An Analysis and Control of Volatile Organic Compound (VOC) Emissions from Petroleum Storage Tanks

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ABSTRACT

Climate change is a growing phenomenon with its effects becoming more prominent to life on earth. According to the latest report by the Intergovernmental Panel on Climate Change (IPCC), some of the effects of climate change are irreversible. However, the implementation of large-scale reduction strategies on emissions may limit climate change over the long-term and provide short term air quality benefits. Petrochemical industries are a major contributor of Volatile Organic Compound (VOC) emissions as the need for storage facilities are expanding to accommodate for the increase in demand of organic liquids storage capacity. The Durban South Basin is a major industrial hub consisting of South Africa's largest capacity oil refinery (SAPREF) and Engen refinery, soon-to-be tank terminal, located near a residential area. Therefore, the implementation of emission monitoring and reduction strategies are critical in ensuring climate resilience and the health and well-being of residents living within close proximity to the refineries.

While there has been some progress in addressing climate change, emission data indicates that storage tanks contribute 42% of VOC emissions to total emissions from oil refineries. Due to limited studies conducted, there is a gap in the knowledge and understanding of proper monitoring and control practices of VOC emissions from petroleum storage tanks in Durban, South Africa. Therefore, the aim of this study is to provide strategies for implementation, such as simulation modelling using Aspen Plus ® and recommended process conditions, to achieve safe control and handling of emissions and to perform an Environmental Impact Assessment (EIA) for analyses of its potential effect on the environment and health of communities.

Estimation of VOC emissions for crude oil and petroleum products (Ultra-Low Sulphur Diesel (ULSD), Unleaded Petrol 95 (ULP 95), Jet Fuel (JET A1) and Marine Gas Oil (MGO) were based on the AP-42 method, Aspen Plus ® simulations, manual flash calculations according to the Rachford-Rice iterative method and empirical correlations (such as the Vasquez-Beggs and Valko-McCain empirical correlation methods). The effects of atmospheric conditions, tank roof type, type of stored organic liquid and varying parameters (such as temperature, pressure and feed flowrate) on the VOC emissions from petroleum storage tanks were assessed to determine the most suitable monitoring method. The potential effect of Nitrogen blanketing (using the API 2000 7th ed. Standards) and Vapour Treatment on the reduction of VOC emissions from petroleum

storage tanks were studied to determine its effectiveness as a control method. This study found that the Aspen Plus ® simulation method is an effective tool in monitoring VOC flashing emissions due to its reliability from its repeatability with the estimation crude oil test system in which the Aspen Plus ® and literature VOC measurement was consistent. Its ability to account for variations using the thermodynamic property models (Soave-Redlich-Kwong (SRK) for crude oil and Peng-Robinson (PENG-ROB)) for the product mixtures) further justifies the use of Aspen Plus ® as an effective monitoring method. Manual flash calculations under-estimated emissions across the organic mixture systems due to its less rigorous approach as it uses simplified equations which includes estimates of process conditions whereas Aspen Plus ® is able to account for variations is process conditions. The estimates determined using empirical correlations were mostly invalid due to the limited appliable range. All mixtures indicated a significant reduction in working and breathing losses when stored in an Internal Floating Roof Tank (IFRT) compared to a Floating Roof Tank (FRT). However, MGO was the exception. It was observed that these tanks should operate at 90 % capacity, with turnovers of 0 – 10 per year and a white painted shell, to ensure minimum emissions. Optimal operating tank temperatures should be maintained at 293.15 – 303.15 K and at pressures below 91 kPa. The installation of vapour recovery units is recommended for FRTs, and these measures are 90 % efficient. Due to the high API gravity of the ULP 95 mixture, the ULP 95 mixture should be targeted as a key mixture for control of VOC emissions as it has the potential to emit greater VOC emissions.

DECLARATION

The work presented in this dissertation was carried out in the Thermodynamic Research Unit in the School of Engineering at the University of KwaZulu-Natal, Durban, from January 2019 to August 2021 under the supervision of Professor P. Naidoo and Doctor K. Moodley.

This dissertation is submitted as the full requirement for the degree M.Sc. (Eng.) in Chemical Engineering.

I, Theasha Naidoo, therefore declare that:

(i) The research reported in this dissertation, except where otherwise indicated, is my original work.

(ii) This dissertation has not been submitted for any degree or examination at any other university.

(iii) This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

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a) Their words have been re-written but the general information attributed to them has been referenced;

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Theasha Naidoo

As the candidate's supervisor, I, Doctor. K Moodley, approved this dissertation for submission.

Doctor K. Moodley

As the candidate's co-supervisor, I, Professor. P. Naidoo approved this dissertation for submission.

Professor P. Naidoo

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NOMENCLATURE

Symbols

API	Stock Tank Oil Relative Density	^{o}API
D	Diameter	ft
E_{Tot}	Total Flash Emissions	ton/year
E_{VOC}	Total VOC Flash Emissions	ton/year
F	Estimated number of temperature swings per month	-
G	Nitrogen inbreathing requirement	scfh
H_L	Stock liquid height	ft
H_{RO}	Roof outage	
H_S	Tank shell height	ft
H_{VO}	Vapour space outage	ft
I	Daily total solar insolation	Btu/ft^2.d
K_E	Vapour space expansion factor	-
K_N	Working loss turnover factor	-
K_P	Working loss product factor	-
K_{Ra}	Zero wind speed rim seal loss factor	lb-mole/ft.yr
K_{Rb}	Wind speed dependent rim seal loss loss factor	
K_S	Vented vapour space saturation factor	-
L_D	Deck seam loss	lb/yr
L_F	Deck fitting loss	lb/yr
L_R	Rim seal loss	lb/yr
L_S	Standing Storage Loss	lb/yr
L_W	Working Loss	lb/yr
MW_{TV}	Tank Vapour Molecular Weight	-

M_V	Molecular weight of vapour	lb/lb-mole
N	Turnovers per year	
N_M	Maximum nitrogen flow rate	scfh
N_T	Total volume of nitrogen required	ft^3/month
N_{TB}	Nitrogen required by the rise and fall of the liquid level owing to the external temperature conditions	ft^3/month
N_W	Nitrogen required by the material flow through the tank	ft^3/month
P*	Vapour pressure function	
P	Pump-out rate	gpm
P_A	Atmospheric pressure	psia
ΔP_B	Breather vent pressure setting range	psi
P_S	Separator Pressure	kPa
ΔP_V	Daily vapour pressure range	psia
P_{VA}	Vapour pressure at daily average liquid surface temperature	psia
Q	Production Rate	bbl/d
R	Ideal gas constant	psia.ft^3/lb-mole.^oR
Rs	Solution Gas Oil Ratio	scf/bbl
R_S	Tank shell radius	ft
S_R	Tank cone roof slope	ft/ft
SGc	Corrected Specific Gravity	-
SG_S	Separator Gas Specific Gravity	-
T_{AA}	Daily average ambient temperature	^oR
T_{AN}	Daily minimum ambient temperature	^oF
T_{AX}	Daily maximum ambient temperature	^oF

T_B	Liquid bulk temperature	^oR
T_{high}	Maximum temperature in tank	^oF
ΔT_{LA}	Daily average liquid surface temperature	^oR
T_{Low}	Minimum temperature in tank	^oF
T_S	Separator Temperature	K
V_{HS}	Average empty headspace	gal
V_T	Total number of gallons discharged from the tank	gal/month
V_V	Tank vapour space volume	ft^3
W_V	Vapour density	lb/ft^3
X_{VOC}	VOC Mass Fraction	lb-voc/lb

Greek letters

α	Tank paint solar absorptance
Δ	Change in

Abbreviations

JET A1	Jet fuel
MGO	Marine Gas Oil
ULP 95	Unleaded Petrol 95
ULSD	Ultra-low sulphur diesel

CHAPTER ONE: INTRODUCTION

The emission of hydrocarbon compounds such as Volatile Organic Compounds (VOCs) to the atmosphere poses a human health hazard and has a negative impact on the environment (Kihlman, et al., 2006). The presence of VOCs combined with nitrogen oxides and sunlight initiate photochemical reactions which give rise to the formation of ozone (O_3) in the troposphere (Kihlman, et al., 2006) (Berezina, et al., 2020). Urban areas have raised serious concerns about the health-related illnesses, such as respiratory tract inflammation, carcinogenic effects and the aggravation of lung diseases (Kihlman, et al., 2006). Shell and BP South African Petroleum Refineries (SAPREF) and Engen Refinery have been noted as the major contributors of atmospheric pollution in the Durban South Area, according to a study conducted by Niranjan (2005). SAPREF and Engen Refinery contribute to 14.1 % and 10.5 % of total VOC emissions in eThekwini respectively, in which 4441 t/a and 3291 t/a of VOC emissions were released from SAPREF and Engen Refinery respectively (eThekwini Health and Norwegian Institute for Air Research, 2007). The Life After Coal Campaign is an ongoing court case in which Sasol and National Petroleum Refiners of South Africa (Natref) are involved in contributing towards air pollution from coal in the Mpumalanga Highveld (Life After Coal, 2021). Ozone in the troposphere is also one of the leading contributors to global warming and poses other major threats to the environment as it damages crops and creates smog (Kihlman, et al., 2006) (UN Environment, 2018). In South Africa, ozone levels in the troposphere are rising rapidly and the effects of climate change are being seen through water scarcity, resulting in issues with water restrictions, as well as crop losses which leads to food insecurity (Sasol Limited, 2019). According to the Working Group I sixth assessment report published by the Intergovernmental Panel on Climate Change (IPCC) in August 2021, a 1.5 ℃ warming may be reached or exceeded in the next twenty years. If emissions continue to rise, a 4.4 ℃ warming may be reached in the world by 2100, leading to catastrophic consequences (IPCC, 2021). Considering the recent widespread fires experienced in Germany, Australia and United States, massive floods in Germany, Belgium and China, and the large loss of ice in the Arctic, the impact and effect of global warming and climate change is being experienced by the entire world (Waskow & Gerholdt, 2021).

To achieve and combat issues related to the United Nations Sustainable Development Goal 13: Climate Change, stringent regulation policies have been implemented to reduce ground level ozone by the monitoring and control of VOCs. This includes several actions undertaken by the

South African Government, of which The South African Carbon Tax Act 15 of 2019, imposes carbon tax on emissions (Government Gazette: Republic of South Africa, 2019), and The National Atmospheric Emission Inventory System (NAEIS) which is an integration between the management of Atmospheric Emission Licenses (AEL) and The National Environmental Management: Air Quality Act 39 of 2004 which instructs process industries to report their estimations of atmospheric emissions (Government Notice, 2015).

South Africa's commitment to a lower-carbon economy is further supported by the Paris Agreement (to which South Africa is a signatory), which aims to "reduce Greenhouse Gas (GHG) Emissions by at least 40% by 2030 and limit the global average temperature increase to well below 2 degrees Celsius" (Nqwababa & Cornell, 2019).

Due to the reliance on fossil-fuel derived energy and the lack of available infrastructure, knowledge and commercialization of renewable energy sources, there are numerous challenges to integrating a low-carbon economy in South Africa (Nqwababa & Cornell, 2019). A leading anthropogenic source of VOC emissions include oil and gas industries in which refinery petroleum storage tanks are the single largest point source of VOC emissions (Howari, 2015). According to Maxwell and Lawal (2016), 31.5% of VOC emissions occur from gasoline or oil storage tanks and IMPEL Network (2000) suggested that tank areas contribute 42% of the total emission sources from an oil refinery. In South Africa, Sasol is one of the highest carbon-emitting companies with total greenhouse gas emissions of 67 632 million tons in 2017, as well as globally with annual greenhouse gas emissions greater than that of the countries such as Denmark, Sweden and Switzerland combined (Cairns, 2019). SAPREF Refinery is another refinery based on the East Coast of South Africa, is the largest crude oil refinery in the country, and hence an obvious candidate for the release of high quantities of VOC emissions. This is evident from the 2016 SAPREF sustainability report in which1906 t/a VOC emissions were reported for 2016, with fugitive emissions being the main contributor to VOC emissions. Fugitive emissions occur from leaks from storage tanks and equipment (SAPREF, 2016). No recent reporting's have been released.

Environmental protection is not the only driving force towards the monitoring and control of VOC emissions. Safety is a critical factor in process industries, especially in the petrochemical industry where the proper containment and management of flammable liquids and vapours need to be considered. Change and Lin (2006) reported that 85% of major industry incidents are attributed to storage tank fires or explosions. The most recent incident reported by Engen

was a fire which occurred in December 2020, resulting in the release of toxic benzene and traumatised community members. Following this and a series of events, Engen Refinery announced its complete shutdown in April 2021. Between 2000 and 2017, the Durban South Basin has seen more than 55 major incidents resulting from fire, in which majority of those were from storage tanks (Nkgadima , 2017).

1.1 Justification

While it is commendable that industries have responded to the new South African legislation such as the implementation of Carbon Tax, there is a lot more work that is needed to be done to address the impacts of climate change. Sasol, for example, has implemented an emission reduction roadmap based on a three-pillar emission-reduction framework which aims to reduce emissions by 10% in South African operations by 2030 (Sasol Limited, 2019). The drive in process optimisation focusing on improving current operations efficiency and the implementation of renewable energy is seen in the reduction strategy outlined by Sasol (Sasol Sustainability Report, 2020).

Currently, a common method used in petroleum industries for VOC emissions estimation was developed by The Environmental Protection Agency (EPA) (United States), which is based on the AP-42 model for air pollutant emission factors and will be discussed further in Chapter 2. Other methods including direct methods such as Leak Detection and Repair (LDAR) or DIAL (SAPREF, 2016), have been utilised to monitor VOC emissions in industry. However, for companies such as Sasol and others to accurately monitor and control their emission reduction targets, more reliable estimation methods using current plant data are required to predict VOC emissions over time. LDAR and DIAL become inadequate in monitoring small leaks and it is not a continuous monitoring method. According to Heath & Liu (2016), technologies such as TANKS Emissions Estimation Software (Version 4.09D), a process simulation software, has been developed and commonly used in industry thus far. However, this process simulator is considered outdated and offers inaccurate estimates due to software issues experienced and is not compatible with modern operating systems (Heath & Liu, 2016). Insight into innovative technologies to provide improved estimates employing rigorous thermodynamic and transport calculations are therefore required to properly control VOC emissions and monitor reduction methods.

One of the most popular reduction and safety methods includes tank blanketing in which a layer of inert gas such as nitrogen is used to fill the headspace of the tank (Parker HannifinCorp, 2016). The inert gas produced by an inert gas generator replaces the displaced volume of crude oil during offloading, whilst maintaining a slight overpressure within the tank. This method maintains safe operating and working conditions where the pressurized blanketed gas is directed to a safe location. However, the inert gas and a high concentration of VOCs are vented to the atmosphere (Childs & Sipkema, 2006) (European Commission, 2006). Another commonly used practice by many industries to reduce VOC emissions include gas-flaring or combustion processes which incinerates the organic compounds produced in the off-gas under extreme temperatures. However, the release of other environmental pollutants such as carbon dioxide and nitrous compounds suggests further investigation into more sustainable reduction methods (Best Available Techniques, 2006).

In context of the research presented, the aim of this study was to quantify the VOC emissions for two types of storage tanks (Fixed roof and Internal Floating Roof), predict the losses for a range of conditions and determine the effect of mitigation strategies on these emissions. The Fixed roof and Internal Floating Roof type storage tanks are most commonly used in petroleum industries for storage of organic liquids and offer significant opportunity for reduction of VOC emissions through control measures. Five organic mixtures were investigated which included: Crude oil, Unleaded Petrol (ULP 95), Ultra-low Sulphur Diesel (ULSD), Jet fuel (JET A1) and Marine Gas Oil (MGO). This included emission calculations on fixed roof and floating roof storage tanks based on the EPA AP-42 standards for all mixtures. ASPEN Plus ® was used to model the storage tanks for the prediction of flashing losses and the effects of various parameters such as temperature and pressure, were investigated.

The objectives of this study are:

I. Determination of VOC emissions from petroleum storage tanks based on the evaluation of measurement methods, namely manual flash calculations, Aspen Plus ® simulations and empirical correlations such as the Vasquez-Beggs (Vazquez and Beggs, 1977) and Valko-McCain (Valko and McCain, 2003).
II. Identification of trends and increase of VOC emissions based on the Air Emission License provided by the aforementioned methods.
III. Development of a predictive method to improve the analyses of VOC emissions from petroleum storage tanks based on ASPEN Plus ®.

IV. Performing an Environmental Impact Assessment based on the toxic substances.
V. Recommendations towards managing VOC emissions based on implementation strategies and Best Available Techniques.

To establish the effects of previous practices, and the consequences of future non-action, an environmental impact assessment of VOC emissions from petroleum storage tanks is conducted in this work using baseline sustainability reports of various petroleum refineries. This assessment highlights the specific need for developing protocols and tools to assist in the monitoring and control of VOC emissions from storage tanks, to reduce the impact on the environment, ensure process safety and abide with new legislature in South Africa.

Five organic mixture systems were considered to understand the uncertainties and limitations involved using the proposed method, in comparison to other options. Manual calculations were considered and compared to the AP-42 method to estimate breathing and working losses and a comparative study was done against empirical correlation estimates. Safe operating conditions were investigated by determining the effect of varying temperature and pressure of the storage tank; and an in-depth study on VOC emission reduction strategies was conducted for implementation in industry.

ASPEN Plus ® was used to determine its ability in modelling and predicting VOC flashing losses from the storage tanks. Due to its ability to offer rigorous estimation of thermodynamic and transport properties, and a rigorous tank safety and design option, it was used to estimate the effect of nitrogen blanketing inbreathing and outbreathing rates. There is a scarcity of research in the literature regarding the estimation of VOC emissions using the Aspen Plus ® platform, and the precision of the methods available in the software.

1.2 Outline of the Thesis Structure

Chapter 1 outlines the introduction, aims and objectives of the research.

Chapter 2 discusses the rationale of the research and presents an overview of the environmental and health effects of VOC emissions, sources of tank emissions, and factors affecting tank emissions. The monitoring methods of air emissions from storage tanks, common mitigation methods, process simulator requirements and South African legislations relating to air emissions are included.

Chapter 3 describes the input parameters required for model development and emissions characterisation parameters.

Chapter 4 focuses on the results obtained from various estimation methods used to quantify VOC emissions, discusses its effect on the environment and displays the resulting effects of utilising reduction strategies or methods.

Chapter 5 integrates the work and draws conclusions to the contributions of this research. Key recommendations for implementing integrative mitigation strategies are also included in this chapter.

CHAPTER TWO: LITERATURE REVIEW OF MONITORING AND MITIGATION OF VOC EMISSIONS FROM PETROLEUM STORAGE TANKS

Climatic factors coupled with urbanization and its dependence on fossil fuel for a multitude of purposes, have caused a rapid increase in hazardous gas emissions globally. Fugitive and flashing VOC emissions are major sources and types of emissions from oil and gas industries. These emissions are gaining much attention due to its ability to form ozone, resulting in pollution, and enhancing the effects of global warming. In the oil and gas industry, storage tanks are employed extensively for storing crude oil prior to process operations as well as storing refined downstream products before transportation. Due to the volatile and flammable nature of the hydrocarbons stored in the tanks, design and safety considerations have been emphasized to reduce environmental pollution and the risk of fires and explosions. The ramifications of VOC emissions have therefore prompted research to reveal the effects and benefits of monitoring and controlling VOC emissions from petroleum storage tanks. This chapter provides a review of literature relevant to petroleum storage tank VOC emissions and the associating factors which influence emissions as well as mitigation methods currently being employed in industry to control and reduce VOC emissions. The thermodynamic property methods were also reviewed for implementation and use in process simulation.

2.1 Volatile Organic Compounds

VOCs can be defined as any organic compound which contain carbon and can take part in atmospheric photochemical reactions. These reactions form ozone when alkyl radicals are oxidized, which subsequently react with atmospheric nitric oxide. The reactions occur at ambient conditions, when atmospheric nitric oxide is present at >10 ppt. Due to VOCs low boiling point and high vapour pressure, VOCs may undergo evaporation at ambient conditions. Its vapour pressure at a temperature of 273.15K is 0.01 kPa (U.S. Environmental Protection Agency, 1992). VOCs are representative of types of chemical species which can be produced naturally through living organisms (biogenic sources) or as a result of human activity (anthropogenic sources) (Mo, et al., 2015). Although there are large amounts of biogenic sources (non-methane) of VOC emissions emitted throughout the world, anthropogenic sources surpass biogenic sources due to increased industrial activities. These anthropogenic sources may arise from industrial processes such as petroleum refining, extraction, storage, and transportation or even through the production of polymers (Rebollar-Perez, et al., 2012).

2.2 Tank Emissions

There are various sources of air emissions from storage tanks during normal operating conditions. Flashing losses are the major source of emissions under normal operation when compared to evaporative losses. For example, the storage vessels used in the oil and gas industries can contain crude oil, volatile organic liquids (VOLs) and various petroleum products and condensates. The produced liquid mixture (at its bubble point) from a crude fractionation train exits a high-pressure separator and enters atmospheric pressure storage tanks in which the liquids are stored. The change in pressure experienced from the transfer of liquids initiates the vaporization of light hydrocarbons from the stored liquid in the tank. This causes the flashed hydrocarbons to accumulate in the headspace of the tank. Due to the atmospheric conditions of the tank, the vapours are vented to the atmosphere. Secondary tank emissions produced from unsteady state processes include Working, Breathing and Loading losses. Generally, the EPA AP-42 standards are used to determine these losses (Burr & Georgeson , 2013). This may include emissions from the transfer of liquid into and out of the tanks by filling or emptying. Emissions caused by temperature increases in the tank may result in thermal inbreathing due to the expansion of the vapour space within the tank. Fugitive emissions may result from point sources or connections on the tank, such as fittings, pumps, gaskets, or flange seals. Other sources of emissions may include sampling methods and emissions during cleaning or maintenance operations. However, tank emissions are not restricted to operational losses and losses from incidents or major accidents such as overfilling, leakages or tank ruptures contribute further to tank losses and VOC emissions (Integrated Pollution Prevention and Control, 2006).

Decreasing emission thresholds are being implemented by the EPA, local agencies and companies including the enforcement of stricter regulation policies based on legislations in South Africa in monitoring and mitigating against the effects of climate change. With the implementation of Carbon tax and stringent air monitoring guidelines, it is imperative that industries adhere to these guidelines. Appendix B presented background information on the legislature, regulations, and carbon tax policies.

The determination of short-term (Daily VOC emissions) and long-term (Annual VOC emissions) emission estimates is therefore crucial in the oil and gas industry. Emission estimates may also be predicted for the use of employing emission control methods such as vapour recovery systems, which include flaring or installing compressors. Therefore, the use

of accurate emission calculation methods is needed to allow for maximum control of emissions as well as the design of facilities and procedures that reduces atmospheric emissions (Burr & Georgeson , 2013).

When determining the quantity of tank emissions to the atmosphere, five main components should be considered, namely: 1) tank parameters, 2) sources of tank emissions 3) the chemical makeup of stored liquid in the tanks, 4) the atmospheric conditions of the tank location and 5) the timeframe for standing time (ERA Environmental Management Solutions, 2019).

2.2.1 Tank Parameters

The quantity of emissions emitted from storage tanks are reliant on the physical characteristics of the storage tank. The type of tanks, type of roof, shape of roof, storage tank shell colour and condition of the tank are all major factors that should be considered prior to the containment of liquids to ensure minimal emissions are being emitted into the atmosphere (ERA Environmental Management Solutions, 2019).

2.2.1.1 Types of Tanks

Several types of storage tanks exist and may be used to store various chemical compounds. Common storage tanks used in industry include external floating roof tanks, internal floating roof tanks, fixed roof tanks, pressure tanks, horizontal tanks, and vapour variable space tanks (Ciolek, 2006). However, floating roof tanks are commonly used in industry to store volatile hydrocarbon liquids such as crude oil and light hydrocarbon products such as jet fuel, diesel, and gasoline. These tanks are preferred due to its ability to keep the volatile vapours sealed below the roof during normal operating conditions, when it is more susceptible to escape (Simon, 2014). A risk matrix is used to determine the potential for implementing control methods to the storage tanks and is based on the rate of emissions. It is a measure of the risk-inspection and is a product of the emission frequency and volume. The score ranges from 1 to 6. Scores are deemed high when its volume and frequency are high and equal to 3 and hence, control measures should be implemented. Table 2-1 to 2-2 provides a summary of the description of various tanks and an indication of the emissions of the type and volume of emissions.

