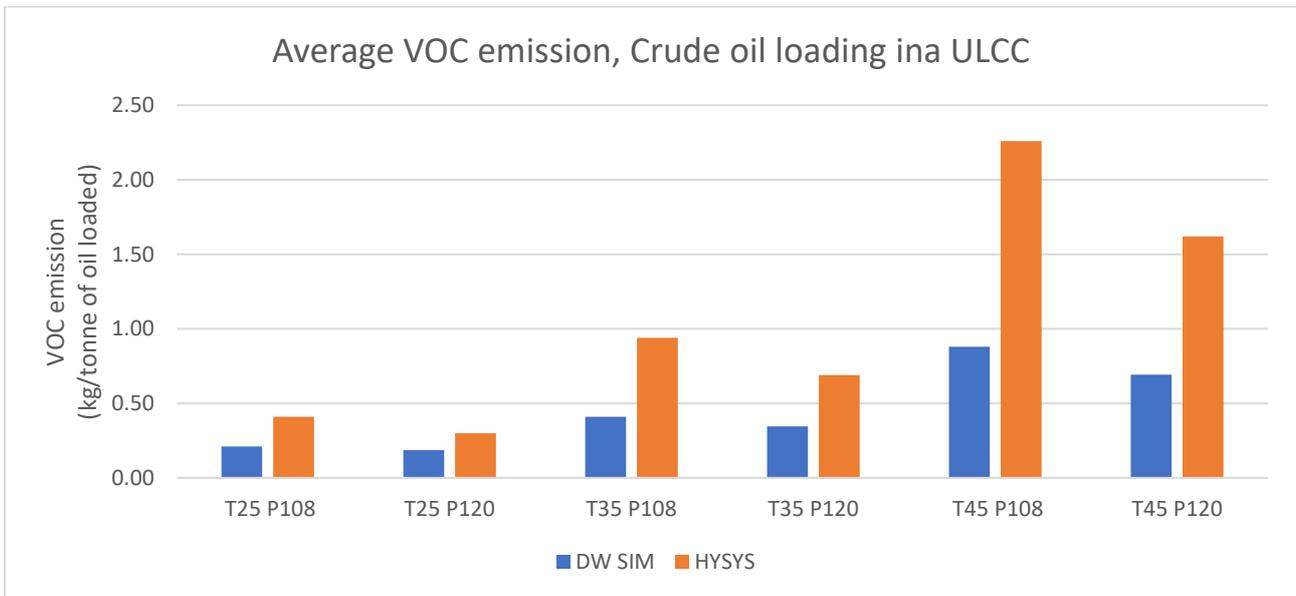Figure A.3 Evaporative loss for crude oil loading operation in an ULCC

Figure A.4 Average VOC emission for crude oil loading operation in an ULCC
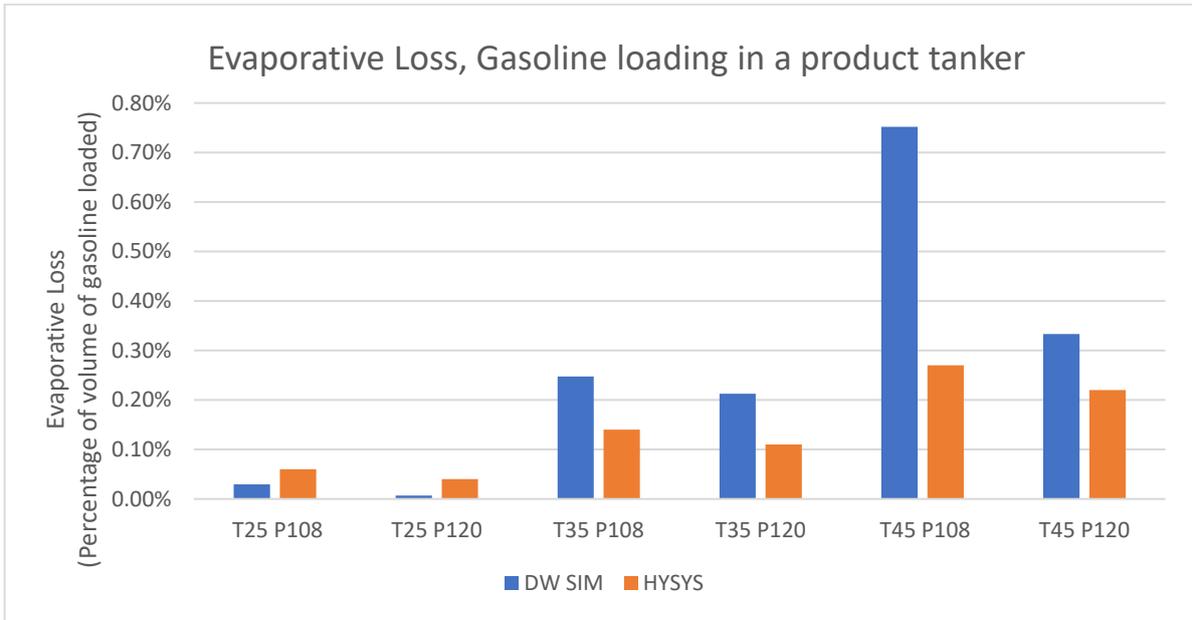
174