Table 2-1: Analysis of the distinct types of tanks (Ciolek, 2006)

	External Floating Roof Tanks	Geodesic Dome Floating Roof Tanks	Pontoon-Type Floating Roof Tanks	Double-Deck Floating Roof Tanks	Fixed Roof Tanks	Internal Floating Roof Tanks	Horizontal Tanks (pressure)	Pressure Tanks	Variable Vapour Space Tanks
Description	Comprises of an open-top floating roof deck which lies on the surface of the liquid in the tank, enabling it to adjust to the liquid level due to filling or emptying. Reduced emissions due to limited vapour space.	Commonly used on external floating roof tanks and is highly suitable for use in locations which experience extreme weather conditions. Reduced emissions due to less wind from the rim seals.	Comprises of an annular pontoon, placed over quarter of the surface of the roof. It contains compartments which alleviate the potential of ruptures or damage to the tank from occurring.	Comprises of a double deck which increases its structural ability, making it more durable to the effects of wind.	Typically, cylindrical, and vertical in shape. May be comprised of a cone or domed shape roof. Operating pressures of 20 mbar or 56 mbar may be used for low pressure and high-pressure tanks respectively. Reduced emissions from nitrogen blanketing or VRUs.	Comprises of a fixed roof and an internal floating deck which adjusts according to the level of liquid in the tank. Non-contact decks are typically used. Reduced emissions due to seals. However, limitations in tank capacity.	Considered small tanks due to its low capacities of 75 – 710 L. May contain pressure-vacuum relief vents, sample wells, and gauge hatches which provides easy accessibility. Above-ground tanks mainly consist of working and breathing losses.	Used to store organic liquids at a high pressure of greater than 103.42 kPa. Consists of vacuum vents which avoid emission losses from changes in temperature and pressure (breathing losses) and boiling losses.	Contain vapour reservoirs which may expand to allow for variations in volume which results from changes in temperature or pressure. Common losses due to filling - breathing and working losses.

Table 2-2: Analysis of the distinct types of tanks (Ciolek, 2006) (Continued)

Material of Construction	Steel Shell	Aluminium Shell with self-supported bolted dome	Steel Shell	Steel Shell	Steel Shell	Steel Shell and Aluminium Deck	Steel Shell with Fibreglass Covering	Steel Shell	Steel Shell
Frequency of Use (Often/ Rare)	Often	Often	Often	Often	Often	Often	Rare	Rare	Rare
Emission Frequency*	1	1	1	1	2	2	2	2	2
Emission Volume*	3	3	3	3	3	3	1	1	3
Emission Score*	3[a]	3[a]	3[a]	3[a]	6[a]	6[a]	2[b]	2[a]	6[a]

* Emission score for filling losses. Taken from references (Best Available Techniques, 2006)[a] and (Ciolek, 2006)[b].

2.2.1.2 Tank Shell Colour and Tank Shell Condition

The colour and condition of a storage tank's shell and roof plays a major role in the quantity of evaporative emissions lost from storage tanks (Stricklin, 2014). If designed properly whilst considering appropriate tank colours and ensuring the shell condition is of good quality, there is a possibility of significantly reducing emissions lost to the atmosphere. Temperature is a major factor that drives evaporative emissions from storage tanks. The temperature of the liquid contents in the tank determines the quantity of emissions released into the atmosphere. The stored liquid in tanks is mainly heated through solar radiation. However, the condition and colour of the paint on the shell and roof, determines the degree to which the stored liquid is heated. Therefore, it is imperative to use paints with a high reflective ability such as those with a low solar absorbance as this paint will allow for slowing retard heating compared to high solar absorbance paints. Hence, tanks with highly reflective paints will maintain a lower temperature of the stored liquid in the tanks, releasing lower emissions. White paint is considered to have a low solar absorbance therefore desired for use in industries to potentially reduce standing losses from storage tanks (Stricklin, 2014). Table 2-3 to 2-4 shows the solar absorbance values for various surface colours at good and poor tank conditions.

Table 2-3: Solar absorbance for various surface colours at a specific surface condition (Stricklin, 2014)

Surface Colour	**Shade or Type**	**Solar Absorptance (∝) Surface Conditions**	
		Good	**Poor**
Aluminium	Specular	0.39	0.49
Aluminium	Diffuse	0.60	0.68
Beige/Cream		0.35	0.49
Brown		0.58	0.67
Gray	Light	0.54	0.63
Gray	Medium	0.68	0.74
Green	Dark	0.89	0.91

Table 2-4: Solar absorbance for various surface colours at a specific surface condition (Stricklin, 2014) (Continued)

Red	Primer	0.89	0.91
Rust	Red iron oxide	0.38	0.50
Tan		0.43	0.55
White	-	0.17	0.34
Aluminium	Mill finish, unpainted	0.10	0.15

The condition and colour of paint used is not justifiable with all types of tanks (Stricklin, 2014). The aforementioned points apply to fixed roof tanks and variable vapour space tanks; however, it may not be directly applicable to external floating roof tanks. Pan-type external floating roofs may benefit from reflective paints as it has the potential to reduce boiling and ultimately reduce the quantity of emissions lost. However, pontoon and double-deck type roofs may not benefit from reflective paints due to its design capability which prevents heat transfer through an insulation barrier. However, reflective paints may be used on the tank walls or shell to aid with the reduction of boiling within the seals to reduce the temperature of the contents within the tank thereby reducing emissions. Reflective paints may be useful to reduce variations with pressure, on pressure tanks. However, colour is not of paramount importance compared to fixed roof or variable vapour space tanks (Taylor & Francis Group, 1971).

2.2.2 Sources of Emissions

There are six main types of emissions which may occur from petroleum storage tanks, namely: 1) breathing losses, 2) standing losses, 3) filling losses, 4) emptying losses, 5) wetting losses and 6) boiling or evaporative losses (Taylor & Francis Group, 1971). Table 2-5 represents the losses from each type of tank.

Breathing losses occur because of thermal expansion of vapours in the tank, barometric changes with pressure or from an increase in vaporization of the product, without altering the level of liquid in the tank, leading to an increase in vapours formed. Breathing losses also commonly occur when changes in pressure or volume thresholds are exceeded, thereby the

losses are forced to escape into the atmosphere. It may occur in most tank types however, fixed roof tanks which lack proper insulation, have no insulation, or designed for vacuum are more prone to experience higher breathing losses. Fixed roof tanks with proper insulation and good condition reflective paint will generally have lower breathing losses. Pressure tanks designed to operate above 17.24 kPa have a very low probability of experiencing breathing losses. Floating roof tanks operate by reducing the vapour space within the tank thereby eliminating the possibility of breathing losses occurring (Taylor & Francis Group, 1971). Similarly, variable vapour space tanks reduce the breathing loss potential (Taylor & Francis Group, 1971).

Standing losses are all losses other than breathing losses and losses resulting from a liquid level change at ambient conditions. A significant quantity of standing losses from floating roof tanks occurs due to poor maintenance or design. A primary seal is a device used to close the gap between the tank wall and the floating deck. Floating roof tanks may utilise mechanical shoes, resilient filled and flexible wiper seal type primary seals. A mechanical shoe seal consists of metallic band made up of a series of sheets which forms a ring and is connected to the tank by mechanical means. Through improper maintenance, the seal and the shoe are improperly connected to the shell of the tank and this provides a source of leakage. This may also provide a means for the release of vapour through the permeable membrane seal which is in the middle of the roof and shoe. Guaging hatches or pressure vacuum vents, various fittings from equipment as well as wind are also other major factors contributing to the release of vapours (Taylor & Francis Group, 1971).

Filling losses occur when the internal pressure of the tank is greater than the relief valve pressure and as a result, the expulsion of vapour occurs from a storage tank during the process of loading or filling the tank. Fixed roof tanks experience a high rate of losses by filling as it has a low-pressure relief, resulting in more filling losses released into to the atmosphere. Due to the increased capacity for the storage of vapours with variable vapour space tanks, variable vapour space tanks have a lower potential of emitting losses during the filling operation. Pressure tanks operate slightly differently, by condensing hydrocarbon vapours to reduce the loss of emissions during the loading process. Floating roof tanks do not exhibit significant filling losses but are subject to other sources of emissions (Taylor & Francis Group, 1971).

Emptying losses occur because of a decrease in partial pressure of hydrocarbon vapours when the vapour space of the tank expands faster than the rate of vaporization, during emptying of the tank. During tank withdrawal, to sustain the atmospheric pressure within the tank, a

sufficient amount of air naturally enters the tank. Once equilibrium of the vapour molecules is reached, the capacity of the vapour space becomes supersaturated with VOC vapours which causes this vapour to be expelled into the air. This is known as the emptying losses. Fixed roof tanks are the most susceptible to emptying losses whereas floating roof tanks are the least. Variable space tanks and pressure tanks may experience emptying losses only if the volume of the vapour exceeds the capacity of the vapour space (Taylor & Francis Group, 1971).

Wetting losses are generally minimal and occur as a result of lowering a floating roof during emptying of a tank which allows for the surface of the wetted tank walls to be exposed. The liquid on the tank walls then vaporize to the atmosphere and are termed wetting losses (Taylor & Francis Group, 1971).

When a liquid boils and vaporization occurs, boiling losses are emitted into the atmosphere. Boiling losses are typically more significant in fixed roof tanks than in a pressure tank (Taylor & Francis Group, 1971).

An additional consideration that is related to conditions of flashing, but ultimately forms part of working losses is pump cavitation. This was assessed for the sales oil stream, exiting the tank as shown in Figure A-1, but can be extended to all pumps associated with the storage process. Pump cavitation is an important consideration during flashing where rapid pressure changes occur, as it is necessary to ensure that vibration, damage, and noise are minimised or prevented (Kelton, 2018) during emptying procedures.

Table 2-5: Losses for each type of tank (Best Available Techniques, 2006)

Types of losses	External Floating Roof Tanks	Geodesic Dome Floating Roof Tanks	Pontoon-Type Floating Roof Tanks	Double-Deck Floating Roof Tanks	Fixed Roof Tanks	Internal Floating Roof Tanks	Horizontal Tanks	Pressure Tanks	Variable Vapour Space Tanks
Breathing	High	High	High	High	High	Medium	High	N/A	Low
Standing	High	High	High	High	High	Medium	High	N/A	Low
Filling	Low	Low	Low	Low	High	Low	High	Medium	High
Emptying	Medium	Medium	Medium	Medium	Medium	High	Medium	N/A	Medium
Wetting	Medium	Medium	Low	Low	High	High	High	High	N/A
Boiling	N/A	N/A	N/A	N/A	Low	N/A	N/A	N/A	N/A

2.2.3 Chemical composition of the Stored Liquid

The type of chemicals stored in storage tanks ultimately determine the type and quantity of emissions produced. Therefore, it is imperative to maintain a comprehensive understanding of the properties of the chemicals being stored in the tank. Properties such as vapour and liquid density and molecular weight should be known (ERA Environmental Management Solutions, 2019). The present study is conducted on volatile hydrocarbons such as components of crude oil and various fuel derivatives. It is therefore necessary to establish the internal and external factors which may affect the physical or chemical properties and the stability of the hydrocarbon products.

2.2.3.1 Hydrocarbon chemical reactions

The chemical stability of a fuel can be characterized by its ability to resist oxidation during operations. Whereas thermal stability is referred to as the ability of a fuel to withstand being degraded at high temperatures (Bentley and Schellhase, 1983). If the stability of the fuel is altered, various undesirable processes such as: polymerisation, condensation of unsaturated compounds or autocatalytic oxidation may occur leading to the formation of resins, gums insoluble deposits and the attack of metals by acidifying compounds (Owczuk & Kotodziejczyk, 2015).

These undesirable processes, in addition to self-oxidation, pyrolysis and thermal oxidation may lead to fuel degradation or may form deposits on the fuel thus affecting the quality and performance of the fuels. Self-oxidation is a common process that occurs with fuels stored in storage tanks over long periods of time. Gasoline, diesel, and turbine oil are most likely to undergo self-oxidation during storage (Bentley and Schellhase, 1983). This spontaneous catalysed reaction occurs as a result of a series of radical-chain reactions. These reactions occur in phases of initiation, propagation, and termination. Pyrolysis is the process whereby the fuel structure decomposes, and heated surfaces may experience thermal oxidation which results in the deposition of unwanted substances, usually in nozzle and sprayers. Thermal oxidation is a process which occurs at elevated temperatures of 473.15 K or higher. Thermal oxidation is commonly experienced with fuels contacted with surfaces of high temperatures (Owczuk & Kotodziejczyk, 2015).

Due to the complex chemical structure of fuel compounds, its susceptible nature to degrade and various oxidation rates, it is difficult to determine an oxidation model from current literature. Therefore, various studies by Owczuk and Kotodziejczyk (2015), Bentley and

Schellhase (1983) and Biernat (2015) indicate that the oxidation rate is governed by the following factors which are dependent of the conditions of the storage tank: 1) physio-chemical fuel properties such as composition of the fuel, 2) atmospheric conditions such as temperature, pressure and humidity and 3) compounds which may aggravate oxidation as well as the materials of construction of a storage tank.

Due to the varying structure of fuel compounds, every hydrocarbon group has a different tendency to undergo oxidation. Owczuk and Kotodziejczyk (2015) report that paraffins are the most susceptible to oxidation, then naphthenes and aromatic compounds are the least resistant due to its chemical structure which lacks long side chains. The ability to undergo oxidation is proportional to the length of side chains and length of carbon atoms present in a molecule, high temperatures, and molecules which exhibit complex structures. Hence, a longer side chain length in a molecule increases the potential to produce oxygenated compounds through the decomposition process (Biernat, 2015). Therefore, branched aromatic compounds are least resistant to oxidation as decomposition of the side chains leads to the formation of various acids, aldehydes and peroxides, as an attack on the aromatic hydrocarbon ring by oxygen may occur. Even though paraffins show resistance to self-oxidation, higher temperatures may lead to a greater possibility of oxidation occurring (Biernat, 2015), (Owczuk & Kotodziejczyk, 2015).

Fuels are comprised of various hydrocarbons which are blended. Therefore, there is a higher tendency for oxidation to occur when these compounds are in contact. This may occur as a combination of highly susceptible and poorly susceptible hydrocarbons to oxidation such as aromatic hydrocarbons and naphthenes, which will yield a higher oxidative stability than naphthenes only. However, studies by Owczuk and Kotodziejczyk (2015) have shown that aromatic hydrocarbons with a 20 – 30 % by concentration, mixed with paraffins and naphthenes may have a lower oxidative stability. This results in a lower production of deposits and tars. That concentration is deemed as the optimal concentration of aromatic hydrocarbons as concentrations on either end of that range may limit oxidation from occurring, thereby, producing a range of larger molecules such as asphalthenes which are insoluble in fuel (Owczuk & Kotodziejczyk, 2015).

Various other external factors such as temperature, pressure, humidity, and the presence of oxygen in the atmosphere may also affect the rate of oxidation of fuels (Owczuk & Kotodziejczyk, 2015).

Temperature can affect conversion rate of fuels via oxidation, which in turn results in a change in the number of products formed from certain processes. An increase in temperature will lead to an increase in the number of products formed at various conversions, during the oxidation process. Hence, the tendency of fuels to undergo oxidation at higher temperatures is high (Biernat, 2015). Therefore, it is vital to monitor the atmospheric temperature of storage tanks which contain fuel, to ensure the effects of temperature are limited to prevent self-oxidation from occurring (Owczuk & Kotodziejczyk, 2015).

Temperature variations within the range of 243.15 K – 323.15 K, can cause changes in the chemical and physical properties of the fuel stored in a storage tank. The chemical effects may be in the form of oxidation, polymerization, corrosion, solid materials, depositions of unwanted substances or may even produce emulsions within the fuels (Biernat, 2015). The physical effects may be experienced in the form of crystallization, creation of new phases and ice crystals or even changes with the water and oxygen solubility (Owczuk & Kotodziejczyk, 2015).

Large amounts of water and oxygen may accumulate in storage tanks due to variations in temperature of the fuel (Kosuru et al., 2021). These temperature variations may lead to irreversible effects. Lower temperatures, however, have a considerable effect such as depositions or dispersion of phases which may remain even with an increase of temperature (Biernat, 2015). This may be more prominent with long chain hydrocarbons which have the potential to stratify and are more likely to settle at the bottom of the tank. However, the effects of lower temperatures on fuel properties are dependent on the content and composition of hydrocarbons present in fuel. For example, precipitation in the form of crystals may occur in diesel, which contains approximately 20 % paraffins, at lower temperatures due to its poor solubility (Owczuk & Kotodziejczyk, 2015).

2.2.3.2 Effect of storage tank design on chemical stability of hydrocarbons

It is also important to ensure that the surface of the storage tanks is properly designed for the protection from direct solar or thermal radiation as the stored products may be reactive at temperatures of 313.15 K or higher. This is due to increased reaction rates as an exponential relationship exists between the rate of reaction and temperature (Biernat, 2015). The converse exists for temperatures of 243.15 K or lower, where the reaction occurs at a reduced rate. Studies by Owczuk and Kotodziejczyk (2015) have shown that the optimal storage temperature

conditions for fuel products lie between the range of 293.15 K – 303.15 K. Between this range, the self-oxidation rate of fuels is considerably low (Owczuk & Kotodziejczyk, 2015).

Pressure is another factor which may affect the oxidation of fuel (Biernat, 2015). Increases in pressure may result in higher oxidation rates. This is because of the breakage of unsaturated hydrocarbon bonds to produce compounds with a longer chain length, as represented by Reaction 1. Hence, leading to the formation of deposits in the form of carbon and resin compounds (Owczuk & Kotodziejczyk, 2015).

$$\text{(monomer) } nCH_2 = CH_2 \xrightarrow{P,T} [\,-CH_2\,-CH_2\,-]_n \text{ (polymer).} \qquad \text{(R1)}$$

Humidity or moisture content is another factor which affects the oxidation rate. Reactions which contain radicals utilise water therefore, water may be present in various forms within the fuel. Water may be dissolved or emulsified in the fuel, dispersion of ice crystals may be found in the fuel or water, or ice may be present on the surface of the tank walls or near the bottom of the tank. These water phases are dependent on the temperature and pressure and may be present as solid or liquid, depending on the atmospheric conditions. At higher temperatures the water solubility will be higher, whereas hydrocarbon compounds with a larger molecular weight will have a lower solubility of water in fuel. At lower temperatures crystallization of water may occur. This could lead to adverse effects as the ice crystals formed may cause blockages in filter or tubing systems (Owczuk & Kotodziejczyk, 2015).

The formation of microorganisms in fuel storage tanks is another consequence of the presence of water (Yemashova et al., 2007). Microorganisms may increase the rate of oxidation as well as the concentration of active agents present on the surface. The pH of the water at the bottom of the tank may also decrease due to the presence of the microorganisms, leading to a possible cause of corrosion of the tank which eventually contributes to emissions (Owczuk & Kotodziejczyk, 2015).

The aforementioned information is an important part in determining the effects of chemical stability of fuel and its derivatives and its effects on emissions. Therefore, various tests have been developed to determine the stability of fuels to ensure good quality fuels are present (Owczuk & Kotodziejczyk, 2015).

2.2.3.3 Methods of determining the stability of fuels

The ASTM D 873 test is a method used to determine the probability of the formation of resin deposits on fuel under long-term storage conditions. This test may also be used to determine the stability of unleaded gasolines and is commonly used in industry. Another test method is the ASTM D 4625 method which exposes the fuel to an oxidation process under a temperature of 316.45 K and uses an IR spectrum to determine the content of resins formed. This test is considered the most reliable method however, it is not commonly used as it is time consuming and expensive. The ASTM D 2274 test has been studied extensively over the past years and yields a good representation between the results obtained from the oxidation stability test and that from using field conditions.

The RANCIMAT method is used for diesel products and utilises an oxidation curve of conductivity versus time to measure the oxidation stability of the fuel (Owczuk & Kotodziejczyk, 2015).

2.3.4 Atmospheric Conditions

Atmospheric conditions such as the temperature or the altitude of the storage tank significantly affects the rate of emissions into the atmosphere. Using recorded weather data from the specific region being studied will improve the accuracy of the emissions estimated (ERA Environmental Management Solutions, 2019). The analyses of conditions applied to this study utilised meteorological data from areas KwaZulu-Natal (Durban), South Africa.

2.3.4.1 South African Climate Conditions and Geographical Location

South Africa is situated in the high-pressure (HP) belt and is considered a subtropical region due to the presence of three HP cells which dominate over the region. The South Indian, Atlantic and Continental HP cells influence the anticyclonic circulation of the atmosphere within the country. High pressure cells or anticyclones may lead to convergence within the upper most part of the atmosphere in the troposphere, divergence close to the surface of the earth or even strong disruptive conditions within the troposphere. These anticyclones may then yield stable atmospheric conditions with satisfactory air conditions, inversions, and slight to no rainfall (Caddick, 2019). These conditions are undesirable for the dispersion of air pollutants within the atmosphere when emitted from the ground or surface level. However, easterly, and westerly waves are common occurrences within the country which may lead to convective activity, which may prevent or disrupt the inversion placed over the country. Hence, air

pollutants may be well dispersed through the atmosphere due to the upward motion of the air pollutants through the atmosphere. The accumulated air pollutants may also dilute and disperse evenly within the atmosphere (Golder Associates, 2019a) (Golder Associates , 2019b)

Warm temperatures (approximately 300 K) are generally experienced throughout the course of the year. However, hot weather with thunderstorms in the afternoon may be experienced in the summer during November to February, whereas mild (approximately 293 K) and dry weather is experienced in winter during May to August. Lower temperatures (approximately 288 K) and lower rainfall are usually experienced in the west coast of South Africa, while higher temperatures (approximately 306 K) and higher rainfall usually occur on the east coast of the country. The dispersal of air pollutants may also be affected by the diurnal wind variations which is controlled by the circulation of the land and sea breeze (Caddick, 2019).

2.3.4.2 Durban Climate Conditions

Durban is regarded as a sub-tropical climate with humid weather conditions. It can be considered as one of the areas within South Africa which experiences the most amount of rainfall, especially during the summer months, which is typically approximately 760 mm in the northern interior part of Durban and around 1250 mm on the coast of Durban. In winter, the presence of the anticyclone leads to drier, milder conditions however, slight rainfall may occur due to the traversing frontal systems. Higher rainfall is desired across regions with considerable industrial activities such as Durban, as rainfall aids in the dilution of air pollutants as well as increases the content of moisture of potential eroding materials to reduce the effects of erosion.

Larger differences in temperatures between atmospheric air and emission plumes allows for the plume to rise rapidly through the atmosphere. Therefore, retrieving ambient temperature conditions provide significant information into determining the mixing potential of the inversion layers within the atmosphere (Shell and BP Refineries , 2018).

Wind is another key climate factor that affects the dispersion of atmospheric air pollutants. The highest diurnal wind velocities in Durban are experienced during the afternoon in the months of summer and winter and the direction of wind is determined by the sea and land breezes. However, calm climate conditions with wind speeds of up to 1 m/s (Golder Associates, 2019a) and gentle winds from a north-easterly direction may be experienced during the winter months. Typically, wind speeds from approximately 0 m/s to 8.2 m/s are experienced in Durban from a west-south westerly and east-north easterly direction. Light northerly winds may also be

commonly experienced with wind speeds of up to 3.1 m/s (Shell and BP Refineries , 2018). Wind is a major contributor to the emissions monitored from external floating roof tanks and affects the rim seals. This is due to wind-induced vibration, as well as convective effects inducing a low-pressure region external to the seal.

2.3.5 Timeframe for fuel Standing Time in Storage Tanks

The time required for a liquid to be stored in a tank prior to its transferral is vital for the understanding of monitoring and controlling of air emissions (ERA Environmental Management Solutions, 2019). Long-term storage of fuel is not desirable, and studies have been conducted to determine its effect on its physio-chemical properties and chemical stability (Owczuk & Kotodziejczyk, 2015).

The Automotive Industry Institute (PIMOT) conducted research by testing and analysing the long-term storage effects of gasoline and diesel. Gasoline storage was studied for four years, and results suggested that the sulphur and microbial content, corrosion of copper and the pH of water were not affected.

However, the factors that were affected included:

- the Research Octane Number (RON) of the fuel which decreased over time due to the production of resins caused by chemical reactions occurring within the fuel
- the quantity of resin, which decreased over a period of a year due to the addition of new fuel into the storage. This resulted in in the requirement of additional time for stabilisation to occur after which oxidation occurred.

However, it was noticed that the resin content increased significantly following the next three years. The number of different hydrocarbon components within the fuel increased exponentially as the fraction of gasoline types that were cracked, increased. This signified that fuel degradation was occurring, suggesting that polymerization, oxidation, and sedimentation processes were occurring. The colouration of the fuel may also be affected. Minor changes in vapour pressure, composition, density, and water content were noticed (Owczuk & Kotodziejczyk, 2015).

The oxidative stability of the fuel was determined using the ASTM D 873 method in which the actual safe storage time of fuel was estimated to be between 6 – 9 years. However, this is

dependent on the amount of cracked fraction gasoline present. For example, a lower cracked fraction means the fuel can be stored for a longer time (Owczuk & Kotodziejczyk, 2015).

Diesel and fuel oils were studied over a period of two years with results indicating that the acidic value, acetone resin content and oxidative stability at a temperature of 368.15 K had changed over time. Similar results obtained from gasoline was obtained from the acetone resin content, where there was an initial decrease in resin content over the first year and after 18 months, an increase in acetone resin was observed (Owczuk & Kotodziejczyk, 2015).

According to a fact sheet presented by BP (2019), petrol or gasoline has a storage life of one year if stored under the proper conditions. This means that the fuel should be stored in a properly sealed container under a sheltered environment. However, if the seals break, the fuel can only be stored for six months at ambient conditions of an average temperature of 293.15 K or it may be stored for three months at a slightly higher average temperature of 303.15 K. BP (2019) also suggests that fuel should only be stored for a period of one month in storage tanks. However, by restoring the volatile compounds which evaporated through introducing a third of a tank full of fresh fuel, the storage life of fuel in storage tanks may be prolonged. This can be done by ensuring the tank level in maintained at 50% capacity to prevent condensation of the water vapour being drawn in. Fuels that comprise of antioxidants, corrosion inhibitors or metal deactivators may also prevent degradation. The deposition of carbon on fuel may also be reduced by using a hot spark plug.

2.3 Monitoring of Air Emissions from Storage Tanks

Various methods have been developed to monitor diffuse emissions from storage tanks. This may include direct measurements, or indirect measurements such as point or remote sensing measurement techniques for estimation of emissions from leakages, equipment and loading and unloading (IMPEL Network, 2000), as well as process simulators and tools, and EPA calculations (CCAC O&G Methane Partnership, 2017).

2.3.1 Direct Measurement of Emissions

Direct emission measurements may be obtained through sampling of emissions from sources and quantitatively measuring it using bagging techniques, leak detection and repair (LDAR) methods, an infrared (IR) detection method or a flame ionization detector FID detector (IMPEL Network, 2000). This study focuses on the indirect measurement methods, However, industries such as Sasol, Engen and BP implement these strategies to reduce emissions. The sustainability

reports published by these industries, outlines its approach to energy management and climate change in adhering to the Carbon Tax Act which came into effect on 1 June 2019. A Carbon Tax rate of R120 per ton of direct emission was imposed to industries which includes flaring, fuel combustion and more relevant to this study, fugitive emissions.

2.3.1.1 Current Direct Measurement Strategies Implemented by Industry

Sasol's ability to implement mitigation methods for the reduction of emissions was possible due to continuous monitoring and sampling of the VOC emissions. The integrity of the sampling methods utilised and continued reporting by an international third-party company ensures accurate measurements (Sasol Sustainability Report, 2020). BP is also focused on ensuring emissions reporting is consistent and transparent to allow for adequate monitoring and control of emissions to achieve its target of net zero by 2050 (BP Sustainability Report, 2020).

2.3.2 Indirect Measurement of Emissions through Estimations methods

Various types of correlations exist to estimate emissions from storage tanks. In this study the Vasques-Beggs (VB), Valko McCain (VM), manual flash calculation method and process simulators were applied (U.S. Environmental Protection Agency, 1992).

2.3.2.1 EPA Correlations

The average emission factor method is the most used method to determine storage tanks working and breathing emissions and is based on emission factors as proposed by the Environmental Protection Agency (EPA). The emission estimate procedures for fixed roof, and internal floating roof tanks were used in this study and are outlined below. These estimates are based on the AP-42 standards as approved by the US Environmental Agency (Ciolek, 2006).

2.3.2.1.1 Fixed Roof Tanks

The following equations can be applied to vertical cylindrical shelled tanks as well as fixed roof tanks in which the liquid contents have a known vapour pressure. The equations are limited to atmospheric storage tanks in which the tanks are vapour- and liquid-tight. The total losses (L_T) from fixed roof tanks are a combination of the standing storage (L_S) and working losses (L_W) all expressed in (lb/year) (1lb = 0.454 kg):

$$L_T = L_S + L_W \quad (2\text{-}1)$$

Where:

L_T = Total losses [lb/year]

L_S = Standing storage losses [lb/year]

L_W = Working losses [lb/year]

The standing storage losses equation estimates the loss of vapours due to breathing of the vapour space of the tank and can be determined as follows:

$$L_S = 365 K_E \left(\frac{\pi}{4} D^2\right) H_{VO} W_V \quad (2\text{-}2)$$

Where:

K_E = Vapour space expansion factor [dimensionless]

D = Diameter [ft]

H_{VO} = Vapour space outage [ft]

K_S = Vented vapour saturation factor [-]

W_V = Stock vapour density [lb/ft^3]

365 = Constant – the number of daily events in a year [year^{-1}]

The working losses can be estimated using the following equation:

$$L_W = N H_{LX} \left(\frac{\pi}{4} D^2\right) K_N K_P K_B W_V \quad (2\text{-}3)$$

Where:

N = Number of turnovers per year [year^{-1}]

H_{LX} = Maximum liquid height [ft]

K_N = Working loss turnover (saturation) factor [-]

Turnovers > 36, $K_N = (180 + N)/6N$

Turnovers ≤ 36, $K_N = 1$

K_P = Working loss product factor [-]

Crude oils, $K_P = 0.75$

All other organic liquids, $K_P = 1$

K_B = Vent setting correction factor [-]

Open vents and maximum vent setting range of $\pm$ 0.03 psig, $K_B = 1$

Refer to Ciolek (2006) for more details regarding the dimensionless factors used in the aforementioned equations.

2.4.2.1.2 Floating Roof Tanks

The total floating roof tank losses (L_{FTL}) under normal operating conditions are a combination of rim seal, deck fitting, deck seam and withdrawal losses as per the following equation:

$$L_{FTL} = L_R + L_{WD} + L_F + L_D \quad (2\text{-}4)$$

Where:

L_R = Rim seal loss [lb/year]

L_{WD} = Withdrawal loss [lb/year]

L_F = Deck fitting loss [lb/year]

L_D = Deck seam loss – internal floating roof tanks only [lb/year]

The rim seal losses may be estimated using the following equation:

$$L_R = (K_{Ra} + K_{Rb}V^n)DP^*M_VK_C \quad (2\text{-}5)$$

Where:

K_{Ra} = Zero wind speed rim seal loss factor [lb-mole/ft.year]

K_{Rb} = Wind speed dependent rim seal loss factor [lb-mole/(mph)^n ft.year]

V	=	Average ambient wind speed at tank site [mph]
N	=	Seal – related wind speed exponent [-]
P^*	=	Vapour pressure function [-]
M_V	=	Average molecular weight of stock vapour [lb/lb-mole]
K_C	=	Product factor [-]

The withdrawal losses can be estimated using the following equation:

$$L_{WD} = \frac{(0.943)QC_SW_L}{D}[1 + \frac{N_CF_C}{D}] \quad (2\text{-}6)$$

Where:

Q	=	Annual throughput [bbl/year]
C_S	=	Shell clingage factor [bbl/1,000 ft^2]
W_L	=	Average organic liquid density [lb/gal]
0.943	=	Constant [1,000 ft^3. gal/bbl^2]
N_C	=	Number of fixed roof support columns [-]
F_C	=	Effective column diameter [ft]

Deck fitting losses can be estimated using the following equations:

$$L_F = F_F P^* M_V K_C \quad (2\text{-}7)$$

Where:

F_F	=	Total deck fitting loss factor [lb-mole/year]

Deck seam losses may exist from bolted deck internal floating roof tanks and can be estimated using the following equations:

$$L_D = K_D S_D D^2 P^* M_V K_C \quad (2\text{-}8)$$

Where:

K_D = Deck seam loss per unit seam loss length factor [lb-mole/ft-year]

Welded deck = 0.0

Bolted deck = 0.14

S_D = Deck seam length factor [ft/ft^2]

Ciolek (2006) contains more information regarding the dimensionless factors in the aforementioned equations.

2.3.2.2 Empirical Correlations

The Vasques-Beggs Equation (VBE) and Valko and McCain (VM) correlations are two common methods to estimate the gas-oil ratio and VOC flashing emissions from storage tanks.

2.3.2.2.1 Vasques – Beggs Equation (VBE)

Empirical equations such as the Vasques-Beggs or Griswold and Ambler GOR Chart methods may be used to estimate hydrocarbon storage tank flashing emissions. The VBE equation is a simple equation that does not require a process simulator. The equation requires eight input variables which include: separator pressure, temperature, specific gravity of the gas, API gravity, hydrocarbon volume, stock tank gas molecular weight, atmospheric pressure, and the VOC fraction of the emissions from the tank (U.S. Environmental Protection Agency, 1992). Some limitations of this method include overestimating or underestimating flashing losses and it does not account for standing and working losses from storage tanks (Sills, 2019).

The method to determine VOC flashing emissions using the VBE was followed based on results published by Gidney and Pena (2009). The separator gas specific gravity at actual conditions can be calculated from the densities of the separator mixture and air.

$$SG_S = \frac{\rho_{SP}}{\rho_{air}} = \left(\frac{MW_{SP}/Z_{SP}}{MW_{AIR}/Z_{AIR}} \right) = \left(\frac{MW_{SP}/Z_{SP}}{28.97} \right) \quad (2\text{-}9)$$

Where:

MW_{SP} = Separator gas molecular weight [lb/lb-mole]

Z_{SP} = Separator gas compressibility [-]

MW_{AIR} = Molecular weight of air, 28.97 [lb/lb-mole]

Z_{AIR} = Compressibility of air, 1 [-]

The corrected separator gas specific gravity is calculated from the following:

$$SG_C = SG_S\left[1.0 + (5.912 \times 10^{-5})(API)(T_S)\log\left(\frac{P_S}{114.7}\right)\right] \quad (2\text{-}10)$$

Where:

API = Stock tank gravity [$°API$]

T_S = Operating separator temperature [°F]

Ps = Operating separator pressure [psia]

The gas-oil ratio of the solution (R_S) measured, scf/bbl, can be estimated using the following method. C_1, C_2 and C_3 are empirically derived constants which are dependent on the API of the mixture.

$$R_S = (C_1)(SG_C)(P_S^{C2})e^{\left(\frac{(C_3)(API)}{T_S+460}\right)} \quad (2\text{-}11)$$

The following equation determines the total VOC emissions (ton/year) from the known solution gas-oil ratio.

$$E_{ToT} = (Q)(R_S)(MW_{TV})\left(\frac{1}{380.8}\right)(365)\left(\frac{1}{2000}\right) \quad (2\text{-}12)$$

Where:

Q = Production rate [bbl/day]

MW_{TV} = Stock tank vapour molecular weight [lb/lb-mole]

380.8 = Molar volume of an ideal gas at 60 °F and 14.65 psia [scf/lb-mole]

The VOC emissions, (ton/year), of each component may then be calculated as follows:

$$E_{VOC} = E_{TOT} \times X_{VOC} \quad (2\text{-}13)$$

Table 2-6 and Table 2-7 represent the empirical correlation constants and criteria for validity of the VBE equation.

Table 2-6: Empirical Constants used in the VBE (TCEQ, 2012)

Coefficient	API $\leq$ 30	API $>$ 30
C_1	0.0362	0.0178
C_2	1.0937	1.187
C_3	25.724	23.931

Table 2-7: VBE conditions for validity (TCEQ, 2012)

Variable	Symbol	Valid Range and Units*
Stock Tank Liquid Relative Density	API	(16 – 58) °API
Separator Pressure	P_S	(50 – 5250) psia
Separator Temperature	T_S	(70 – 295) °F
Separator Gas SG at P_S and T_S	SG_S	(0.56 – 1.18)
Solution Gas Oil Ratio (GOR)	R_S	(20 – 2070) scf/bbl

*1 °API $= \left(\frac{141.5}{SG} - 131.5\right)$, 1 psia $= 6.89476$ kPa, $(1°F - 32) \times \frac{5}{9} + 273.15 = 255.928K$, $1\frac{scf}{bbl} = 0.1781\frac{m^3}{m^3}$

2.3.2.2.2 Valko and McCain (VM)

The Valko and McCain empirical correlation method estimates the gas-oil ratio and hence, the flashing losses from the storage tanks. Valko and McCain used data from 881 samples taken from the fluid from a reservoir to determine the range of separator gas-oil ratios. This was used to develop the correlations by Gidney and Pena (2009). The proposed correlations for use in determining the gas-oil ratios and VOC emissions for the given stock tank API gravity (°API), separator pressure (psig) and separator temperature (°F) is as follows.

Z_n, an empirical correlation developed to determine the gas-oil ratio is solved using the following:

$$Z_1 = -8.005 + 2.7(\ln P_S) - 0.161(\ln P_S)^2 \quad (2\text{-}14)$$

$$Z_2 = 1.224 - 0.5(\ln T_S) + 0 \quad (2\text{-}15)$$

$$Z_3 = -1.587 + 0.0441\ (\text{API}) - 2.29 \times 10^{-5}(\text{API})^2 \quad (2\text{-}16)$$

$$Z = Z_1 + Z_2 + Z_3 \quad (2\text{-}17)$$

Hence, the stock tank gas-oil ratio (R_S) is obtained as follows:

$$R_{ST} = \exp\left(3.955 + 0.83Z - 0.024Z^2 + 0.075Z^3\right) \quad (2\text{-}18)$$

The flashing VOC emissions may be obtained using equations (2-12) and (2-13).

Where, the range of the correlation data sets are represented in Table 2-8.

Table 2-8: Validity range of each parameter used in the Valko McCain Correlation (Gidney & Pena, 2009)

Parameter	Variable	Range and Units*
Separator Pressure	P_S	(12 – 950) psig
Separator Temperature	T_S	(35 – 194) °F
Stock Tank Gravity	API	(6 – 56.8) °API
Separator Gas-oil Ratio	R_{SP}	(8 – 1817) scf/bbl
Stock Tank Gas-oil Ratio	R_{ST}	(2 – 527) scf/bbl
Separator Gas Specific Gravity	SG_S	(0.566 – 1.292)
Stock Tank Gas Specific Gravity	SG_{ST}	(0.581 – 1.598)

*$1\ °\text{API} = \left(\frac{141.5}{\text{SG}} - 131.5\right)$, 1 psia = 6.89476 kPa, $(1°\text{F} - 32) \times \frac{5}{9} + 273.15 = 255.928\text{K}$, $1\frac{\text{scf}}{\text{bbl}} = 0.1781\frac{\text{m}^3}{\text{m}^3}$

2.3.2.3 Process Simulators

Process simulation methods include models which use mass and energy balances and equations of states (EOSs) to predict and estimate flash emissions from a petroleum process. Some examples of such process simulator packages include Aspen Plus ®, HYSIM, HYSIS, WINSIM, PROSIM, PROMAX. This method of estimating hydrocarbon storage losses requires inputs such as temperature, pressure, flow, and other parameters. Even though this method is complicated and software licensing may be expensive, it produces the most accurate estimation of VOC emissions compared to the other estimation methods, therefore it is preferred (kdheks.gov, 2006).

The role of process simulators in chemical industries are continuously growing and evolving and serve a major part in developing models which describe the macroscopic behaviour of various chemicals. Therefore, emphasis has been placed on the development of modern, more

accurate process simulators and thermodynamic property models to accurately describe a variety of chemical components. Various separation processes such as gas separation, the separation of hydrocarbon components or crude oil in refineries and the separation of highly non-ideal compounds, utilise process simulations (Adams, 1986). This work focuses on modelling crude oil and hydrocarbon streams from petroleum refineries for the purpose of estimating emissions from petroleum storage tanks.

Petroleum liquids consist of a highly complex hydrocarbon mixture consisting of a broad range of hydrocarbons such as methane, long chain paraffins, aromatic and polyaromatic compounds. Other components such as nitrogen, carbon dioxide and hydrogen sulphide may also be present in petroleum fuels. Due to the complex nature of the fuel, it is difficult to accurately model the system using process simulators. Therefore, much research has been conducted throughout the years to obtain good thermodynamic property models which improves the efficiency of using process simulators and allows for accurate predictions. Even though the accuracy of thermodynamic models may be questioned, much uncertainty of modelling petroleum fluids arises from sampling and analysing the fuels using gas chromatography. Due to the wide range of large organic isomers with very similar properties that exist, it is not possible to model heavy petroleum compounds accurately therefore, C_{11} + compounds are regarded as a single stream. This may also lead to certain inaccuracies in predicting the properties of the fuel (Avaullee, et al., 1997).

The most widely used thermodynamic property models used in chemical industries are the van der Waals-type cubic equations of state (EOS) property models which include Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and Pate-Teja (PT) (Aspen Technology Inc., 2001). RK EOS was one of the first adjustments made to the van der Waals EOS which offered significant improvements to the attraction term. This EOS is most suitable for low to moderate pressure systems. The SRK EOS is an adjustment to the RK EOS in which it incorporates a temperature-dependent attraction term. This EOS is highly suited for vapour liquid equilibrium (VLE) systems however, it is not suited for liquid compressibility predictions. The PR EOS is highly suited for predictions of hydrocarbon systems used in gas processing, refineries and petrochemical processes as liquid densities and vapour pressures may be predicted with reasonable accuracy. The PT EOS is an equation consisting of three-parameters. This EOS is also highly suited for hydrocarbon processes and may give acceptable predictions of density and vapour pressure of heavier, polar compounds (Behbahani, et al.,

2014). This work focuses on the use of the SRK and PR EOS, as most model binary interaction parameters for the relevant systems are available in the literature. The following section provides a brief description of the thermodynamic models used.

2.3.2.3.1 Soave-Redlich-Kwong (SRK) Equation of State (EOS)

The EOS proposed by Soave (1972) is a modification of the Redlich-Kwong EOS which was derived from the van der Waals equation originally shown below:

$$\left(P + \frac{a}{v^2}\right)(v - b) = R\,(1 + \alpha\, t) \tag{2-19}$$

Where:

P = Externally measured pressure

v = Externally measured molar volume

R = Gas constant (8.314472) [$J.mol^{-1}.K^{-1}$]

α = Kinetic Energy of the molecule

This equation was later written in the form:

$$P\,(T, v) = \frac{RT}{v - b} - \frac{a}{v^2} \tag{2-20}$$

This indicates that the pressure is a result of the repulsive term $P_{rep} = RT\,/\,(v - b)$ and the attractive term $P_{att} = -a/v^2$. Expressing the parameters, a and b in terms of its critical conditions, temperature and pressure, the following equation arises:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \tag{2-21}$$

$$b = \Omega_b \frac{R\,T_c}{P_c} \tag{2-22}$$

Where: Ω_a = 27/64 and Ω_b = 1/8

The van der Waals equation can then be written as a cubic equation in the form of a third-degree polynomial in terms of its volume:

$$v^3 - v^2 \left(b + \frac{RT}{P} \right) + \frac{a}{P} v - \frac{ab}{P} = 0 \tag{2-23}$$

However, Clausius (1880) modified the Van der Waals EOS to increase the accuracy of the model by introducing a constant parameter denoted "c" into the volume of the attractive term as well as introducing a temperature dependency to the attractive time.

$$P(T, v) = \frac{RT}{v - b} - \frac{a/T}{(v+c)^2} \tag{2-24}$$

Redlich-Kwong (1949) proposed another model based on the van der Waals EOS in which the attractive term was again modified to improve the phase behaviour of the fluid at lower and higher densities.

$$P(T, v) = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{2-25}$$

Where:

$$a(T) = a_c \alpha(T) \; ; \; b = \Omega_b R T_c / P_c \tag{2-26}$$

$$a_c = \Omega_a R^2 T_c^2 / P_c \text{ and } \alpha(T) = \sqrt{T_c / T} \tag{2-27}$$

$$\Omega_a = \frac{1}{\left[9\left(\sqrt[3]{2} - 1\right)\right]} \approx 0.4274 \tag{2-28}$$

$$\Omega_b = \frac{\sqrt[3]{2} - 1}{3} \approx 0.08664 \tag{2-29}$$

The RK EOS introduces a temperature dependency into the attractive term, like the Clausius equation. The parameter *a* is a product of the constant coefficient and the alpha function which is equal to one at the critical point. This model was a widely used cubic equation which resulted in accurate predictions of basic fluids with acentric factors approximated as zero. However, this model lacked accuracy with more complex fluids with acentric factors that were not zero (Privat & Jaubert, 2012).

The RK EOS was further developed to produce the SRK EOS in which the alpha function was replaced by a general temperature dependence term. Soave (1972) introduced a three-parameter

EOS by considering the acentric factor instead of the two-parameter EOS used by Redlich-Kwong (1949). The acentric factor varies with the length and spatial arrangement of the molecules therefore, the molecular size and the effects of shape are considered with this model (Privat & Jaubert, 2012). The SRK EOS can be described as follows:

$$P\,(T, v\,) = \frac{RT}{v - b} - \frac{a\,(T)}{v\,(v + b)} \tag{2-30}$$

Where:

$$a\,(T) = a_c\,\alpha\,(T)\;;\; b = \Omega_b RT_c/P_c \tag{2-31}$$

$$a_c = \Omega_a R^2 T_c^2/P_c \text{ and } \alpha\,(T) = [\,1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)]^2 \tag{2-32}$$

$$m = 0.480 + 1.574\,\omega - 0.176\,\omega^2 \tag{2-33}$$

$$\Omega_a = \frac{1}{\left[9\left(\sqrt[3]{2}-1\right)\right]} \approx 0.4274 \tag{2-34}$$

$$\Omega_b = \frac{\sqrt[3]{2}-1}{3} \approx 0.08664 \tag{2-35}$$

The alpha function is referred to as Soave's alpha function. This model exhibited a more accurate trend to experimental data when tested for accuracy by fitting to experimental hydrocarbon vapour pressure data (Privat & Jaubert, 2012).

2.3.2.3.2 Peng-Robinson (PR) Equation of State (EOS)

Peng-Robinson (1976) aimed to improve the accuracy of the SRK EOS through modification of the m-function and of the volume-dependent attractive term and is described as follows:

$$P\,(T, v) = \frac{RT}{v - b} - \frac{a\,(T)}{v\,(v + b) + b\,(v - b)} \tag{2-36}$$

Where:

$$a\,(T) = a_c\,\alpha\,(T)\;;\; b = \Omega_b RT_c/P_c \tag{2-37}$$

$$a_c = \Omega_a R^2 T_c^2/P_c \text{ and } \alpha\,(T) = [\,1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)]^2 \tag{2-38}$$

$$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2 \quad (2\text{-}39)$$

$$X = \frac{1}{3}\left(-1 + \sqrt[3]{6\sqrt{2}+8} - \sqrt[3]{6\sqrt{2}-8}\right) \approx 0.2531 \quad (2\text{-}40)$$

$$\Omega_a = 8\frac{(5X+1)}{(49-37X)} \approx 0.45723 \quad (2\text{-}41)$$

$$\Omega_b = X/(X+3) \approx 0.077796 \quad (2\text{-}42)$$

The PR EOS is commonly used in industries and offers great accuracy for hydrocarbon systems as it accurately predicts the phase behaviour of certain polar and associated molecules such as paraffins, naphthene's, aromatics etc. (Privat & Jaubert, 2012).

Peng-Robinson (1978) offered a slight adjustment to the m-function to improve the accuracy of prediction of heavier molecules i when $\omega_i > \omega_{n-decane} = 0.49$. The following m-functions can be used:

$$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2 \quad (2\text{-}43)$$

$$\text{if } \omega \leq 0.491$$

$$m = 0.379642 + 1.487503\,\omega - 0.164423\,\omega^2 + 0.016666\,\omega^3 \quad (2\text{-}44)$$

$$\text{if } \omega > 0.491$$

Volume predictions were improved by Peneloux, et. Al. (1982). This consisted of the addition of a constant *c* which was added to the *v* and b terms as: *v* + *c* and *b* + *c*. This volume translation *c* can be described by the following correlations which uses the Rackett compressibility factor, Z_{RA}.

$$c = \frac{RT_c}{P_c}\left[0.1156 - 0.4077\,Z_{RA}\right] \text{ for the SRK EOS} \quad (2\text{-}45)$$

$$c = \frac{RT_c}{P_c}\left[0.1154 - 0.4406\,Z_{RA}\right] \text{ for the PR EOS (1976)} \quad (2\text{-}46)$$

The Stryjek and Vera (1986) EOS is a modified version of the Peng-Robinson EOS (1976), which was an improvement and used to account for its use in polar, non-polar, associating, and non-solvating mixtures.