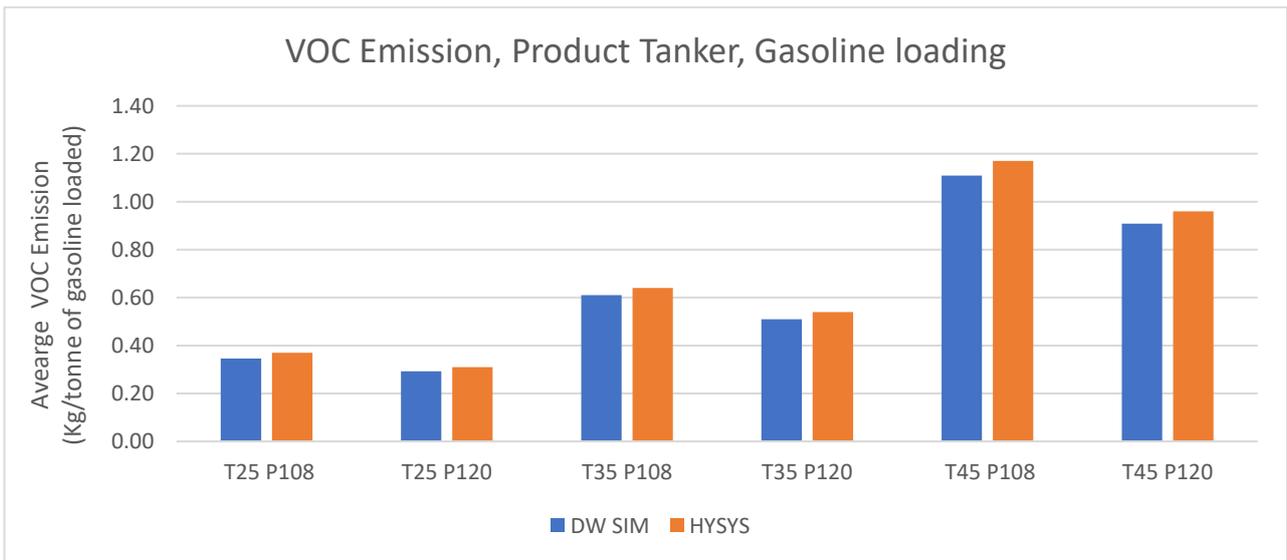Figure A.5 Evaporative loss for gasoline loading operation in a Product tanker

Figure A.6 Average VOC emission for gasoline loading operation in a Product tanker

	Evaporative Loss *(Percentage of volume of oil loaded)*	DW SIM	HYSYS
Loading crude oil in Aframax tanker	T25℃ P108kPa	0.11%	0.18%
	T25℃ P120 kPa	0.08%	0.13%
	T35℃ P108 kPa	0.25%	0.38%
	T35℃ P120 kPa	0.11%	0.27%
	T45℃ P108 kPa	0.38%	0.84%
	T45℃ P120kPa	0.06%	0.62%
Loading crude oil in ULCC	T25℃ P108kPa	-0.07%	0.09%
	T25℃ P120 kPa	-0.02%	0.06%
	T35℃ P108 kPa	0.10%	0.23%
	T35℃ P120 kPa	0.08%	0.15%
	T45℃ P108 kPa	0.28%	0.63%
	T45℃ P120kPa	0.30%	0.43%
Loading gasoline in Product tanker	T25℃ P108kPa	0.03%	0.06%
	T25℃ P120 kPa	0.01%	0.04%
	T35℃ P108 kPa	0.25%	0.14%
	T35℃ P120 kPa	0.21%	0.11%
	T45℃ P108 kPa	0.75%	0.27%
	T45℃ P120kPa	0.33%	0.22%

Table A.1 Simulation results by DWSIM and Aspen HYSYS for evaporative loss for crude oil and gasoline loading

VOC Emission (kg/tonne of oil loaded)		DW SIM	HYSYS
Loading crude oil in Aframax tanker	T25℃ P108kPa	0.41	0.73
	T25℃ P120 kPa	0.37	0.56
	T35℃ P108 kPa	0.74	1.46
	T35℃ P120 kPa	0.64	1.09
	T45℃ P108 kPa	0.80	2.90
	T45℃ P120kPa	1.32	2.26
Loading crude oil in ULCC	T25℃ P108kPa	0.21	0.41
	T25℃ P120 kPa	0.19	0.30
	T35℃ P108 kPa	0.41	0.94
	T35℃ P120 kPa	0.35	0.69
	T45℃ P108 kPa	0.88	2.26
	T45℃ P120kPa	0.69	1.62
Loading gasoline in Product tanker	T25℃ P108kPa	0.35	0.37
	T25℃ P120 kPa	0.29	0.31
	T35℃ P108 kPa	0.61	0.64
	T35℃ P120 kPa	0.51	0.54
	T45℃ P108 kPa	1.11	1.17
	T45℃ P120kPa	0.91	0.96

Table A.2 Simulation results by DWSIM and Aspen HYSYS for VOC emission for crude oil and gasoline loading