2.3.2.3.3 Crude Oil Test System

The crude oil test system VOC emissions were monitored using the methods outlined in Table 2-9 by Burr & Georgeson (2013). The simulation-based method used in this case was ProMax, in which the crude oil compositions and tank conditions were based on the compositions found in Appendix A and the Peng-Robinson equation of state. This simulation method has a function for determining the working and breathing losses of the crude oil tank which is based on the EPA AP-42 method. The total working and breathing losses using the ProMax method was 12.65 tons/yr. A comparison of the ProMax results against direct and indirect methods is tabulated in Table 2-9. It was noted by Burr & Georgeson (2013) that the VOC flashing emissions predicted using the ProMax method was 18% higher than direct estimates and it yielded the closest measurement to the direct measurement result. These results also indicated the over-prediction (such as E&P) and under-prediction (such as Vasqez-Beggs and GOR) methods. Using methods such as those which over or under-predicted emissions may pose significant challenges to operators when compliance testing or reporting needs to be conducted.

Table 2-9: Flashing Losses from Various Methods (Burr & Georgeson , 2013)

Flashing Losses and Methods	VOC (ton/yr)
Vasquez-Beggs	19
Gas-Oil Ratio	23
Generic Exploration and Production (E&P) Tank	34
Direct Measurement	94
ProMax Flash Only	111
Exploration and Production (E&P) Tank	236

These conclusions and the Vasquez-Beggs and GOR methods were used in this study to predict emissions from a crude oil, unleaded petrol, ultra-low sulphur diesel, jet fuel and marine gas oil storage tanks. Aspen Plus ® simulation method was used instead of ProMax due to the availability of the software. Similarly, these results were compared against the different methods, including manual flash calculations to determine the effectiveness of using Aspen Plus ® as a monitoring method.

2.3.2.4 Manual Flashing Calculations

Flashing losses from petroleum storage tanks were estimated using a flash vessel simulated by a process simulator. The principles governed by the flash calculations are described in this section.

Flashing occurs when a pressurized liquid feed entering through a flash drum, is partially vaporized when flashed adiabatically to a lower pressure, to produce a vapour phase and liquid phase. This typically occurs in a single-staged equilibrium distillation column. Isothermal flashing follows the Rachford and Rice procedure, and adiabatic flashing (Q = 0) occurs through an iterative approach using the same procedure, to determine the temperature, compositions, flow rates and pressure of the phases produced. The iteration occurs by guessing a value of operating pressure then determining the values of φ, V, x, y and L by using the following equations (Seader, et al., 2011). The specified variables are: F, T_F, P_F, Z_1, Z_2, ……,Z_c, T_V, P_V, Where: C refers to the number of species or components. 1,2,….., C, and F represents the feed (with composition z_i), V represents the vapour (with composition y_i) and L (with composition x_i) represents the liquid. T and P are the temperature and pressure respectively. Ki is the equilibrium constant of component i and φ is the vapour fraction.

The Rachford-Rice iteration procedure involves the following steps:

(1) $$T_L = T_V \quad (2\text{-}47)$$

(2) $$P_L = P_V \quad (2\text{-}48)$$

(3) $$f\{T_V\} = \sum_{i=1}^{C} \frac{z_i(1 - K_i)}{1 + \varphi\,(K_i - 1)} = 0 \quad (2\text{-}49)$$

(4) $$V = F\varphi \quad (2\text{-}50)$$

(5) $$x_i = \frac{z_i}{1 + \varphi\,(K_i - 1)} \quad (2\text{-}51)$$

(6) $$y_i = \frac{z_i K_i}{1 + \varphi\,(K_i - 1)} = x_i K_i \quad (2\text{-}52)$$

(7) $$L = F - V \quad (2\text{-}53)$$

(8) $$Q = h_V V + h_L L - h_F F \quad (2\text{-}54)$$

The vapour pressures are determined from the Antoine Equation using the Antoine constants A, B and C, provided in literature. It is imperative however, to ensure the pressure (mmHg) and Temperature (K) ranges are adhered to for accuracy.

$$\ln P_i = A - \left(\frac{B}{T + C}\right) \tag{2-55}$$

Raoult's law assumes ideal gas phase and is used to determine the vapour fraction of each component.

$$y_i P = x_i P_i^{sat} \tag{2-56}$$

Where,

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P_i} \tag{2-57}$$

The vapourised fraction is obtained from step (3) through an iterative approach and the molar fractions are obtained from steps (5) and (6). Hence, the vapour flowrates are calculated from a mass balance across the tank and the pressure after iteration is the storage tank operating pressure.

2.3.2.5 Effectiveness of Continuous Monitoring Methods

The indirect methods as proposed in this section can be used to complement the direct monitoring methods. It offers a useful tool in estimating emissions through prediction using the empirical correlations and process simulators, in which the VOC emissions can be monitored continuously daily. It offers an advantage to direct methods as methods such as the leak detection methods is conducted through inspection and may not offer accurate results due to human error. Whereas, flashing loss calculations may be useful in determining the nitrogen blanketing pressures for control of emissions, however, it needs to consider the fluctuations in feed flowrate and compositions of the varying mixtures. The process simulation method is also useful in accurately predicting and optimizing the operating conditions of a storage tank to ensure the release of minimal emissions.

2.4 Mitigation Methods and Safe Storage Practices

Reducing VOC emissions is a leading concern in chemical industries therefore, this section aims to discuss traditional and current practices employed in industries used to mitigate VOC emissions. Safety is also of paramount importance in industries and the precedence to reduce emissions should not compromise the safety of people or the environment, especially when working with flammable substances such as hydrocarbon fuels.

2.4.1 Tank Blanketing

The offloading of crude oil or petroleum products from storage tanks may result in the displacement of air into the tank. Since hydrocarbon gas occupies the vapour space of the tank, this poses the risk of reaching the explosive range of the hydrocarbon and air mixture. Tank blanketing is therefore used to fill the vapour space above the liquid thus reducing the risk of exposure to the flammable region (Childs & Sipkema, 2006).

Tank blanketing is a process used to control the vapour pressure in a storage tank containing volatile liquid chemicals. This is done to ensure a safe working environment for workers by preventing the risk of a fire and explosion and prevents corrosion of equipment and the environment. Tank blanketing involves the use of a pure gas which is used to cover the surface of the liquid in a storage tank. Typically, nitrogen, carbon dioxide or argon is used. However, nitrogen is commonly preferred due to its wide availability and is less reactive than carbon dioxide and it is inexpensive compared to argon (Connaughton , 2019). This method avoids the entrance of air and moisture into the tank thereby, preventing contamination and chemical oxidation of the liquid contents (Emerson, 2019).

According to European Commission (2006), Nitrogen blanketing as a VOC emission control method is 50 – 99% efficient. This wide range is attributed to factors such as the insulation thickness and the conservation vent set point.

Tank blanketing or “padding” involves the flow of a 95% to 99.9% purity, low-pressure, nitrogen gas to the headspace of the tank (Connaughton , 2019). This makes up for the volume created by tank filling or thermal changes thus, preventing excessive pressure build-up (Emerson, 2019). Inert gas can be produced by burning fuel gas using inert gas generators which produces carbon dioxide and nitrogen gas. This slightly over pressured inert gas is then used to replace the volume of the displaced crude oil or petroleum products during storage of

the hydrocarbon liquid. An oxygen content of less than 8 % should be maintained in the tank to ensure an inert mixture (Childs & Sipkema, 2006).

The nitrogen required estimations were presented by Air Products and Chemicals (2019).

The total volume of nitrogen required (ft^3) per month, is obtained from the nitrogen required by throughput and the nitrogen required by thermal breathing.

$$N_T = N_W + N_{TB} \tag{2-58}$$

Where:

N_W = Nitrogen required by working throughput [ft^3]

N_{TB} = Nitrogen required by thermal breathing [ft^3]

The nitrogen required by working throughput is estimated by:

$$N_W = \left(\frac{V_T}{7.48}\right) \tag{2-59}$$

Where:

V_T = Total volume discharged from the tank per month [gal]

The nitrogen required by thermal breathing is estimated by:

$$N_{TB} = V_{HS}\left(\frac{T_{HIGH} - T_{LOW}}{555}\right)\frac{1}{7.48} \tag{2-60}$$

Where:

V_{HS} = Average empty headspace [gal]

T_{HIGH} = Maximum temperature in tank [°F]

T_{LOW} = Minimum temperature in tank [°F]

The peak nitrogen requirement for tanks greater than 840 000 gallons in capacity can be obtained from:

$$N_M = 8.021P + G \tag{2-61}$$

Where:

P = Pump-out Rate [gpm]

G = Nitrogen Inbreathing Requirement [scfh] – in Appendix A

The API 2000 7th edition standards by API (2013) described the equations for estimation of the inbreathing and outbreathing rates. The inbreathing rate is defined as the tank blanketing regulator flow and is the sum of the maximum pump out rate and temperature drop.

$$\dot{V}_{IR} = (8.02 \times \text{Max pump out rate}) + (3.08C(V_{tk})^{0.7}R_i) \quad (2\text{-}62)$$

Where:

V_{tk} = Tank Volume [bbl]

R_i = Insulation Factor (Assumed 1) [-]

The outbreathing rate is defined as the vapour recovery regulator flow and is the sum of the maximum pump in rate and the temperature rise.

$$\dot{V}_{OR} = (16.04 \times \text{Max pump in rate}) + (1.15Y((V_{tk})^{0.7} \times 5.618)R_i) \quad (2\text{-}63)$$

Where, the C-factor and Y-factor (Latitude) are represented as follows:

Table 2-10: C-Factors at average storage temperatures

Latitude	C-Factor			
	Vapour Pressure Similar to Hexane		Vapour Pressure Higher than Hexane or Unknown	
	Average Storage Temperature			
	< 77°F	77°F < 77°F		> 77°F
Below 42°	4	6.5	6.5	6.5
Between 42° and 58°	3	5	5	5
Above 58°	2.5	4	4	4

Table 2-11: Y-Factors at a Latitude

Latitude	**Y-Factor**
Below 42°	0.32
Between 42° and 58°	0.25
Above 58°	0.20

2.4.2 Vapour Treatment

Vapour treatment systems may be used in industries as a form of emission control technology to reduce VOC emissions from petroleum storage tanks. Typically, vapour treatment systems may be used from vapours released from fixed roof tank vents. The vapour from these tanks is collected and transferred via pipeline to a vapour recovery unit (VRU) or a thermal oxidiser. Incinerators, heaters, gas engines or flaring are commonly used techniques for oxidation of the vapours emitted. Whereas, VRU systems incorporate adsorption, absorption, membrane separation and condensation technologies to reduce VOC emissions (Best Available Techniques, 2006).

Vapour recovery units are primarily used in industries to reduce flashing losses from storage tanks. However, this system may also be used to reduce evaporative losses. The VRU operates by recovering the hydrocarbon vapours displaced from filling operations to be re-used. The two processes involved with the VRU includes: 1) Separating the air/hydrocarbon mixture and 2) Liquefying the separated hydrocarbon vapours (Best Available Techniques, 2006).

The separation process involves pressure-swing adsorption on activated carbon, a washing process which uses an absorbent fluid with a low volatility through an absorption process, selective membrane separation and condensation through cooling and compression. The liquefying process involves reabsorption processes, condensation which occurs on a cold surface and a compression process (Best Available Techniques, 2006).

Various types of VRUs exist and the most used VRUs in industry include twin bed pressure swing process using adsorption, a stream of lean oil used in a cold liquid absorption process, indirect liquid condensation using a refrigerant and selective membrane separation by using a selective hydrocarbon surface. The efficiency of these technologies may differ depending on the type of product used. For example, n-butane may yield a higher efficiency compared to methane. The efficiency of the overall reduced emissions may be increased using two of the aforementioned systems in series. However, this may incur additional capital and operating costs for a small increase in efficiency in comparison to using a single stage process. VRUs should also only be used to treat significant sources of emissions. According to the Dutch guidelines for air emissions, a significant source of emission is considered when "the emission of a discontinuous source exceeds 1000-fold the value of the hourly mass stream" on an annual basis (Best Available Techniques, 2006). Emission reduction using VRUs for tank farms with a capacity less than 50 000 m^3 should have a minimum of emission reduction potential of 97% with maximum VOC concentrations of 35gr/m^3 (IMPEL Network, 2000).

Adsorption is a process whereby vapour or gas components attach to the surface of a solid substance. Adsorption for the use of reducing air pollutants or the control of VOC emissions includes creating a large ratio of surface-to-volume using a highly porous solid adsorbent particle of carbon. This large surface area of the carbon particle allows for gas molecules to adsorb (U.S. Environmental Protection Agency, 1992). A bed of activated carbon is typically used in which the air/hydrocarbon mixture is passed through (Rudd & Hill, 2001). Industries generally use vapour-phase carbon adsorbers for the reduction of VOC emissions in which it is used in low VOC concentration waste gas streams. Once the organic molecules are removed

through adsorption by remaining on the carbon, the carbon dioxide and air particles escape to the atmosphere. A more concentrated desorption process may be used for disposal or re-use of the components (U.S. Environmental Protection Agency, 1992).

Stripping or vacuum may be used to regenerate the bed in cases of saturation and where adsorption no longer occurs. A 95-99 % efficiency may occur when using this method and is dependent on the carbon mass present in the bed, the degree to which regeneration occurs and the type of adsorbent material used. The adsorption method is highly exothermic therefore, proper control needs to be employed to ensure hot spots do not occur and inert gases should be used instead of air (Rudd & Hill, 2001).

Trained personnel are required to operate the system and for maintenance. It may be used for a wide range of products and flowrates; however, some problems may arise with certain products such as crude oil which form by-products within the bed. Disadvantages of this method includes high energy consumption, production of carbon dioxide, regular replacement of carbon and a high hazardous potential from the exothermic nature of the process (Best Available Techniques, 2006).

Absorption is a process whereby a liquid solvent is used to selectively remove specific components from a stream of gas (U.S. Environmental Protection Agency, 1992). The released vapour from loading operations enters through the bottom of a packed absorption column and contacts the chilled liquid absorbent as it counter-currently flows up through the column. This process allows for the removal of hydrocarbon components from a mixture of air/vapour in which the absorbent removes the hydrocarbons through dissolution. Remaining air from the process is released to the atmosphere and the absorbent liquid is stripped to be re-used (Rudd & Hill, 2001).

A lean absorbent with a low volatility is generally used in the absorption process. The type of absorbent used is dependent on the required efficiency and the vapour composition. A cooling process may be required for the absorbent prior to use, to decrease its volatility. An example of the type of gasoline which can be used is kerosene, for gasoline products. Kerosene at a temperature of between 238.15 to 248.15 K may be more suitable than using a low temperature gasoline which will yield a lower efficiency (Best Available Techniques, 2006).

Absorption can be used for a wide range of flowrates and products, similar to adsorption. A major benefit of this method is the safe handling of this process. No safety requirements are

required unless using a hazardous chemical as the absorbent. Studies conducted have also shown that a 99 % efficiency may be attributed to the use of terpenes, a cleaning agent, to absorb VOCs. This fluid operates at ambient conditions and may also be able to absorb certain odours. However, this process is relatively expensive and may require large amounts of energy for operational purposes (Best Available Techniques, 2006).

Condensation is a process whereby the released vapour is cooled using a condenser and liquid nitrogen as the cooling medium. This is required to reduce the VOC concentration of gas exiting the condenser which is achieved by low temperatures (Rudd & Hill, 2001). Refrigeration may also be used to achieve the low temperatures required for condensation (U.S. Environmental Protection Agency, 1992). Condensation then occurs through a heat exchanger by allowing the vapours to condense on the exchanger surface. The heat exchanger conditions are reliant on the product boiling point and efficiency of recovery. A cryogenic condenser may also be used as another stage to increase the efficiency (Best Available Techniques, 2006).

Safety practices involved with the condensing method includes ensuring professionally trained personnel attend to operation issues as exposure to the coolant may lead to potential injuries. Some limitations of this method include operating the condenser at appropriate temperature conditions to ensure blockages and polymerisation are avoided. Variations with flow may also affect condensation and only certain products may be treated with this method. The products that can be used depending on the design temperature of the condenser. Negative environmental effects will occur if ozone depleting refrigerants are used (Best Available Techniques, 2006). Condensation is a highly expensive method therefore, it is sometimes used in conjunction with other units (U.S. Environmental Protection Agency, 1992).

Membrane separation is a process whereby separation of hydrocarbons or organic vapours from air occur through the use of a semi-permeable membrane through which the air/vapour mixed is passed. The organic compounds move through the membrane which is selectively permeable to specific organic compounds such as the smaller VOCs. A vacuum pump is generally used to aid this process by creating a driving force (Rudd & Hill, 2001).

A differential pressure across the membrane determines the efficiency which requires a compressor, a vacuum pump or both, at either ends of the membrane to maintain this. Due to this and the requirement of a double set of moving vapour equipment, membrane technology is considered relatively expensive with high operating costs. Membrane separation is suited for

use in fixed roof tanks which uses vapour balancing and large vapour volume systems. The only safety consideration is the protection against vacuum conditions when a compressor is also used (Best Available Techniques, 2006).

2.4.3 Mitigation Methods Used in Industry

2.4.3.1 Sasol

Sasol is committed to meeting net zero by 2050 and supporting the Paris Agreement. Sasol's emissions profile is significantly high, and this is mainly attributed to the type of feedstock (coal) used in its operations in the Fischer Tropsch process. However, Sasol is focused on introducing net zero feedstocks such as hydrogen, renewables as well as sustainable carbon. This will play a vital role in the reduction of emissions; however, this transition is a long-term approach and Sasol has implemented a framework which focuses on a short-term approach to reduce global emissions by 30 % by 2030 (Sasol Sustainability Report, 2020).

This is further substantiated by the mitigation methods implemented at its Secunda and Natref Plants in which the recommissioning of five regenerative thermal oxidisers (RTOs) at its Secunda operations noted a 10.51 kt reduction in VOC. The installation of seven RTOs in the tar operations was able to mitigate VOC emissions from 114 sources. Optimizing the vapour recovery unit also assisted in reducing VOC emissions as well as the implementation of analytical monitoring methods which provided an overview of the tanks which are compliant, and which require further improvement. The Natref plant saw an improvement in reduction of VOC emissions through the installation of secondary seals on some crude oil, petrol, and heavy oil storage tanks. The implementation of vapour recovery units and geodesic dome roofs with internal floating disks on one petrol and two crude oil storage tanks allowed for adequate dispersion of the VOC emissions (Sasol Sustainability Report, 2020).

2.4.3.2 Engen

Engen Refinery is also committed to ensuring scope 1 direct emissions are minimised. However, Engen has seen an increase of approximately 2 tons of carbon dioxide equivalent from 2015 to 2019. This includes direct emissions from fuel combustion, flaring and fugitive (VOC) emissions. Whilst they continue to assess the risks of its operations and its effect on climate change, they have not made significant improvements in mitigating their emissions yet

and has reported that a risk management system will be included in future reporting and business requirements (Engen 2019 Integrated Report, 2019).

2.4.3.3 BP

BP has outlined a strategic approach into achieving its net zero target by 2050. Its ambition focuses on aims for BP to achieve net zero as well as the word to achieve net zero. BP has managed to achieve a 15 % reduction in scope 1 direct emissions from 2019 to 2020. This was done through the optimization of process operations such as improvements in energy efficiency and reducing venting and flaring to the atmosphere (BP Sustainability Report 2020, 2021).

2.5 Summary

The strategies and information provide great insight into the existing literature of VOC emissions, factors affecting tank emissions, monitoring methods of air emissions, strategies to reduce the emissions through mitigation means with safe handling practices of flammable compounds such as petroleum fuels as well as analysing the most suitable thermodynamic properties when using process simulators. This ensures proper environmental management and sustainable development in South Africa and the world.

CHAPTER THREE: METHODOLOGY

This chapter aims to outline the methodologies applied in estimating VOC emissions using the techniques described in Chapter two. It presents the systematic approach used in the research design with the relevant data inputs and models. Due to the diversity of oil and petroleum products and the complexity of sourcing industrial plant data, five types of organic liquid mixtures consisting of crude oil and petroleum products (ULSD, ULP 95, MGO and JET A1) were utilized to determine its contributing effects to VOC emissions in the Durban South Area, South Africa and thus applied elsewhere in similar refineries. A comparative analysis was then conducted against the various scenarios and, mitigation strategies were implemented to determine the recommended VOC reduction potential from storage tanks. This chapter further states all assumptions made in the execution of this work.

3.1 Research Methodology

Figure 3.1 outlines the procedures involved in identifying the steps in the workplan. A thorough review of the literature was done with the collection and analysis of data to determine the VOC emissions and factors affecting VOC emissions. The effect of mitigation and control techniques to reduce emissions were also conducted. This study involved three main steps to analyze and control VOC emissions from petroleum storage tanks. Due to the difficulty in obtaining experimental data, a thorough review of the literature was done to acquire the data for analyses. The second step involved the analyses of data through monitoring techniques and the third step included control methodologies for the mitigation of emissions and recommendations to curb these releases.

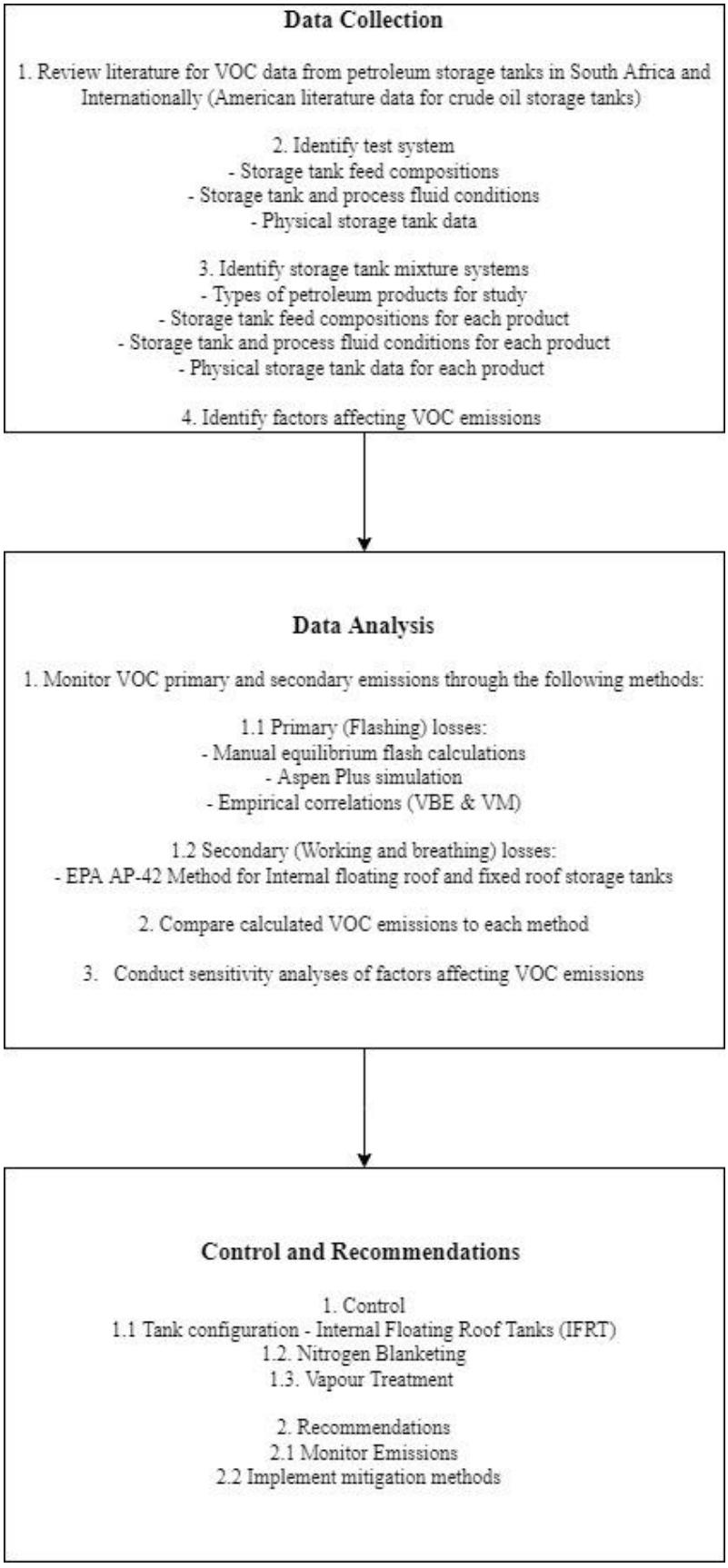


Figure 3-1: Workflow diagram of research methodology to compare VOC emission estimation and mitigation strategies.

3.2 Data Acquisition

A literature review on various petroleum oil and product mixtures in storage tanks in South Africa and worldwide was conducted to determine compositions and conditions of the storage tank. This was done due to the limited and partial availability or confidentiality of experimental plant data of storage tanks in South African industry. In the majority of these reports, overall figures available in annual reports are provided for example, or specific case study documents.

3.2.1 Test System

A test system was initially chosen for replication and verification of the methods presented in this study. This consisted of the data presented in Burr and Georgeson (2014) in which samples were retrieved through direct measurement from a crude oil storage tank at wellsite named WTB 1. Thirteen samples were collected by Dunn and Mountrail Counties, from the upstream separator liquid of the atmospheric storage tank at the separator pressure. Low pressure samples were collected by third party consultants in which the sample was retrieved at the valve inlet of the oil line, to the separator.

The bulk of the mixture consisted of C10+ components in which a pseudo component was used to identify the C10+ mixture from the measured specific gravity and molecular weight. The separator temperature and pressure, storage tank temperature and sales oil flowrate were noted and are shown in, Table 3-6. The crude oil test system is assumed to be representative of a typical crude oil storage tank which can be applied to South African systems.

These samples were analyzed through gas chromatography to determine the pressurized liquid compositions of each component. The data obtained is represented in Table A-1 of Appendix A.

3.2.2 Organic Liquid Mixtures

Four organic liquid mixtures, based on the following petroleum product storage tanks: ULSD (Ultra-Low-Sulfur-Diesel), ULP 95 (Unleaded Petrol 95), JET A1 (jet fuel) and MGO (Marine Gas Oil), were studied. These are common grades found in refineries and apply to Sasol or SAPREF. The storage tanks, proposed by Lanele Group (Pty) Ltd. is in the storage terminal at Ambrose Park, in Bayhead, port of Durban and is known as the Lanele Oil Terminal 1 (Lot 1) project. The data utilized in this study was obtained from the Environmental Impact Assessment (EIA) conducted by Golder Associates Africa (Pty) Ltd. The data was sampled through air dispersion modelling in which a Gaussian Plume model or AERMOD view

simulation software was used to obtain air emission concentrations, based on meteorological conditions of the area. Figure A-1 in Appendix A shows the process flow diagram and data (compositions and conditions) of the storage tanks and process fluids, utilized in this study. The unidentified components were incorporated as a bulk (pseudo) component which is representative of the mixture.

3.3 Data Analysis

VOC emissions were estimated from the data obtained for the test system and the four organic liquid mixtures for comparative and control purposes. Primary losses consisted mainly of flashing losses and were estimated using manual flash calculations, Aspen Plus ® Simulations, and empirical correlations. Secondary losses were estimated using the EPA AP-42 methodology (refer to section 7.1 *Organic liquid storage tanks* of the document), through manual calculations.

3.3.1 Primary 'Flashing' Losses

Flashing losses for the five organic liquid systems (Crude oil, ULSD, ULP 95, JET A1 and MGO) were estimated using the Rachford-Rice (Seader, et al., 2011) iterative manual equilibrium flash calculations, Aspen Plus ® process simulation method and empirical correlations based on the VBE (Gidney & Pena, 2009) and VM (Gidney & Pena, 2009) methods. A comparative analysis was conducted against the base cases and the effect of feed flowrate, storage tank temperature and pressure on emissions rates were determined. Table 4-1 represents the VOC emissions monitored from the flash methods of the five organic liquid systems. The conditions at which these methods were applied were tabulated in Appendix A. The crude oil base case was based on the conditions stipulated by Burr and Georgeson (2014) and the petroleum systems were based on the conditions in the studies by Golder Associates Africa (Pty) Ltd. (Golder Associates, 2019a). Table 4-2 indicates the VOC vapour fractions for the base casesThe five organic liquid storage tank systems are representative of a typical tank farm in which crude oil and the petroleum products are stored. According to the study conducted by Peacock (2010) and Burr and Georgeson (2014), direct emissions from the crude oil storage tank were quantified as 94 ton/year. This was used as a basis to determine the quality of estimation of the emissions from the various flashing methods.

3.3.1.1 Manual Equilibrium Flash Calculations

The VOC flashing losses for all storage tanks were estimated using the manual equilibrium flash calculations by the Rachford-Rice iterative methodology. The Rachford-Rice method is an ideal approximation method and equations (2-47) and (2-54) in Chapter 2 were used. An excel spreadsheet was used with the solver function to vary the pressure due to changes in temperature and determine the vapour fraction of the mixtures. This was used to calculate the vapour and liquid fractions of the mixtures along with the molecular weight of the mixture. The rate of VOC emissions of each component was determined.

3.3.1.2 Aspen Plus ® Simulation

Aspen Plus ® a simulation tool was used to determine the VOC emissions of each storage tank and for comparison of the results against the other methods applied in this study. The simulation results were compared against the ProMax simulation method used in the study by Burr and Georgeson (2014) for validation of the test system. An investigation of the thermodynamic property model was conducted to determine the most suitable property method for modelling and predictive applications in the atmospheric storage tanks. Regression analyses and consistency tests performed in this work (as seen In Appendix A) for each component of each mixture suggested the use of the SRK property method for the crude oil test system and PR for the petroleum product mixtures. These cubic equations of state method are justifiable for use in refinery and petrochemical applications over a wide range of temperatures and pressures (Aspen Technology Inc., 2001). The system, as represented in the flow diagram in Figure 3-2, consisted of passing the organic liquid of given compositions and conditions through a control valve. The tank temperature and pressure were set according to the specified conditions and the VOC emissions were monitored at the tank conditions. The remaining liquid product leaving the storage tank after flashing occurred, was pumped to determine if pump cavitation occurred, and the pumped liquid was used to determine the secondary losses. Table 3-1 provides the list of the input and output variables required.

Table 3-1: Input and output variables required for the Aspen Plus simulation

Input Variables	Output Variables
Pressurized liquid from separator stream	VOC flowrate
Pressurized liquid from separator temperature	Product liquid flowrate
Pressurized liquid from separator pressure	
Outlet valve pressure	
Storage tank temperature (internal)	
Storage tank pressure	
Pump pressure	

3.3.1.3 Empirical Correlations

Empirical correlations were used to determine the total VOC flashing emissions from a storage tank. The Gas-Oil Ratio (GOR) is an important parameter used to estimate the VOC emission rates in the VBE and VM correlation. Gidney and Pena (2009) conducted studies on these empirical correlations to develop improvements with the correlations. Flashing losses were estimated using all four empirical correlations to determine the reliability of the correlations for VOC emission monitoring.

3.3.2 Secondary 'Working and Breathing' Losses

Secondary losses consisting of working and breathing losses were determined by using the residual product liquid from the storage tanks, physical tank data and EPA's AP-42 methodology (Ciolek, 2006) through manual calculations, for each organic liquid mixture. The type of storage tank, tank location, paint colour and quality, tank dimensions and roof type were all critical factors which affected the rate of breathing and working losses in atmospheric storage tanks. Therefore, data analyses consisted of monitoring the trends involved in varying each factor through a sensitivity analyses with a comparative analysis to determine the effect of fixed-roof storage tanks and internal-floating roof storage tanks. The calculations were performed for each mixture to check the repeatability. The accuracy of the data was observed by the trends which were compared to each other and literature, with statistical inferences of line of best fit equation and the coefficient of determination (R^2). Table 3-2 lists the input variables required for determination of the fixed roof storage tank which consist of standing and working losses. Table 3-3 represents the input and output variables of the internal floating

roof tank which consists of rim seal losses, withdrawal losses, deck fitting and deck seam losses.

Table 3-2: Input variables required for fixed roof storage tank calculations[a]

Standing storage loss [lb/year]	Working loss [lb/year]
Tank diameter [ft]	Number of turnovers per year [per year]
Stock Vapour density [lb/ft^3]	Maximum liquid height [ft]
Vapour space outage [ft]	Diameter [ft]
Vented vapour saturation factor [-]	Working loss turnover saturation factor
Vapour space expansion factor [-]	Working loss product factor [-]
	Vent setting correction factor [-]
	Vapour density [lb/ft^3]

[a]1 ft = 0.3048, 1 lb/ft^3 = 16.0185 kg/m^3

Table 3-3: Input variables required for internal floating roof storage tank calculations

Rim seal loss [lb/year]	Withdrawal loss [lb/year]	Deck fitting loss [lb/year]	Deck seam loss [lb/year]
Zero wind speed rim seal loss factor [lb-mole/ft.year]	Annual throughput [bbl/year]	Total deck fitting loss factor [lb-mole/year]	Deck seam length factor [ft/ft^2]
Average ambient wind speed at tank site [m/h]	Average organic liquid density [lb/gal]	Vapour pressure function [-]	
Average molecular weight of stock vapour [lb/lb-mole]	Tank diameter [ft]	Average molecular weight of stock vapour [lb/lb-mole]	
	Effective column diameter [ft]		

[a] 1 lb-mole/ft.year = 1488.164 g-mole/m.year, 1 bbl/year = 0.16 m^3/year, 1 m/h = 1.61 km/h, 1 ft = 0.3048,1 lb/gal = 119.83kg/m^3, 1 ft/ft^2 = 0.328 m/m^2

3.3.3 Control Methods

Quantification of the VOC emission analyses led to the determination of the effectiveness of control methods for the potential reduction of VOC emissions from petroleum storage tanks. According to the Best Available Techniques on Emissions from Storage Tanks (European Commission, 2006). Table 3-4 recommends the most effective mitigation strategies which were implemented in this study to determine its effect in mitigating the VOC emissions.

Table 3-4: Control Method Efficiency and Dependent Variables (European Commission, 2006)

Control Method	Efficiency (%)	Dependent Variables
Tank Configuration – Internal Floating Roof Tank (IFRT)	≥ 90	Tank size Type of stored product Turnover rate (per year)
Pressure and Vacuum Relief Valves (PVRV)	5 – 13	Storage pressure
Nitrogen Blanketing	50 – 99	Storage conditions Type of stored product
Vapour Treatment	≥ 99	Type of stored product

3.3.3.1 Tank Configuration

The tank configuration was used as a control measure to reduce secondary losses from storage tanks through the EPA AP-42 method as studies conducted by European Commission (2006) suggested that a 90 % efficiency can be achieved through IFRTs compared to a FRT without control measures in place. The effect of controlling VOC emissions through tank configuration was determined by comparing a Fixed Roof Tank (FRT) and an Internal Floating Roof Tank (IFRT). The variables which were varied and contributed to the difference in tank emissions included: meteorological conditions such as tank temperature, diameter of the tank, the type of liquid stored in the tank and the number of turnovers of the tank. This was done through altering the EPA AP-42 FRT and IFRT equations. However, European Commission also suggested that a smaller tank diameter and fewer turnovers results in lower efficiency. Further reduction strategies were implemented to determine the maximum reduction potential through the

implementation of an IFRT. This was done using primary liquid seals and secondary rim mounted seals.

3.3.3.2 Nitrogen Tank Blanketing

Nitrogen blanketing was used to control secondary losses such as working and breathing losses from FRTs in which a slight overpressure in the tank was maintained. The method involved the creation of an excel spreadsheet in which the nitrogen blanket was sized according to the API 2000 7th Edition venting procedure to determine the reduction efficiency based on the emission rate. This was compared to the efficiency suggested by European Commission (2006) given as 50 – 99 %. The following variables were varied to determine the effect of this control method on the potential of reducing emissions: type of stored product, storage pressure, vent set point and insulation thickness. Aspen Plus ® was then used to determine the venting requirement using the safety analysis feature where the nitrogen inbreathing and outbreathing rates were obtained according to the specification represented in Appendix A (Vogel, 1985). Table 3-5 provides the conditions used in the calculations performed.

Table 3-5: Nitrogen Tank Blanketing Pressure Conditions (Perfect Fluid Control Equipment Manufacturing Co. Ltd, 2020)

Condition	Pressure (kPa)
Nitrogen Supplying Pressure	300 – 800
Nitrogen Blanketing Set Pressure	1
Nitrogen Bleeding Pressure	1.5
Respiration Valve Exhalation Pressure	2
In-Breathing Pressure	-0.8

3.3.3.3 Vapour Treatment

According to European Commission (2006) and Golder Associates Africa (Pty) Ltd (Golder Associates, 2019a) vapour treatment has the potential to reduce VOC emissions from storage tanks by at least 99 %. Therefore, this control measure was utilized to control FRT breathing or filling emissions. European Commission (2006) suggested that the implementation of a two-stage process increases the efficiency by a further 0.9 % which includes a membrane treatment

unit and a thermal oxidizer. Therefore, the economic insensitive is poor. These efficiencies are dependent on the type of product stored in the tank. Therefore, the efficiencies were used as a factor multiplied to the VOC emission rates monitored from the various products in FRTs and the controlled emissions were noted. The results were compared to the emissions observed by Golder Associates Africa (Pty) Ltd (Golder Associates, 2019a).

3.4 Summary of the Models Used

3.4.1 Aspen Plus ® and Thermodynamic Property Methods

Aspen Plus ® is a process simulation method used to model the storage tank mixtures and were based on the various conditions and feed flowrates and compositions. According to Aspen Tech (2013), the following property methods may be applied to petroleum-based process simulations: Peng-Robinson (PENG-ROB), Redlich-Kwong-Soave (RKS), (Soave-Redlich-Kwong) SRK and SRK-Kabadi-Danner (SRK-KD). The SRK property model is justifiable for producing reasonable results across all temperature and pressure ranges and is highly recommended for use in petrochemical and refinery applications. Its suitability for non-polar and mildly polar mixtures of hydrocarbons and light gases makes it an appropriate model for use in this system. PENG-ROB property method is also advantageous for implementation here due to its preferred use for polar, non-ideal hydrocarbon mixtures and light gases and its results are acceptable at all temperatures and pressures (Aspen Tech, 2013).

3.4.2 Manual Flash Calculations

The manual flash calculation utilises the Rachford-Rice isothermal, iterative approach in which the multi-component flash calculations were based on K-values estimated from 2-57. This is useful in determining the flashing losses.

3.4.3 Empirical Correlations

The two types of empirical correlations utilised in this study were VBE and VM. The major factors affecting the emissions from empirical methods include separator pressure and temperature and API gravity of the organic mixture.

3.5 Test System – Analysis of a crude storage tank

The process flow diagram shown in Figure 3-2 presents the simulation as applied in this work for the Aspen Plus ® method of the test system as presented in Section 4.1. The input parameters and results are presented in Table 3-6.

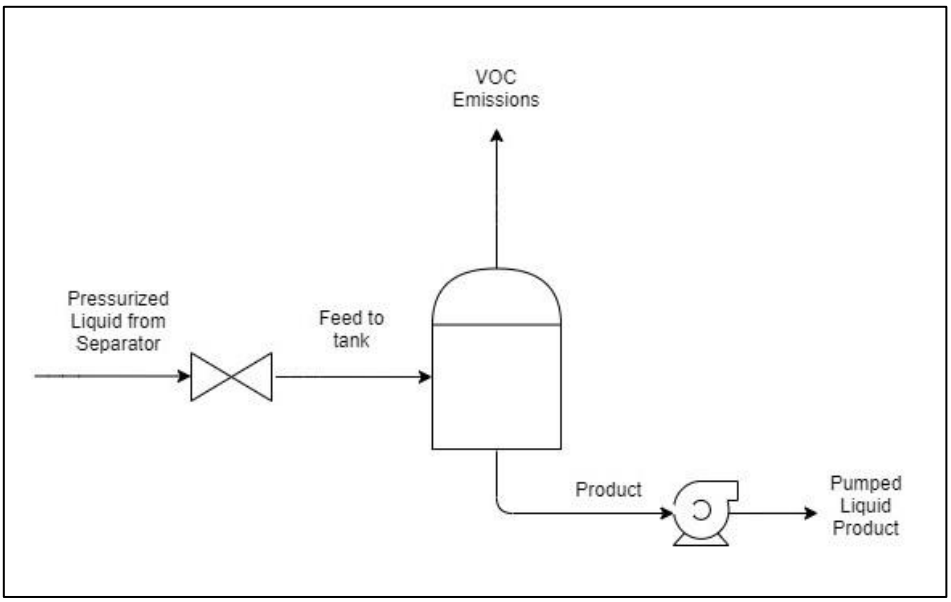


Figure 3-2: General Schematic of Crude Oil and Petroleum Product Mixtures Simulation

Table 3-6: Input Parameters for Crude Oil Aspen Plus ® Simulation *(Burr & Georgeson , n.d.)*

Input Parameter	Value
Sales Oil Flowrate (bpd/ton/year)	188/9 479.73
Storage Tank Pressure (psia/kPa)	13.98/96.39
Storage Tank Temperature (F/K)	64.2/291.04
Separator Pressure (psig/kPa)	42/289.58
Separator Temperature (F/K)	66/292.04
C10+ Molecular Weight	262.7
C10+ Specific Gravity	0.87872

For the analysis of the VOC emissions and trends from a crude oil storage tank, a simulation involving a flash tank with a crude oil mixture was established. The information used was gathered from literature. This exercise was conducted as a test system for replication and as a comparative study against the literature experimental data presented by Burr and Georgeson (2014). The uncertainties in the flashing losses were determined using the following methods:

process simulation (Aspen Plus ®), empirical correlations (VBE and VM) and uncertainties in the secondary losses with the EPA method.

A sensitivity analysis was then conducted to determine the effects of tank temperature, pressure, and feed compositions on emission properties. Recommended control measures were suggested and implemented based on these measures while also considering the factors affecting VOC emissions, as discussed in Chapter 2. Figure 3-2 shows the schematic of the simulation and Table 3-6 and Table A-1 presents the stream data input.

3.5.1 Determination of Flashing Losses using Aspen Plus ®

The flashing losses of the crude oil test system were analysed according to its property method and VOC emission trends due to operational parameters.

3.5.1.1 Thermodynamic Property Method

Burr and Georgeson (2014) suggested the use of PENG-ROB or SRK equations of state for crude oil simulations on Aspen Plus ®. To confirm the appropriate property method, model predictions and regressions were conducted using experimental thermodynamic data of the various mixture combinations available via the NIST database. Then, according to Burr and Georgeson (2014), an operating pressure and temperature of 96.38 kPa and 291.04 K respectively were applied, where the slight vacuum reduced the escape of vapours, which are typically appreciable in fixed roof storage tanks at small changes in temperature, pressure, and liquid levels (Solken, 2021). The regression analysis was performed to estimate the interaction parameters of the binary pairs of the key components where parameters were missing, or poorly predicted the experimental data. This helped to improve the accuracy of the simulation as the updated parameters provide a more realistic characterization of the component phase behaviour. A thermodynamic consistency test of the vapour-liquid equilibrium data consisting of the area test, and based on the Gibbs-Duhem equation, was performed for each binary pair. The data sets representing the highest consistencies at the given conditions were deemed the most reliable data and was used to determine the root mean square error (RMSE) of each model. Section A.2.2 in Appendix A tabulates the consistency test results and RMSE of each binary pair for each model. It was noted that the SRK EOS yielded an overall lower RMSE of an average of 99.25 and was deemed the most suitable for the mixture considered, as it best describes the equilibrium data for all components present.

3.5.1.2 Analysis of the VOC Emission

The crude oil storage tank was modelled as a flash vessel on Aspen Plus ®, with the schematic of the flow diagram represented in Figure 3-2. The pressurized liquid stream from the separator was passed through a control valve and set at a pressure drop of 100 kPa to reduce the pressure of the feed stream entering the tank. This allowed for control of the change in pressure across the tank to ensure minimum vapour emissions are released. Table 3-6 and Table A-1 in Appendix, represent the stream and unit details, including inputs to the simulation. The VOC emissions were monitored as the vapour stream and the liquid stream exiting the tank was used to estimate the secondary emissions via the AP 42 standards.

3.5.1.3 Pump Cavitation

The flashing due to cavitation can ultimately result in VOC emissions. To minimize this effect in this study, vapour pressures of each component present in the sales oil stream was computed using experimental data from NIST. It was extracted from Aspen Plus ® and the minimum pressure at which pump cavitation occurred was determined to be 197 kPa. The pump was then set at an operating pressure of 200 kPa to avoid the formation of vapour cavities reducing pump impact and additional losses.

3.6 Summary

This chapter outlined the approach and methodology taken in analyzing and controlling VOC emissions from petroleum storage tanks of various organic liquids in the Durban South Area. This included a description of the approach utilized in conjunction with the calculation methods and data inputs involved in the collection of data from literature sources, analyses of the raw data using various monitoring techniques to determine the effect of the monitoring methods on VOC emissions and the analyses of control methods to determine the potential reduction efficiency of VOC emissions with the recommended strategies for implementation.

CHAPTER FOUR: RESULTS AND DISCUSSION

This chapter presents the emission calculation results from five types of organic liquids consisting of crude oil and four petroleum product mixtures. These five systems were considered based on the storage tank conditions, stored products and stream components, and analysed to illustrate and quantify the effects of VOC emissions. The effects of VOC emissions were examined in terms of its impact on the environment and the health and safety of the people in surrounding areas in relation to the current and proposed mitigation strategies.

Thereafter, an in-depth analyses of mitigation techniques were conducted to determine the potential reduction effect of VOC emissions from the tanks. The comparative study allowed for the identification of mitigation methods for use in the petroleum industry to efficiently reduce VOC emissions, to promote sustainability and reduce environmental impact.

4.2 Analysis of the Crude Oil Test System

The Aspen Plus simulation of the crude oil test system indicated that 110.2 tons/year of VOC emissions at a temperature of 291.04 K and pressure of 96.38 kPa were produced. Figure 3-2 and Table 3-6 represents the simulation model and input conditions used. This flashing loss contributed to 1.1% of the feed flowrate of 9371.5 ton/year and was calculated based on the feed flow of the crude oil to the tank to determine the total contribution of VOC emissions emitted. This may seem a small contribution of VOC emissions, however, 110.2 tons/year exceeds the allowable threshold of 100 tons/year permitted by Golder Associates Africa (Pty) Ltd (Golder Associates, 2019a). Therefore, control measures such as nitrogen blanketing or tighter control of tank conditions are necessary. The recovery of the products in the vapour stream, as represented in Figure 4-1, is indicative of the components recovered in the VOC stream from the feed stream. The lighter hydrocarbon components of methane (90.4%), ethane (58.0%) and propane (28.1%), show significant recovery, whereas the heavier hydrocarbons were entrained in the sales oil mixture. The latter contributes to breathing and working losses.

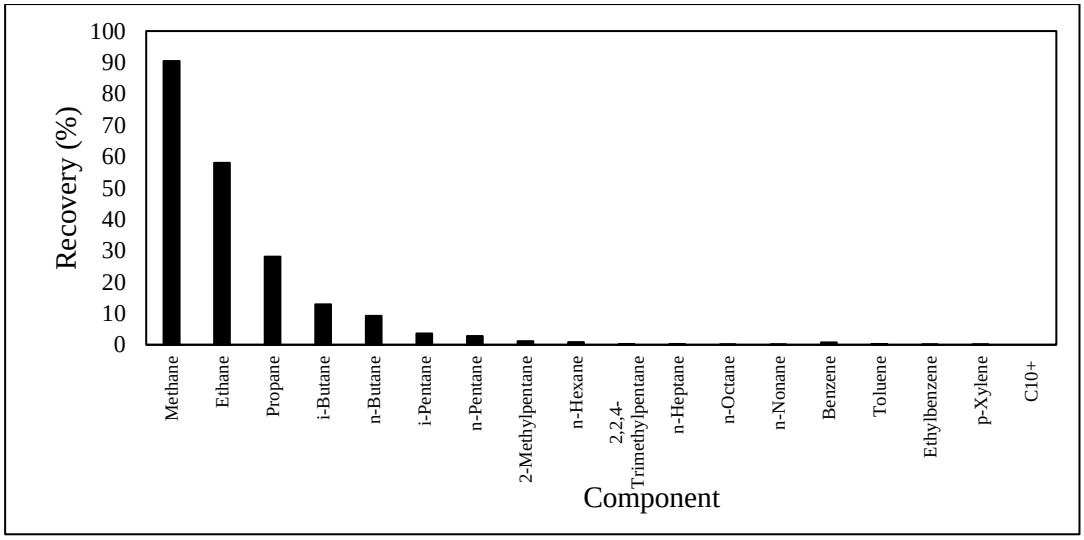


Figure 4--1: The percentage recovery of components in the VOC emissions stream at 291.04 K and 96.38 kPa

Figure 4-2 shows that approximately 38.3% of the total VOC emitted from the tank (by mass) was propane, 25.6% was ethane and 24.4% was butane. Lower amounts of pentane (7.5%) and methane (7.1%) and trace amounts of heavier hydrocarbons, consisting of alkanes and aromatics were observed. The loss of these light hydrocarbons, rich in alkanes, to the atmosphere (as VOC emissions) were expected due to the high pressure drop of 143 kPa, experienced across the tank during flashing.

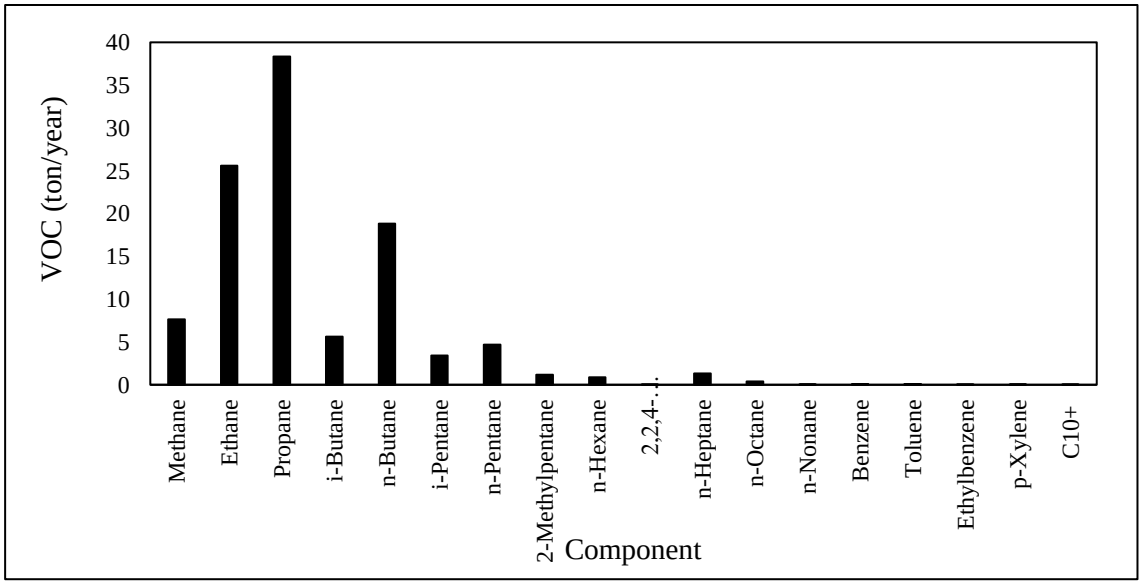


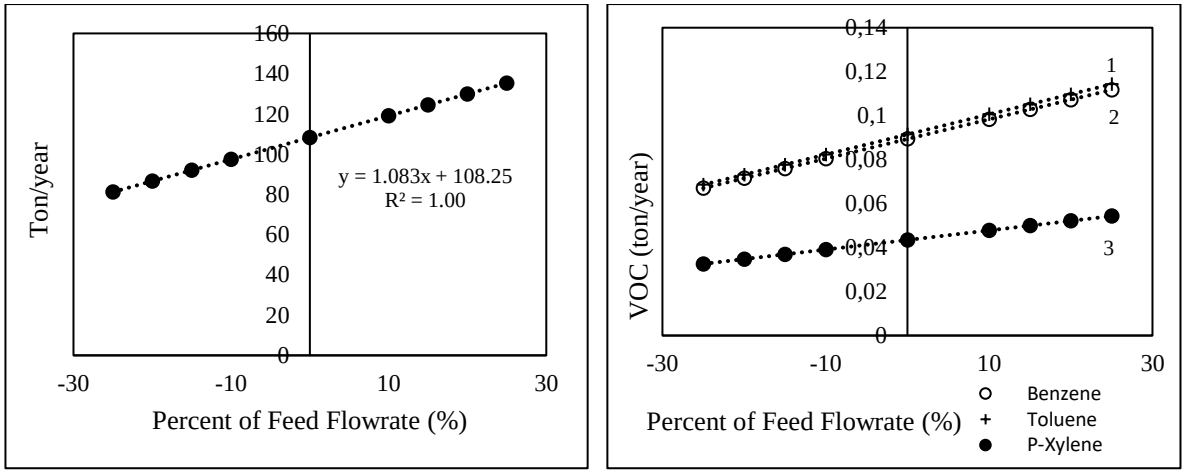
Figure 4--2: VOC emission rate (ton/year) per component in the crude oil storage tank operating at 291.04 K and 96.38 kPa

From the test system results, Figure 4--2 shows that C1-C4 alkanes/isoalkanes are abundant in the emission stream. These alkanes contribute to ground-based ozone pollution due to the global warming potential as greenhouse gas components (Helmig et al. 2016). Suffocation, cardiac arrest, unconsciousness, and seizures are some of the major health effects which may be caused from exposure to high concentrations of these alkanes (McKee, et al., 2014). The significant alkane emission flow rates ranging from 5 – 39 ton/year into the atmosphere from crude oil storage tanks only, validates the need to implement control measures such as nitrogen blanketing or tighter control of tank conditions during operation to mitigate those emissions.

4.2.1 Sensitivity Analysis of Crude Oil Test System

The sensitivity of feed flowrates, tank temperature and tank pressure were determined for the crude oil test system to observe the effects of these varying conditions on the flashing of the storage tank and resulting VOC emissions. This was done using Aspen Plus ® V11.

Figure 4-3 (a) illustrates the effect of a $\pm$ 10 – 25 % variation on the feed flowrate, with a base feed flowrate of 9 479.73 ton/year, on the VOC emission rate at a tank temperature of 291.04 K and pressure of 96.38 kPa. A direct, linearly proportional relationship exists between the feed and VOC emission rate with a regression analysis indicating a coefficient of determination (R^2) of 1.00. Hence, a strong relationship exists between the variables. This trend further suggests that with a $\pm$ 5% variation in feed flowrate, a variation of + 5.41 ton/year in VOC emission rate was noted. Similarly, the emissions of hazardous components such as benzene, toluene and p-xylene in the feed are illustrated in Figure 4-3 (b). An increasing trend is also observed indicating that higher VOC emissions of these components are released when it is abundant in the feed mixture. The gradients of benzene and toluene are approximately twice that of p-xylene, indicating a higher rate of production of VOC emissions. The repercussions of increasing quantities of VOC emissions of these hazardous components are further discussed in the Environmental Impact Assessment in section 4.4.



a) b)

Figure 4-3: The effect of ± 10 – 25% feed flow variation on a) VOC emission rate and b) feed of hazardous components, from the crude oil test system storage tank with a feed flowrate based of 9479.73 ton/year (Toluene (1): y = 0.0009x + 0.091, R^2 = 1.00; Benzene (2): y = 0.0009x + 0.089, R^2 = 1.00; P-xylene (3): y = 0.0004x + 0.044, R^2 = 1.00)

The temperature of the crude oil storage tank is another parameter which affects the quantity of VOC emissions of flashing losses. Figure 4.4 and Figure 4.5 illustrates the effect of crude oil tank temperature, at Durban ambient conditions, on the VOC emission rate at a pressure of 96.38 kPa. The maximum, minimum and average temperatures of Durban, as indicated by Burr and Georgeson (2014) and represented in Appendix A, Table A-3, were used to determine the maximum, minimum and average VOC emissions from the crude oil storage tank at a pressure of 96.38 kPa, seen in Figure 4-4, for a period of 12 months. It was noted that the VOC emissions were highest during the warmer summer months (December – May) with average VOC emissions ranging between 114.11 – 141.65 ton/year. Whereas the lowest emissions were recorded in the colder winter months (June – November), ranging between 101.77 – 125.83 ton/year. The lowest emissions (101.77 ton/year) were recorded in July, in which the average temperature was the lowest at 16.5 ℃.

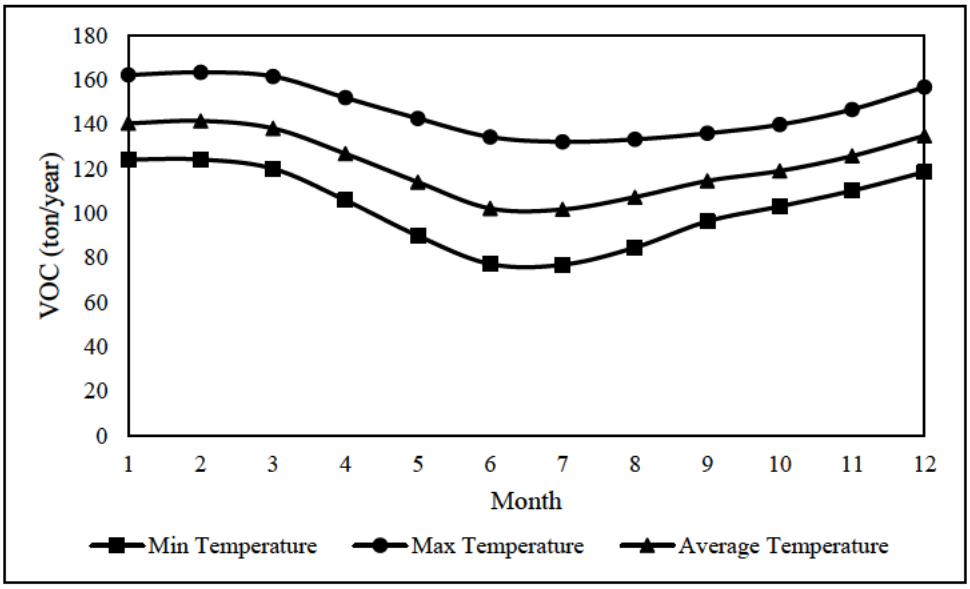


Figure 4-4: The effect of the maximum, minimum and average crude oil storage tank ambient temperatures in Durban, on the VOC emissions at 96.38 kPa

Further to this, average summer and winter temperatures in Durban were estimated at 25 °C and 18 °C respectively and used as the base temperatures. Variations in increments of 2 °C were applied to this and graphically represented in Figure 4-5, in which the scatter was plotted from the moving average. The summer temperatures were varied between 22 and 30 °C and yielded VOC emissions ranging between 129.00 – 176.15 ton/year. Winter temperatures were varied between 14 and 22 °C and yielded VOC emissions ranging between 90.80 and 129.00 ton/year. A second order relationship was obtained from both trends with correlation coefficients of 1.00. The sensitivity in temperature was noticed to be $\pm$ 8.71 – 12.61 ton/year of VOC emissions with an increase or decrease in temperature increments of 2 °C. Hence, suggestive of a great change in VOC emissions with a small change in temperature. To ensure VOC emissions, remain below the threshold of 100 ton/year as suggested by Golder Associates Africa (Pty) Ltd. (Golder Associates, 2019b), a temperature of 16.1 °C should be maintained. Due to the continuous fluctuations in atmospheric temperatures surrounding a storage tank, this justifies the need to implement control measures.

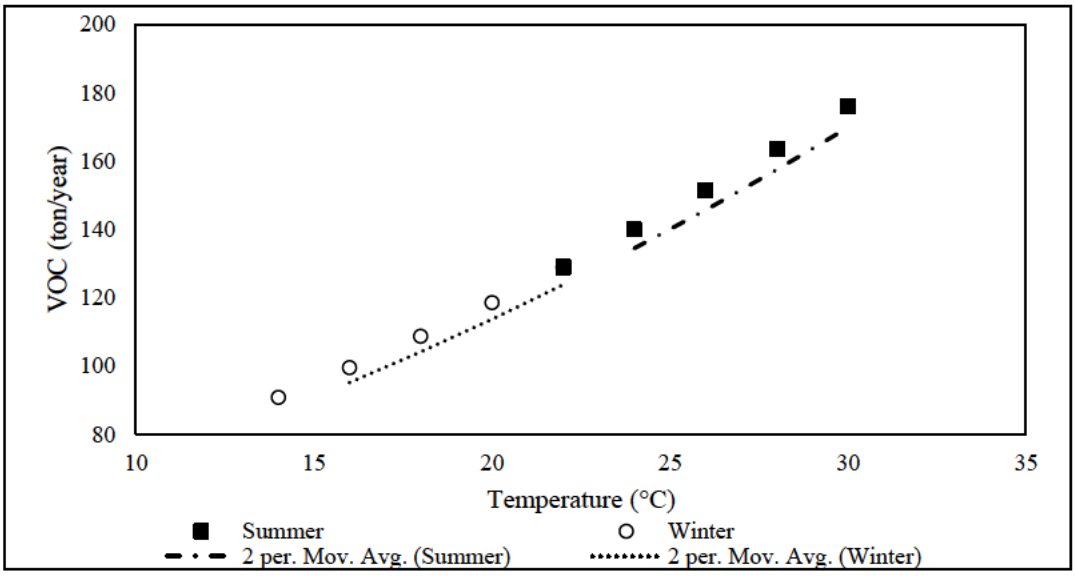
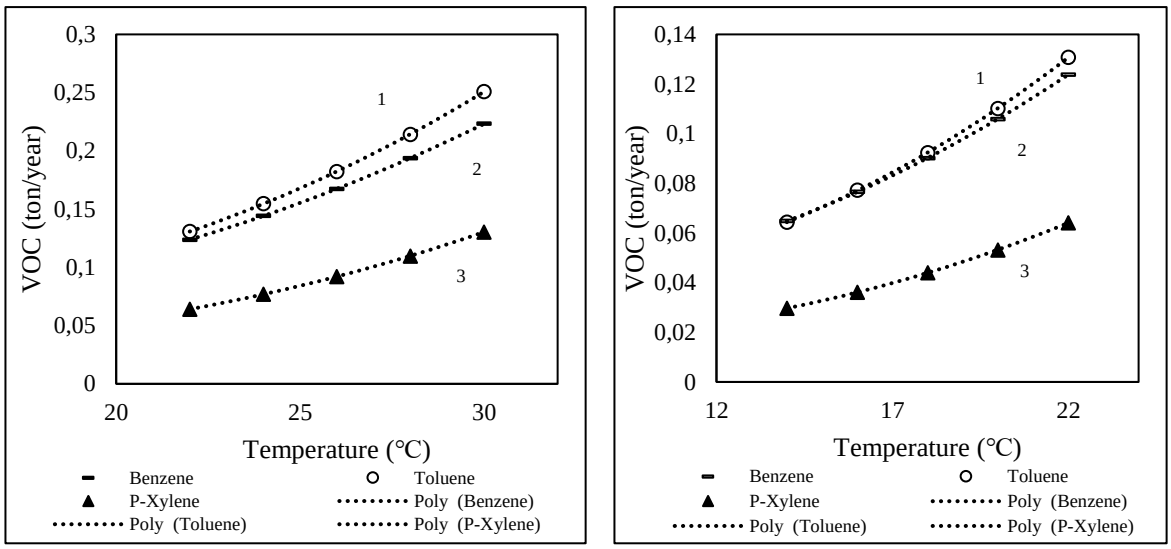


Figure 4-5: The effect of seasonal temperature variation on the crude oil storage tank VOC emission rates at 96.38 kPa (Moving averages represents the direction of trends during summer and winter)

Studies by Tamaddoni et al. (2013) have shown that an increase in tank temperature results in an increasing evaporation rate of crude oil and thereby hydrocarbon gas emissions from the tank increases. This verifies the increasing relationship that exists between the temperature of the tank and VOC emissions calculated in this study and justifies the need for proper control of tank temperature such as more frequent monitoring and predictions to reduce emissions. Figure 4-6 (a and b) illustrates the effect of temperature on the hazardous components: benzene, toluene, and p-xylene on the VOC emissions from the crude oil storage tank. A similar relationship is noted with VOC emissions of these components, with increasing VOC emissions as temperatures increase. Benzene has the greatest effect with temperature, having higher VOC emission rates whereas p-xylene was noted to emit the lowest VOC emissions. This is expected due to the properties of the two components as benzene has a lower boiling point compared to p-xylene.



a) b)

Figure 4-6: The effect of temperature on emission rates of hazardous components in the crude oil test system tank at 96.38 kPa a) 1: $y = 0.0005x^2 – 0.012x + 0.15$; 2: $y = 0.0004x^2 – 0.0075x + 0.1035$; 3: $y = 0.0003x^2 – 0.0085x + 0.0946$ b) 1: $y = 0.0003x^2 – 0.0033x + 0.048$; 2: $y = 0.0003x^2 – 0.0018x + 0.041$; 3: $y = 0.0002x^2 – 0.0023x + 0.026$

Another parameter which affects VOC emissions is the storage tank pressure. Figure 4.7 illustrates the effect of tank pressure on the VOC emissions released from the crude oil storage tank at winter (18 ℃) and summer (25 ℃) temperatures.

According to Juta and Company (Pty) Ltd. (2018), the maximum storage pressure of a tank containing an organic liquid, without the use of a pressure vessel, is 91 kPa. However, studies performed by Tamaddoni et al. (2013) observed that storage tank pressures should be maintained at pressures slightly higher than atmospheric pressure (e.g. greater than 101.325 kPa) with the use of inert gas injections, to reduce emissions. Therefore, the maximum pressure to which the tank was varied was 140 kPa. As represented in Figure 4-7, an increase in pressure results in a decrease in crude oil evaporation from the tank and hence, less VOC emissions are released from the tank. The tank has a greater sensitivity to pressure at lower pressures, where it was observed that within an 18.75 kPa change in pressure, VOC emissions varied between $\pm$ 15.66 – 198.28 ton/year in winter and $\pm$ 20.48 – 217.23 tons/year in summer. Figure 4-7 indicated that the greatest VOC loss was at lower pressures. Furthermore, VOC emissions ranged between $\pm$ 87.23 – 523.11 ton/year and $\pm$ 66.75 – 608.89 ton/year in winter and summer, respectively. This justifies the need for the implementation of nitrogen blanketing at

higher operating pressures, preferably over 100 kPa, in which the VOC emissions remain below 100 ton/year, as per Burr and Georgeson (2014). The large variation in emissions within the pressure range of 18 – 140 kPa, can be attributed to the sensitivity of VOC emissions to tank operating pressure and the 18.75 kPa interval increase in pressure. It was notably observed from the scatter from Figure 4-7 that the difference between the points (VOC emissions) decreased with increasing pressure.

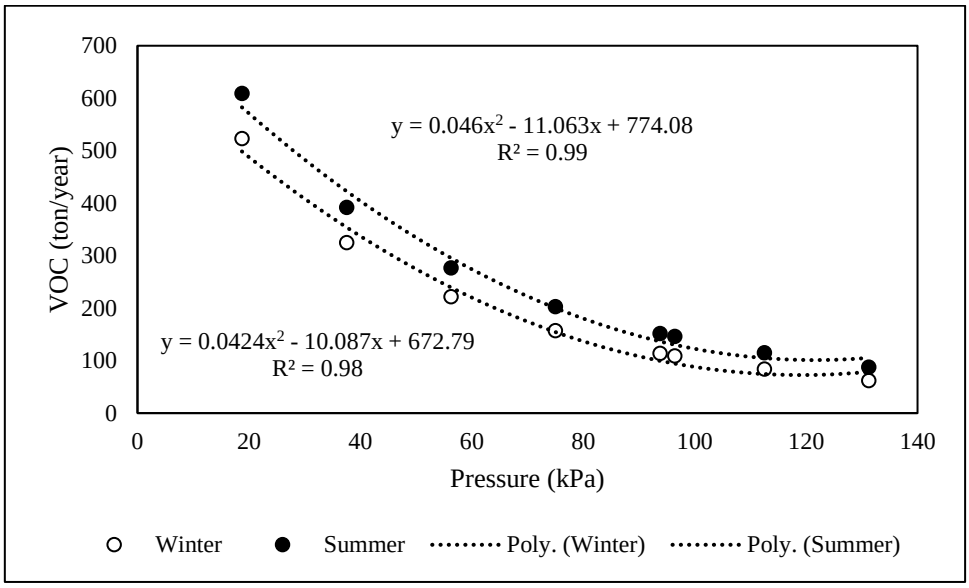


Figure 4-7: The effect of varying pressures of the crude oil on VOC emissions test system storage tank at winter (18 ℃) and summer (25℃) temperatures

4.3 Monitoring of Primary Flashing Losses

4.3.1 Base Case: VOC Emissions from Organic Liquid Storage Tank Systems

Manual equilibrium flash calculations (using K-charts) predicted emissions 161.5 % higher than direct measured emissions, whereas Aspen Plus ® predicted emissions 15.1 % higher than the VOC emissions measured through direct methods. This is likely due to the rigour of the thermodynamic models used in the Aspen Plus ® simulations. Emissions predicted from empirical correlations were significantly lower than direct measurements with deviations of 97.2 % and 85.8 % lower for the VBE and VM methods respectively. These methods have shown similar precision in the original reported studies and in other applications in the literature (Gidney & Pena, 2009). The manual flash method grossly under-estimated the flashing losses whereas the empirical correlation methods under-estimated the flashing losses. It can therefore be noted that the flashing method used to monitor VOC emissions has a

significant role in determining the level of importance stated during the reporting and compliance phase when meeting regulatory legislature, which, determines the degree of necessity to implement control methods. Since the flashing losses predicted from Aspen Plus ® was only slightly over-estimated and closer to direct measurements, it verifies the Aspen Plus ® simulation method as a preferred method to model and predict the emissions in this case. This slight over-estimation of emissions allows for the parametric factors such as varying environmental conditions to be accounted for. A sensitivity analysis can also be used to determine the VOC emissions at varying environmental conditions.

Table 4-1: VOC emissions estimated from the various flash methods of the five organic liquids at its base conditions

Flash Method	VOC (ton/year)				
	Crude oil	**ULP 95**	**ULSD**	**JET A1**	**MGO**
Manual	245.84	453 413.13	5.30	8.87	1.45
Aspen Plus ®	108.25	7 011 810.24	6 284.26	9 634.79	1 659.72
Vasquez-Beggs	2.66	2 898.64	9 126.10	7 540.83	3 014.04
Valko-McCain	13.33	28 021.61	18 913.19	16 438.98	6 200.95

Table 4-2: VOC Vapour fraction estimated from the various flash methods of the five organic liquids at its base conditions

Flash Method	VOC Vapour Fraction				
	Crude oil	**ULP 95**	**ULSD**	**JET A1**	**MGO**
Manual	0.026	0.013	0.00063	0.00092	0.00060
Aspen Plus ®	0.011	0.89	0.00047	0.00092	0.00037
Vasquez-Beggs	0.056	0.10	0.16	0.17	0.16
Valko-McCain	0.056	0.10	0.16	0.17	0.16

For the manual flash calculations, the crude oil storage tank was operated at 17.89 ℃ and 96.38 kPa, as the test system discussed in section 4.1. The petroleum product tanks were all examined at 30.0, 22.8 23.5 and 25.0 ℃ and 88.1, 116.0, 58.1 and 106.7 kPa for JET A1, MGO, ULP 95 and ULSD, respectively and the compositions are provided in Appendix A. These pressures were obtained by varying the pressure of the tank, using an iterative approach, through the

solver function on MS Excel to determine the operating pressure of the storage tanks and the vapour fraction of the liquid. Hence, the VOC emissions from the vapour stream were determined. From the analysis and Table 4-2, it was found that the highest emissions were given off from the storage tank containing crude oil and ULP 95 (Vapour mass fraction of 0.026 and 0.013 respectively) and the lowest emissions were emitted from the MGO storage tank (Vapour mass fraction of 0.00060), when estimated using the manual equilibrium flashing method. However, the emissions estimated from Aspen Plus ® (except for crude oil) is considerably lower than the emissions estimated from the manual flash calculation and the empirical correlations. The emissions estimated from the crude oil storage tank using the manual flash calculation method was determined to be $\pm$ 55.96 – 98.92 % higher than with Aspen Plus ® and empirical correlation-based methods. The estimated emissions, comparing manual calculations to Aspen Plus ®, from ULP 95, ULSD, JET A1 and MGO were determined to be $\pm$ 93.5 – 99.91 %, higher using Aspen Plus ®, respectively. However, this is attributed to the differences in operating pressures of the tanks at which flashing occurs and is accounted for, by considering the uncertainty in the pressure between the operating pressure using the manual flash method and Aspen Plus ®. This significant difference between the manual flash method and Aspen Plus ® could be attributed to the assumptions upon which the manual flash calculations are based. The non-ideal behaviour of the system, interaction parameters and activity coefficients, as accounted for, by the thermodynamic property method in Aspen Plus ® simulations, were not accounted for in the manual flash method. The separator and valve pressure changes were not considered as the manual flash method only accounts for changes within the storage tank. This justifies the considerable difference in emissions as the pressure drop across the tank contributes significantly to the rate of emissions emitted from the tank. These factors may contribute to the decreased emissions observed/obtained from the manual flash calculations, which is likely under-estimated by the method for these cases.

Similar to the estimation of VOC emissions from the crude oil test system analyzed in section 4.1., Aspen Plus ® simulations were conducted on all five organic liquid system storage tanks, to model, quantify and predict the emissions. As discussed in section 4.1.1, the SRK thermodynamic property method was selected to model the crude oil storage tank. However, after analysis, the PENG-ROB (Aspen Tech, 2013) property method was selected for the petroleum product systems (ULP 95, ULSD, JET A1 and MGO). This was a result of the lower RMSE values yielded from the consistency tests performed on Aspen Plus ®. Section A.2.2 in Appendix A represent the consistency and RMSE for each binary pair for each model results.

It was observed that the overall lower RMSE values (for the PENG-ROB property method) were: 10.07, 7.50, 8.59, and 7.50 for ULP 95, ULSD, JET A1 and MGO, respectively.

Emissions from the ULP 95 storage tank estimated using Aspen Plus ® were observed as most appreciable. This could be attributed to the lower pressure within the tank at which flashing occurs and a pressure drop of 85.33 kPa was noted across the tank estimated from Aspen Plus ®. This was $\pm$ 2.03 times higher than the pressure drop of the tank estimated from manual flash calculations. The emissions for the other five tanks showed comparable results due to the lower to negligible uncertainties in the operating pressures of the tanks.

The empirical correlation methods used to monitor the VOC emissions in this study were the VBE and VM (Gidney & Pena, 2009) gas-oil ratio methods. It was noted that the emissions from both the correlations were significantly higher than the estimations from the manual flash calculation and lower than Aspen Plus ®. The difference in the normalized emissions between the two correlations were as follows: 1.2, 2100, 620, 750 and 610 g/m^3 for crude oil, ULP 95, ULSD, JET A1 and MGO respectively. The difference in emissions between the VBE and VM empirical correlations ranged between $\pm$ 10.67 – 25 122.97 ton/year in which the minimum and maximum difference in emissions were observed for the crude oil and ULP 95 storage tanks respectively. This is justifiable as the API gravity for the ULP 95 mixture was the highest at 79.21^o and lighter mixtures such as this, allows for the flashing of more hydrocarbon vapours into the atmosphere.

4.3.2 Analysis of the Parametric Variations for the Organic Liquid Storage Tank Systems

Variations in the percentage of feed flow and temperatures of the five organic liquid storage tank systems were conducted and a comparative analysis reporting the effect and sensitivity of the parameters on the VOC flashing emissions is presented. Flashing losses from a storage tank are typically driven by environmental conditions such as the temperature of the tank (whether it is regulated or at ambient conditions). The rate of organic liquid pumped into the tank is also a major contributing effect and determines the rate of vapour flow out the tank. Therefore, the tank temperature and feed flowrate were varied based on average summer and winter conditions in the Durban area (over the temperature range of 14 – 30 ℃) and $\pm$ 10 – 25 % of the base feed flowrate entering the tank. Table 4-3 to Table 4-7 represent the variations of VOC emissions with feed flowrate using the different flash calculation methods. Similar to the test system discussed in section 4.2., the emissions increased linearly with feed flowrate. Furthermore, the emissions estimated using manual flashing methods were considerably lower

than Aspen Plus ® and the empirical correlations. The emissions which were deemed invalid from the VBE and VM correlation, were marked with an asterix in the results shown in Table 4-3 – Table 4-10.

The manual flash calculations revealed the greatest sensitivity to the feed flowrates as a 5.0 % difference resulted in an average of $\pm$ 41.94, $\pm$ 0.59, $\pm$ 0.11, $\pm$ 10 356.66 and $\pm$ 0.41 tons/year for the crude oil, JET A1, MGO, ULP 95 and ULSD storage tanks respectively. Again, using Aspen Plus ® as the basis due to its close similarity to direct methods in predicting emissions, the manual calculations under-estimated the emissions as it was found to be $\pm$ 0.0031 – 0.55 ton/m^3 lower than Aspen Plus ® results for crude oil, JET A1, MGO and ULSD storage tanks. The VBE correlations underestimated the emissions for all tanks except for MGO. Similarly, the VM empirical correlation under-estimated the emissions for the crude oil, ULP 95 and Jet A1 storage tanks.

Understanding the effect of the variations with feed flowrates allows for the development of control strategies for VOC emissions exiting the tank by ensuring the flowrate entering the tank is optimized to limit the amount of VOC emissions. Aspen Plus ® is thus, further justified as an appropriate method for use in monitoring emissions, as it can track this relationship with higher accuracy than manual methods and correlations.

Table 4-3: Comparative analysis of VOC emissions with varying flow rate using different flashing methods for crude oil

Percent of Feed flow	VOC (tons/year)			
	Manual	Aspen Plus ®	Empirical correlations	
			Vasquez-Beggs	Valko-McCain
-10	377.43	97.42	2.40*	12.00
-15	356.46	92.01	2.26*	11.33
-20	335.49	86.60	2.13*	10.67
-25	314.53	81.19	2.00*	10.00
0	419.37	108.25	2.66*	13.33
10	461.31	119.07	2.93*	14.66
15	482.27	124.49	3.06*	15.33
20	503.24	129.90	2.55*	16.00
25	524.21	135.31	3.33*	16.66

*Invalid result (Solution Gas Oil Ratio, Rs, not within limits of 20-2070 scf/bbl)

Negative value indicates percent below feed flow. Positive value indicates percent above feed flow.

Table 4-4: Comparative analysis of VOC emissions with varying flow rate using various flashing methods for JET A1

Percent of Feed flow	VOC (tons/year)			
	Manual	Aspen Plus ®	Empirical correlations	
			Vasquez-Beggs	Valko-McCain
-10	7.99	9 155.49	6 786.75*	14 795.08
-15	7.54	8 646.86	6 409.71*	13 973.14
-20	7.10	8 138.22	6 032.67*	13 151.19
-25	6.66	7 629.58	5 655.63*	12 329.24
0	8.87	10 172.77	7 540.83*	16 438.98
10	9.76	11 190.05	8 294.92*	18 082.88
15	10.20	11 698.69	8 671.96*	18 904.83
20	10.65	12 207.33	9 049.00*	19 726.78
25	11.09	12 715.96	9 426.04*	20 548.73

*Invalid result (Solution Gas Oil Ratio, Rs, not within limits of 20-2070 scf/bbl)

Negative value indicates percent below feed flow. Positive value indicates percent above feed flow.

Table 4-5: Comparative analysis of VOC emissions with varying flow rate using various flashing methods for MGO

Percent of Feed flow	VOC (tons/year)			
	Manual	Aspen Plus ®	Empirical correlations	
			Vasquez-Beggs	Valko-McCain
-10	1.31	1 492.67	2 712.63*	5 580.85
-15	1.24	1 409.68	2 561.93*	5 270.80
-20	1.16	1 326.79	2 411.23*	4 960.76
-25	1.09	1 243.89	2 260.53*	4 650.71
0	1.45	1 658.46	3 014.04*	6 200.95
10	1.60	1 824.34	3 315.44*	6 821.04
15	1.67	1 907.24	3 466.14*	7 131.09
20	1.75	1 990.13	3 616.84*	7 441.14
25	1.82	2 073.12	3 767.55*	7 751.18

*Invalid result (Solution Gas Oil Ratio, Rs, not within limits of 20-2070 scf/bbl)

Negative value indicates percent below feed flow. Positive value indicates percent above feed flow.

Table 4-6: Comparative analysis of VOC emissions with varying flow rate using various flashing methods for ULP 95

Percent of Feed flow	VOC (tons/year)			
	Manual	Aspen Plus ®	Empirical correlations	
			Vasquez-Beggs	Valko-McCain
-10	93 209.95	6 310 629.21	7 905.38*	25 219.45*
-15	88 031.62	5 960 038.70	7 466.19*	23 818.37*
-20	82 853.29	5 609 448.19	7 027.00*	22 417.29*
-25	77 674.96	5 258 857.67	6 587.82*	21 016.21*
0	103 566.61	7 011 810.24	2 898.64*	28 021.61*
10	113 923.27	7 712 991.26	9 662.13*	30 823.77*
15	119 101.60	8 063 581.77	10 101.32*	32 224.85*
20	124 279.93	8 414 172.28	10 540.51*	33 625.93*
25	129 458.26	8 764 762.79	10 979.69*	35 027.01*

*Invalid result (Solution Gas Oil Ratio (Rs) and API not within acceptable limits of equation)

Negative value indicates percent below feed flow. Positive value indicates percent above feed flow.

Table 4-7: Comparative analysis of VOC emissions with varying flow rate using various flashing methods for ULSD

Percent of Feed flow	VOC (tons/year)			
	Manual	Aspen Plus ®	Empirical correlations	
			Vasquez-Beggs	Valko-McCain
-10	5.02	5 655.93	8 213.49*	17 021.87
-15	5.05	5 341.66	7 757.18*	16 076.21
-20	5.10	5 027.47	7 300.88*	15 130.55
-25	5.15	4 713.29	6 844.57*	14 184.89
0	5.20	6 284.38	9 126.10*	18 913.19
10	5.27	6 912.75	10 038.71*	20 804.51
15	5.33	7 227.02	10 495.01*	21 750.17
20	5.41	7 541.21	10 951.32*	22 695.83
25	5.50	7 855.39	11 407.62*	23 641.49

*Invalid result (Solution Gas Oil Ratio, Rs, not within limits of 20-2070 scf/bbl)

Negative value indicates percent below feed flow. Positive value indicates percent above feed flow.

Table 4-8 represents the variations of temperature on VOC emissions for the five systems using manual flash calculations and Aspen Plus ®. As suggested by Golder Associate Africa (Pty) Ltd. (Golder Associates, 2019b), the temperatures in winter and summer in Durban range between 14 – 22 ℃ and 24 – 30 ℃ respectively, hence, the temperatures were varied accordingly. Similar to the results obtained with the test system, the trends exhibited the same behaviour of increasing VOC emissions with temperature. Comparison of the manual flash calculations with Aspen Plus ® for each of the systems indicated that emissions estimated using manual calculations were lower than emissions estimated using Aspen Plus ® for all the systems except crude oil. The average deviation of emissions using manual calculations with respect to Aspen Plus ® predictions were 94 – 127 % for all the systems. It was observed that crude oil manual calculation had the greatest over-prediction and ULP 95 manual calculation had the smallest over-prediction of emissions. However, the ULP 95 storage tank Aspen Plus ® emission results indicate that flashing of the mixture was not predicted under the winter temperatures at the specified pressure of 14.67 kPa using Aspen Plus ® and is only predicted to occur at 58.09 kPa using manual flash calculations. This suggests that environmental conditions play a role in the estimation of VOC emissions when using Aspen Plus ® and should be taken into consideration during emission predictions.

Empirical correlations were varied according to separator temperature and pressure inputs to determine the gas-oil ratio and hence, the resulting VOC emissions for each of the five storage tank systems. The separator temperature was varied from 20 – 150 ℃ as this was the operating range in which the VBE (Vazquez and Beggs, 1977) and VM (Valko and McCain, 2003) correlations were deemed valid as the required specifications for all parameters utilised in the equations were met. This temperature variation was applied to both the VBE and VM correlations. It was noted that the VOC emissions decrease with temperature with both correlation methods and VBE correlations estimated lower emissions compared to VM. The difference between the two correlation methods ranged between the following: 3.53 – 10.3, 1 343.03 – 9 927.49, 284.9 – 3 594.56, 14 956.02 – 19 716.88 and 954.18 – 11 023.15 ton/year, for crude oil, JET A1, MGO, ULP 95 and ULSD respectively.

Various constraints exist with both the empirical correlations. Therefore, for the results to be valid, the boundaries for each parameter had to be met. The limitations are presented in Table 2.5 and 2.6 in Chapter 2. It was observed, from Table 4-3 to Table 4-7, that the validity of the empirical correlations was very restrictive with only a few emission measurements being valid

when using the VBE correlation as the gas oil ratio was calculated to be out of the specified range of the VBE equation. Using the VBE correlation, all the emissions estimated with the variations of flowrate between $\pm 10 - 25$ % (in Table 4-3 to Table 4-7) were invalid as the gas-oil ratios were below 20 scf/bbl for crude oil, JET A1, MGO and ULSD storage tanks. Contrary to the VBE equation, VM-based correlation estimates met most constraints for almost all the storage tank systems except for ULP 95, which was deemed invalid due to its API value exceeding 56.8^{o} (Results shown in Table 4-6). It was noted that the prediction of ULP 95 emissions was not possible due its high API value of 79^{o} which exceeded the VBE and VM constraints of 58^{o} and 56.8^{o} respectively (Results in Table 4-6). Similarly, all the emission estimates from all storage tank systems using the VBE correlation method, with varying separator temperatures in Table 4-9 results were deemed invalid as the gas-oil ratios were below 20 scf/bbl and the separator pressure was set to below the accepted 50 psia. For the VM-based correlation estimates, all estimates for all systems, at temperatures above 90 ℃ were discarded due to its invalidity as the correlation is only able to be used for prediction at temperatures below 90 ℃. The emissions with varying pressures were only valid between 600 – 1000 kPa for all systems using the VBE-based correlation method as the separator pressure constraints were limited to a range of 344 – 36 197 kPa (Table A-70 and Table A-71 shows this). All estimated emissions using the VM-based correlation method met the given constrains and were therefore deemed valid for all the systems, except ULP 95, for reasons discussed above. These results prove that monitoring emissions through the use of the VBE and VM correlation methods is unreliable, including for several common hydrocarbon mixtures at standard conditions. It is recommended that these equations are applied only when all conditions are within the applicable ranges. The variability with the type of organic mixtures, lack of specified conditions and limited parameter limits of the correlation equations contributed to the unreliability of the use of the empirical correlations for prediction of VOC emissions.

Table 4-8: Comparative analysis of VOC flashing emissions, for the different monitoring methods, at varying temperatures of the five organic liquid storage tank systems

Season	Temperature (℃)	VOC (ton/year)									
		Crude oil		JET A1		MGO		ULP 95		ULSD	
		Manual	Aspen Plus ®	Manual	Aspen Plus ®	Manual	Aspen Plus ®	Manual	Aspen Plus ®	Manual	Aspen Plus ®
Winter	14.00	190.19	90.79	7.93	1099.92	1.45	872.72	30 409.41	-	5.02	2 813.17
	16.00	215.42	99.51	8.01	1099.92	1.45	1 006.96	113 718.20	-	5.05	3 243.58
	18.00	245.84	108.78	8.40	1099.92	1.45	1 164.45	199471.20	-	5.25	3 748.60
	20.00	247.89	118.61	8.10	1099.92	1.45	1 348.79	272308.096	-	5.10	4 339.77
	22.00	291.35	129.01	8.20	1099.92	1.45	1 564.01	371581.18	-	5.15	5 030.13
Summer	24.00	352.73	139.96	8.31	1099.92	1.45	1 814.70	508423.079	7 554 733.80	5.20	5 834.38
	26.00	446.28	151.47	8.44	1099.92	1.45	2 106.00	632019.17	7 007 010.91	5.27	6 769.08
	28.00	607.15	163.54	8.50	1099.92	1.45	2 443.70	767617.34	7 832 941.31	5.30	7 852.81
	30.00	953.88	176.15	8.57	1099.92	1.45	2 550.65	881796.24	7 832 941.31	5.33	8 427.73

Table 4-9: Comparative analysis of VOC flashing emissions, using empirical correlations, at varying separator temperatures of the five organic liquid storage tank systems

Separator Temperature (℃)	VOC (ton/1000/year)									
	Crude oil		JET A1		MGO		ULP 95		ULSD	
	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain
21.10	0.00265*	0.013	7.78*	17.71	3.10*	6.70	9.43*	29.15*	9.40*	20.42
37.78	0.00259*	0.0108	6.83*	13.28	2.74*	4.97	6.98*	25.14*	8.31*	15.17
65.56	0.00247*	0.00865	5.59*	9.26	2.27*	3.41	4.26*	21.19*	6.85*	10.44
93.33	0.00236*	0.00729*	4.63*	7.00*	1.90*	2.55*	2.56*	18.70*	5.73*	7.82*
121.11	0.00224*	0.00633*	3.86*	5.55*	1.60*	2.01*	1.43*	16.91*	4.83*	6.15*
146.11	0.00214*	0.00567*	3.29*	4.63*	1.38*	1.66*	0.71*	15.66*	4.15*	5.10

*Invalid Result (VM temperatures > 90℃, VBE Gas Oil Ratio is not within the limit of 20-2070 scf/bbl)

Table 4-10: Comparative analysis of VOC flashing emissions, using empirical correlations, at varying separator pressures of the five organic liquid storage tank systems

Separator Pressure (kPa)	VOC (ton/1000/year)									
	Crude oil		JET A1		MGO		ULP 95		ULSD	
	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain	Vasquez-Beggs	Valko-McCain
200	0.00114*	0.0071	7.54*	16.44	3.01*	6.20	8.78*	28.02*	9.13*	18.91
400	0.00274*	0.00203	18.11*	59.24	7.22*	23.43	22.77*	71.76*	21.86*	71.03
600	0.00458	0.00318	30.19	95.73	12.01	38.24	39.46*	137.04*	36.39	115.79
800	0.00659	0.0043	43.36	128.00	17.24	51.19	58.13*	231.49*	52.23	154.99
1000	0.00874	0.00545	57.41	158.33	22.80	63.22	78.40*	360.59*	69.10	191.43

*Invalid Result (VM temperatures > 90℃, VBE Gas Oil Ratio is not within the limit of 20-2070 scf/bbl)

4.3.3 Monitoring of Secondary Breathing and Working Losses

Annual atmospheric working and breathing losses were estimated using the equations developed by the American Petroleum Institute (API) and the U.S. Environmental Protection Agency (EPA). A comparative analysis of the factors affecting the rate of VOC emissions from five petroleum liquids/products (Crude oil, ULSD, ULP 95, Jet A1 and MGO) and two types of tanks (FRT and IFRT) are presented in this section.

The total annual atmospheric emissions for various petroleum liquids are presented in Table 4-8 and are based on the production rates and conditions as presented in

Table **4-11**. Emissions from all five storage tank systems are compared to the emissions standard of 100 ton/year (Peacock, 2010). Burr and Georgeson (2014) estimated breathing and working losses for crude oil to be 12.65 ton/year using the ProMax utility, whereas the EPA calculations estimated 4.35 ton/year from fixed roof tanks. This 65.5 % difference in the emissions estimate is a possible indication of an over-prediction with the ProMax utility method as EPA equations are continuously under development to improve accuracy. However, these improvements are not necessarily conclusive.

A comparison of the emission levels from two types of tanks: FRTs and IFRTs are shown in Figure 4-8. The highest source of emissions from FRTs were observed at Tank 3 (ULP 95) with an emission rate of 1486.29 ton/year and the lowest at Tank 5 (MGO) of 0.064 ton/year. The total emissions estimated from Tanks 3 and 4 were found to be 1386.29 and 473.85 ton/year, respectively, which are higher than the threshold standard of 100 tons/year of VOC emissions, whereas the total emissions from Tanks 1, 2 and 5 were lower than the threshold. The highest emitting, Tank 3, may be due to its contents as the vapour pressure (58.17 kPa at 296.66 K) of petrol is higher than the other products at this temperature, thus yielding a high VOC emission rate. Emissions from the IFRTs were observed to be significantly lower for all petroleum products except for MGO which was higher and the emissions were increased by 86.2 %. Jet A1 was found to have the greatest reduction in emissions levels, with an IFRT, by 99.7 % with ULP 95, ULSD and crude oil being lowered by 99.4 %, 99.5 % and 91.3 % respectively. These observations can be viewed in Table 4-9 and may be justified by the fact that IFRTs react to varying temperature changes through the floating roof mechanism which allows for the pressure to be maintained within the tank without the need for atmospheric venting. Whereas fixed roof tanks use venting as a technique for controlling pressure changes as varying temperature conditions are experienced (Jackson, 2006). These significant

reductions in emission levels may justify the replacement of FRTs with IFRTs in storage tank facilities where possible as a first step to reduce emissions.

Table 4-11: Tank conditions for emissions estimations from various petroleum liquids

Tank	Product	Throughput (m^3)	Production Rate of Oil (bpd)	Turnovers (per year)	Roof Shape	Colour	Solar Absorptances
T1	Crude Oil	2604.13	18550	26.00	Conical	Medium grey	0.68
T2	ULSD	622800.00	343434.01	24.00	Geodesic dome	White	0.17
T3	ULP 95	90000.00	12407.30	6.00	Geodesic dome	White	0.17
T4	JET A1	120000.00	24814.60	9.00	Geodesic dome	White	0.17
T5	MGO	188000.00	30237.04	7.00	Geodesic dome	White	0.17

T – Tanks
ULSD – Ultra-low Sulphur Diesel
ULP 95 – Unleaded 95 Petrol
JET A1 – Jet Fuel
MGO – Marine Gas Oil

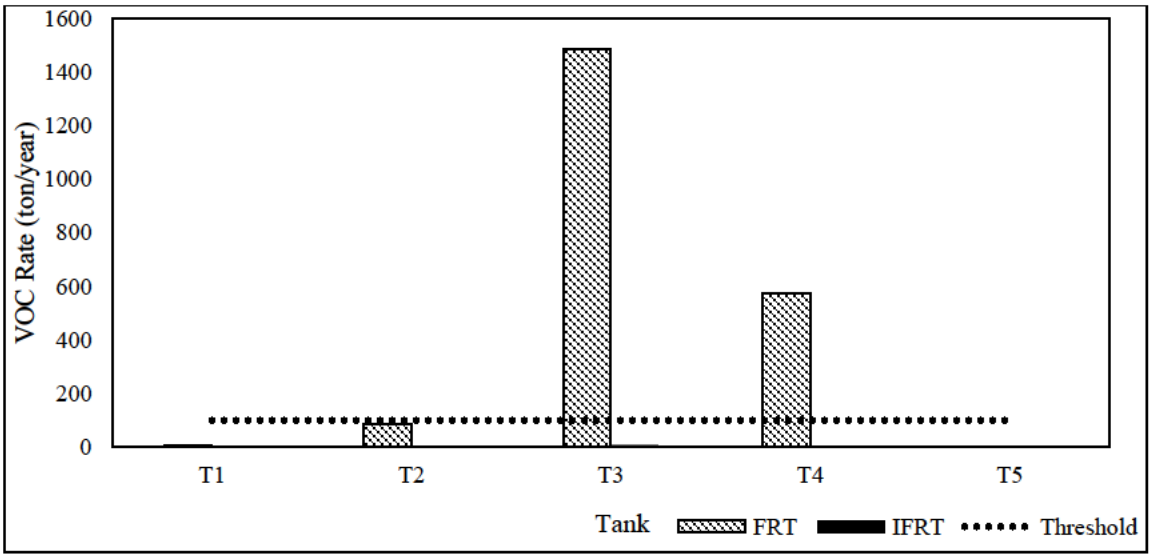


Figure 4-8: VOC rate of five petroleum liquid types (Tank 1: crude oil, Tank 2: Ultra-low Sulphur Diesel (ULSD), Tank 3: Unleaded Petrol (ULP 95), Tank 4: Jet Fuel (JET A1) and Tank 5: Marine Gas Oil (MGO)) from a Floating Roof Tank (FRT) and Internal Floating Roof Tank (IFRT)

The normalized rate of emissions with respect to throughput is represented in Figure 4-9 for a FRT and IFRT. Tanks 3 and 4 were found to emit the highest rate of VOCs in a FRT while Tank 5 emitted the lowest rate. Comparatively, Tanks 1 and 3 emitted the highest rate in an IFRT and Tanks 2 and 4 emitted the lowest. These observations suggest that petrol, jet fuel and crude oil may have the greatest potential for emitting VOCs into the atmosphere from the secondary losses. Studies conducted by Jackson (2006) revealed that 87.0 % of total VOC emissions from a storage tank facility may be attributed to the release from petrol, 3 % from crude oil and 10 % from the other refined petroleum products. This corresponds with the estimates produced in this work. Diesel has a higher molecular weight with lower vapour pressures, suggesting lower emission rates from this product as verified by the estimates presented in Figure 4-9.

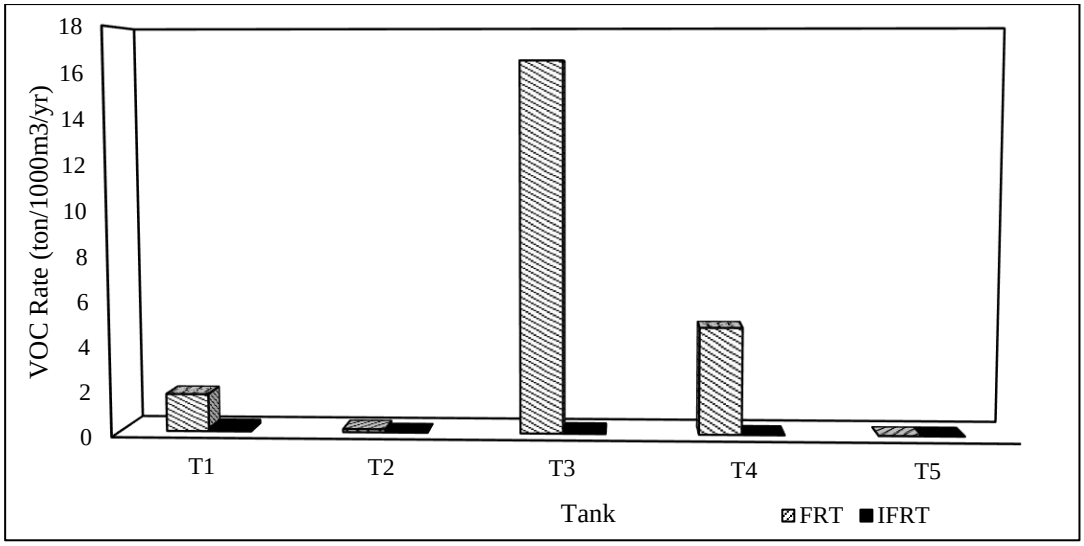


Figure 4-9: Normalized VOC rate of six petroleum liquid types (Tank 1: crude oil, Tank 2: Ultra-low Sulphur Diesel (ULSD), Tank 3: Unleaded 95 Petrol (ULP 95), Tank 4: Jet Fuel (JET A1) and Tank 5: Marine Gas Oil (MGO)) from a Floating Roof Tank (FRT) and Internal Floating Roof Tank (IFRT)

4.3.3.1 Variations in Breathing and Working Losses

The factors affecting breathing and working losses from FRTs and IFRTs were varied to determine its effect on the VOC emissions. Figure 4-10 (a-e) illustrates the effect of the colour of the storage tank through the paint solar absorptance factors (as illustrated in Table 2-2, Chapter 2) on the rate of VOC emissions from the five types of organic liquids: crude oil, ULSD, ULP 95, JET A1 and MGO.

Consistent trends were observed for all hydrocarbon liquids, in both FRTs and IFRTs. The paint factor, relating to a specific tank colour, is directly proportional to the VOC emissions rate in which a linear, increasing relationship exists. A distinct observation from Figure 4-10 is the difference in VOC emissions between FRTs and IFRTs in which IFRTs have a significantly lower VOC emission rate. It can also be noted that the IFRT emission rates have a slight increase in VOC emission with the paint factor compared to the FRT. A grey, medium shade painted storage tank was initially specified in Burr and Georgeson (2014) for crude oil, therefore, using this as the basis, a maximum reduction in VOC emissions was noted in using a white painted tank with absorptance factor of 0.17. Reduction in VOC emissions by 15.6 % and 10.6 % from FRTs and IFRTs respectively, was determined with a 6.1 % and 4.4 % increase in emissions using a red painted tank which has an absorptance factor of 0.89. This follows the trends illustrated by the figures in which white paint has the lowest

absorptance factors and red paint has the highest. This suggests that the paint factor is an appropriate parameter in controlling VOC emissions in FRTs and IFRTs. The petroleum products of USLD, ULP 95, JET A1 and MGO were all analysed using a white storage tank as specified by Golder Associates Africa (Pty) Ltd. (Golder Associates, 2019b) and hence, the lowest VOC emissions affected by paint factor, were recorded.

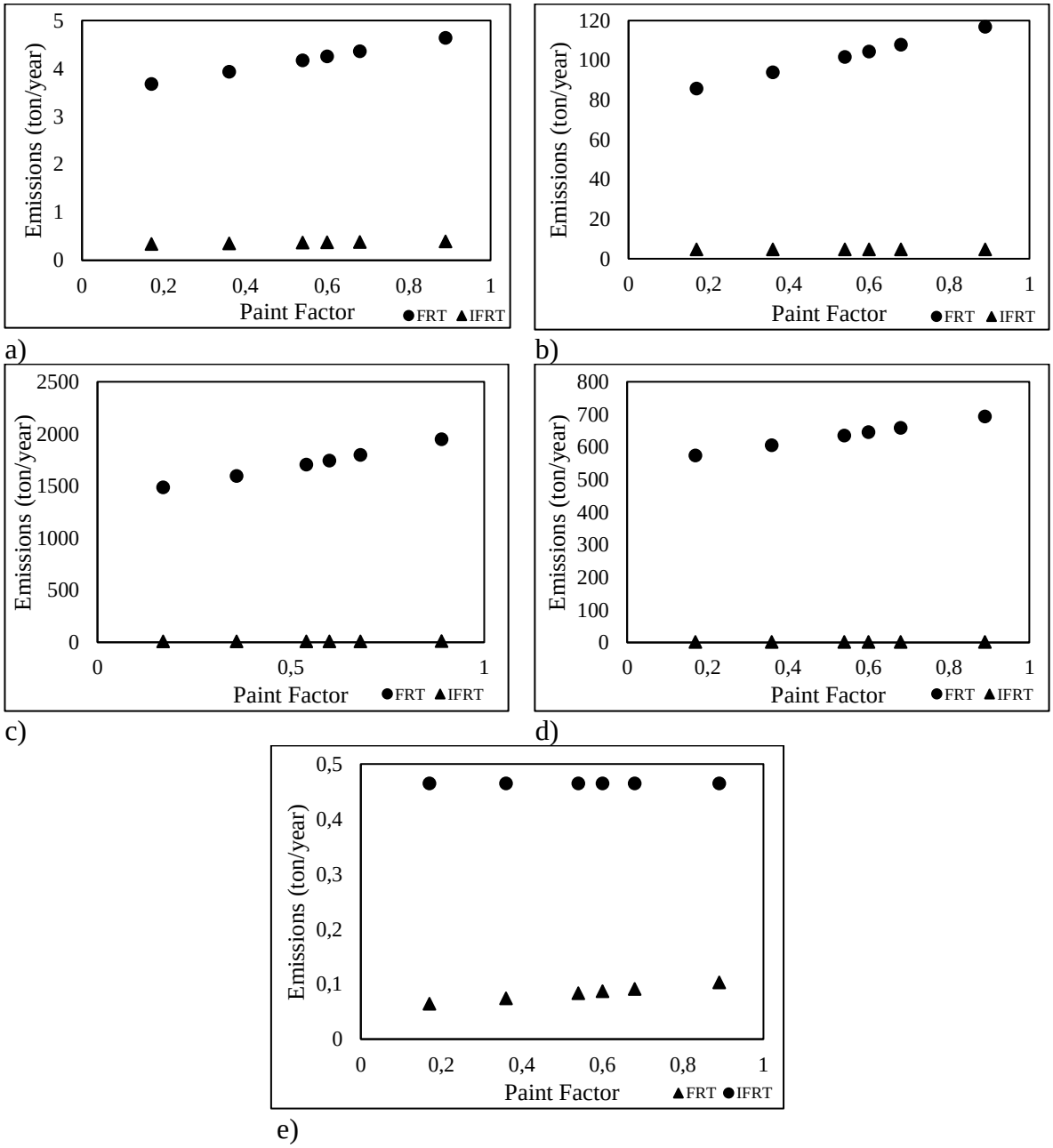


Figure 4-10 (a-e): The effect of paint factor (tank colour) on the emissions from a crude oil, ULSD, ULP 95, JET A1 and MGO storage tank, respectively

The breathing losses of a storage tank result from changes in the level of liquid within the tank. The effect of the changing liquid levels on the emissions were monitored by varying the capacity of the tanks. Figure 4-11 represents the trends obtained when the capacity of the various organic liquid systems was varied from 0 – 100 %. The observed trends from this study resembled the trends of filling and emptying volumetric flow rates, displayed as capacity in this study, from Rota, et al. (2001). While all systems exhibited a generally consistent trend with a slight reduction in emissions with increasing capacity, ULP 95 had the highest rate of emissions and MGO had the lowest rate of emissions. The sensitivity of the emissions to changes in the capacity of the tank remains low and varies for each system. A 10 % increase in capacity reduced the emissions slightly by an average of: $\pm$ 1.6 % for crude oil, $\pm$ 0.12 % for ULSD, $\pm$ 0.59 % for ULP 95, $\pm$ 0.44 % for JET A1 and $\pm$ 1.7 % for MGO. The reduction in emissions with increasing capacity may be attributed to the fact that the vapour space of the tank is reduced when the tank is filled to a higher capacity and hence, this reduces the build-up of vapours in the tank and ultimately reduces the expulsion of vapours to the atmosphere (Rota, et al., 2001). The crude oil storage tank was on average filled at 50 % of its capacity (Burr & Georgeson, 2014), whereas the other systems were filled at an average on 75 % of its capacity (Golder Associates, 2019b). Considering that the effect of increasing capacity only slightly affects the reduction potential of the emissions, tanks should continue to operate at these capacities or close to maximum capacity of 90 % to prevent over-filling and to ensure the effects environmental conditions such as varying temperature and pressure are accommodated for.

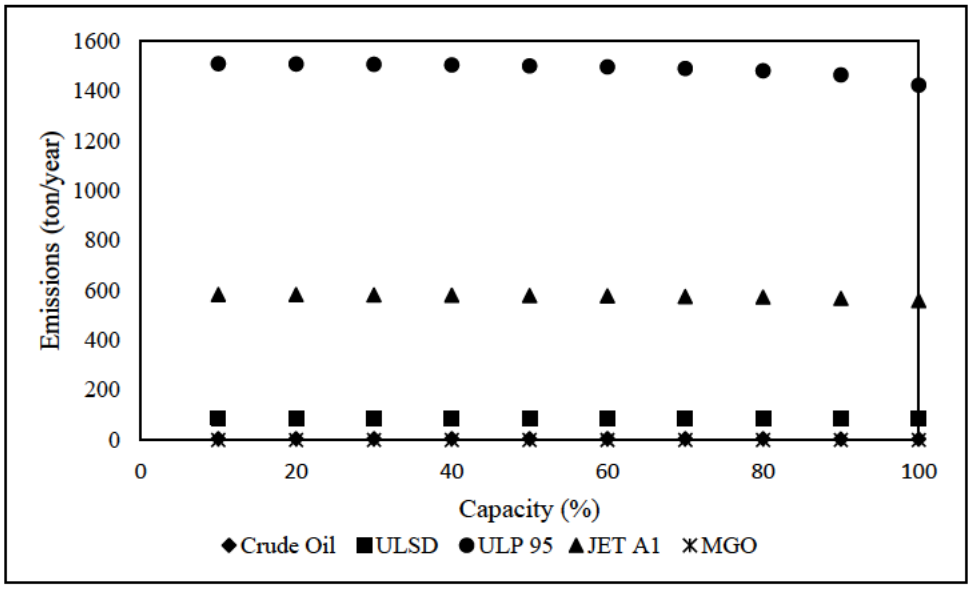


Figure 4-11: The effect of tank capacity on emissions from five petroleum liquid types in a fixed roof storage tank

The effect of the production rate of the various systems on the VOC emissions were determined and presented in Figure 4-12 (a-e). Similar trends were observed for all the systems in which emissions increased linearly with production rate. Notably, the sensitivity of the emissions to the production rate for each system differed slightly for both the FRT and IFRT with a R^2 value of 1 noted for all graphs. For a FRT the analysis of the slopes suggested that ULP 95 exhibited the highest slope of 87.5 kg/year.bpd. This steeper gradient suggested that a larger increase in emissions occurred over the increasing range of the production rate. MGO was observed to have the smallest slope of 20 kg/year.bpd, suggesting that a smaller increase in emissions occurs with an increase in production rate. For the IFRT, crude oil was noted to have the highest slope of 600 kg/year.bpd and MGO has the lowest slope of 2 kg/year.bpd. ULP 95 and JET A1 emissions in an IFRT were low due to the chemical constituents of the fuel cut at the varying production rates. Therefore, for emissions to remain at a minimum, the production rate should be controlled accordingly to ensure the threshold limits are maintained. The linear models obtained from the trends in Figure 4-12 (a-e) can be used to control the emission rate by ensuring it remains below 100 ton/year (Golder Associates, 2019b).

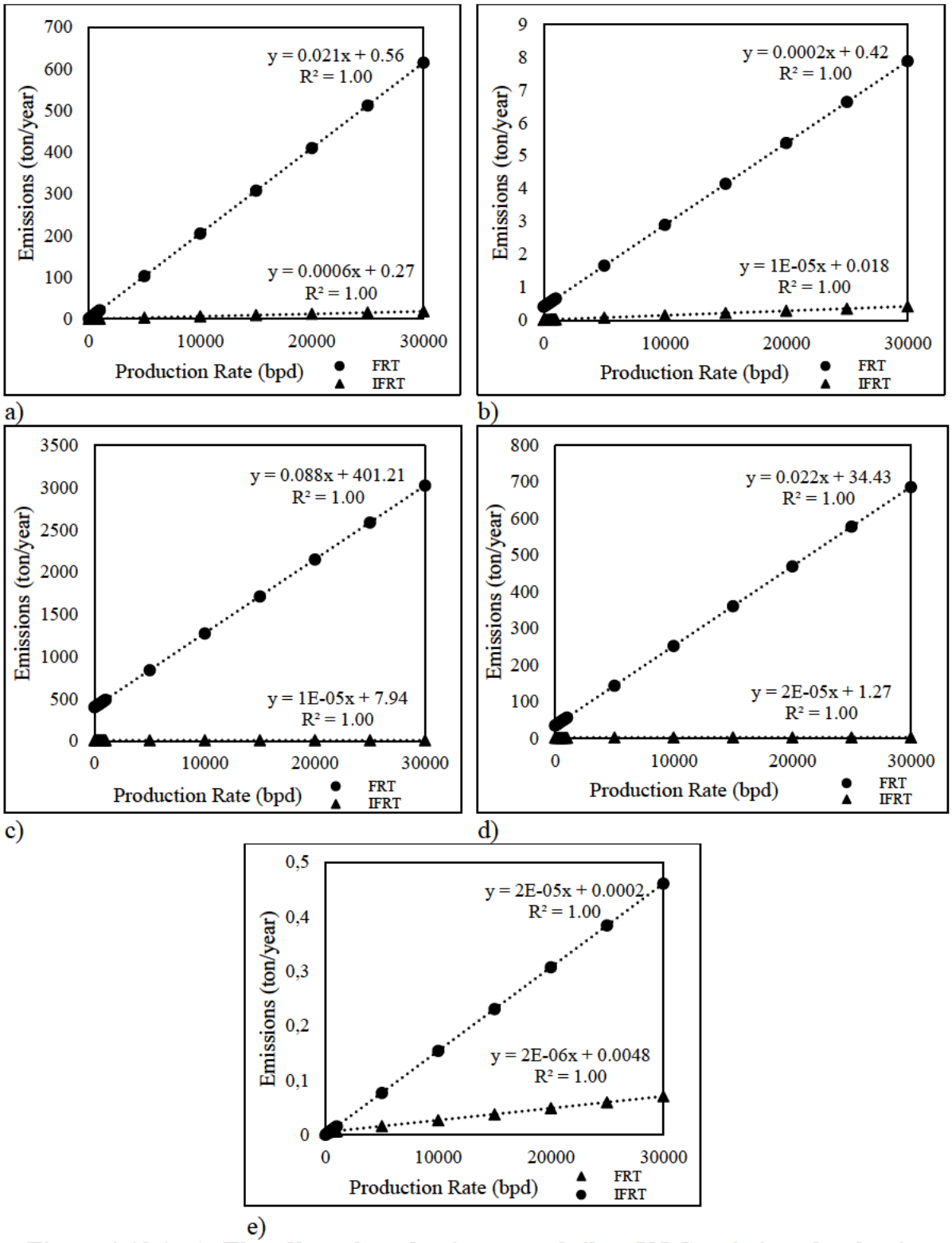
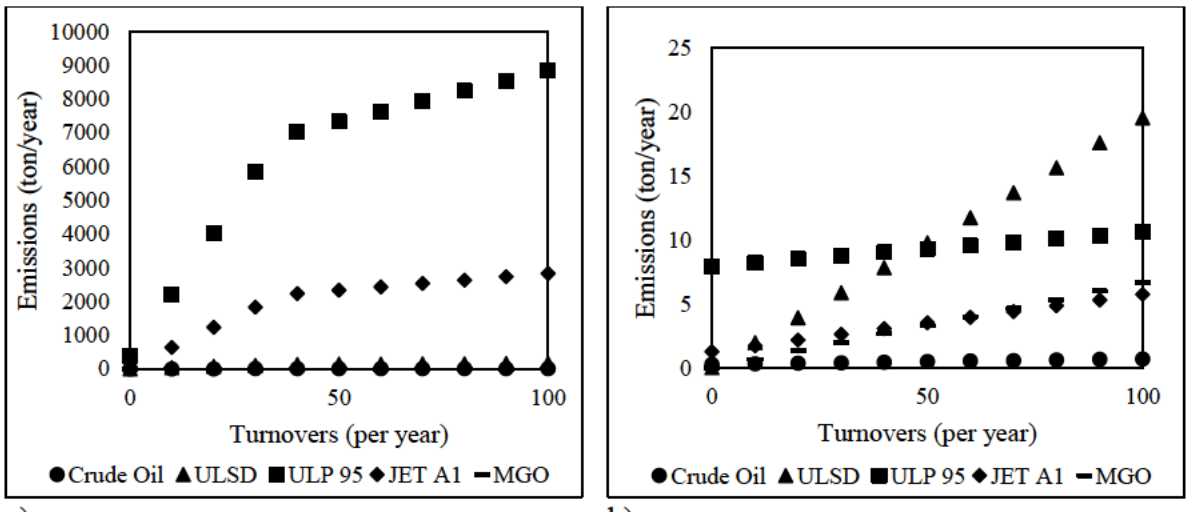


Figure 4-12 (a-e): The effect of production rate of oil on VOC emissions for the six types of petroleum liquids, (a) crude oil, (b) ULSD, (c) ULP 95, (d) JET A1 and (e) MGO respectively, in a FRT and IFRT

Figure 4-13 (a-b) represented the sensitivity of the emissions on the turnovers from a FRT and IFRT. According to Kirmeyer, et al. (1995), the average storage time of an organic liquid, is known as the turnover. It is therefore a useful parameter to determine during the design and operation of storage tanks and can be used to ensure emissions remain at a minimum. The guidelines proposed by Kirmeyer, et al. (1995), suggested an average detention time of storage tank contents is 3 days. However, studies by Owczuk and Kotodziejczyk (2015) suggested a safe storage period of fuel as 6 – 9 years. However, the literature also suggested that diesel and fuel oils should be stored for an approximate period of 2 years and petrol should be stored for approximately 1 year. This is to ensure that fuel degradation, polymerization, oxidation, and sedimentation do not occur. The turnovers increased until 40 per year, and then began to plateau whereas the IFRT showed a constant linear increasing trend. ULP 95 was again, observed to emit the highest emissions in the FRT tank with increasing turnovers, whereas in the IFRT the effect of turnovers had a slight impact on the emissions of ULP 95 compared to the other mixtures. Crude oil was observed to have the lowest emissions with a relatively flatter slope for both the FRT and IFRT, suggesting that the increase of the rate of emissions is smaller as the turnovers increase. The turnovers should, therefore, be maintained at a minimum to ensure emissions are reduced. This coupled with the storage time suggested by literature, to ensure the quality of the organic mixtures is not compromised, implied that operation of the storage tanks should occur with approximate turnovers of 0 – 10 (per year).



a) b)

Figure 4-13 (a-b): Graphs showing the effect of turnovers on a FRT and IFRT

Temperature is a critical parameter which affects the breathing losses in a storage tank. Figure 4-14 (a-e) represents the effect of this under the conditions in Durban where the temperature ranged between 10 – 40 ℃. Similar to the trends observed by the variation of temperature with flashing losses, it was noted that an increasing, linear trend exists for all mixtures, except for ULP 95, in both the FRT and IFRT. ULP 95 differs in that the emissions increase exponentially from a FRT suggesting the need to implement stricter control methods for this storage tank. This is expected due to the higher vapour pressure and compositions of the mixture, as previously discussed. Emissions from FRTs were considerably higher for all mixtures except for MGO, compared to the IFRT. The average increased deviations from the simulated IFRT were noted as follows from Figure 4-14 (a-e): $\pm$ 876.7, $\pm$ 2 407.6, $\pm$ 20 436.4, $\pm$ 34 435.4 % for crude oil, ULSD, ULP 95, JET A1 respectively. MGO was noted to show an average decreased deviation of $\pm$ 77.7 % from the IFRT. Optimum temperatures for operation are suggested in section 4.3.2 – operational controls, of VOC emissions.

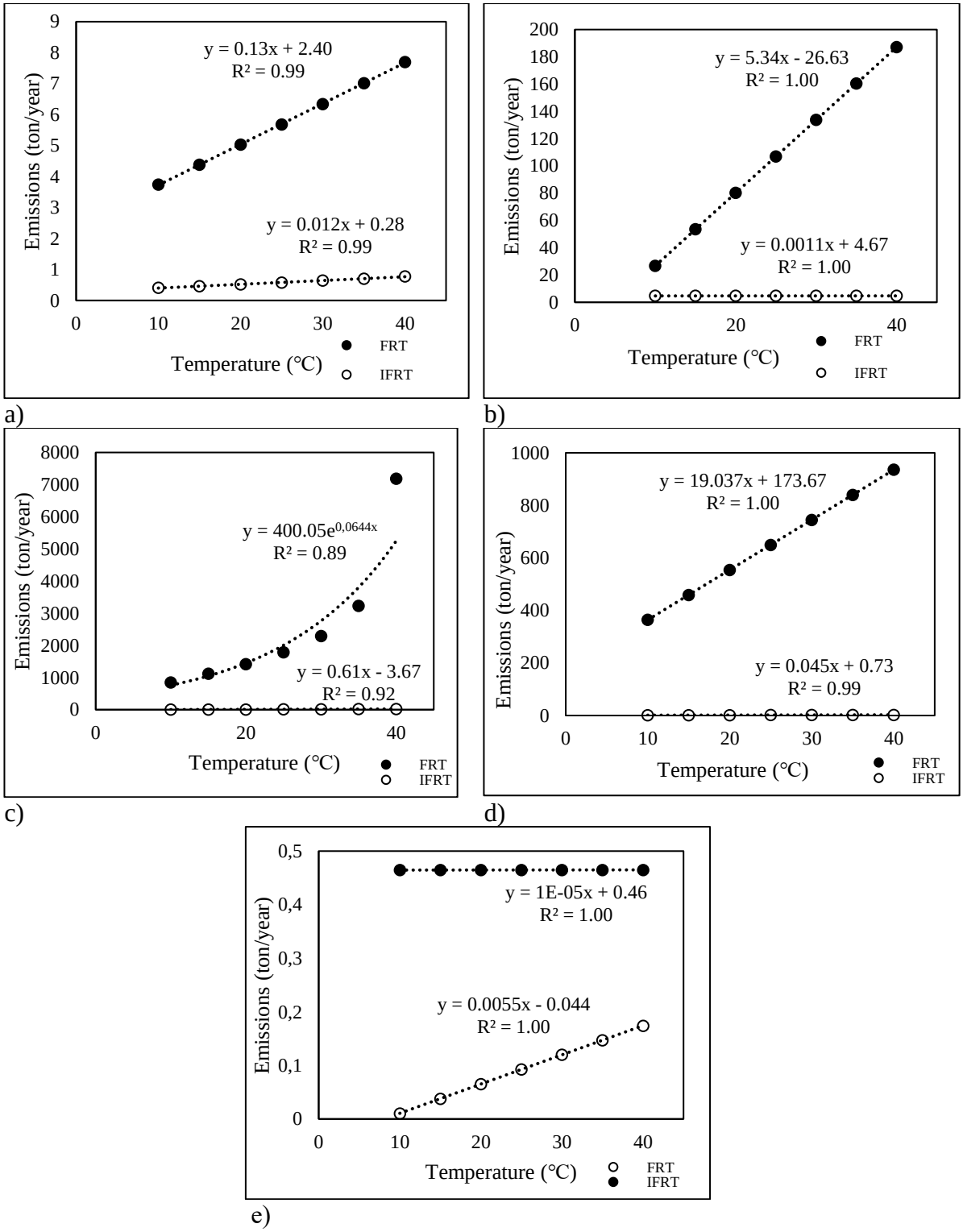


Figure 4-14 (a-e): The effect of daily average ambient temperature on VOC emissions of the five types of petroleum liquids using the EPA method, (a) crude oil, (b) Ultra-low Sulphur Diesel (ULSD), (c) Unleaded Petrol (ULP 95), (d) Jet Fuel (JET A1) and (e) Marine Gas Oil (MGO) respectively, in a Floating Roof Tank (FRT) and Internal Floating Roof Tank (IFRT).

4.4 Control of VOC Emissions

This section discusses the operation and implementation of some control methods on the VOC emissions in storage tanks. The need for implementing these mitigation procedures were necessitated by the Sustainable Development Goals (SDGs): 13 (Climate Action) and 11 (Sustainable Cities and Communities) and outlined in the frameworks of the sustainability reports in major Petroleum Industries such as BP and Sasol, and other the studies. The control schemes studied were based on physical and operation control methods to determine its efficiency in handling the VOC emissions from flashing losses and working and breathing losses, where applicable.

4.4.1 Physical Controls

The physical control methods studied consisted of tank configuration with working and breathing losses, vapour treatment with efficiencies applied to the flashing losses using Aspen Plus ® and working and breathing losses using the manual calculations, and nitrogen blanketing and pressure relief valves of working and breathing losses for the five different cases of organic mixtures.

4.4.1.1 Tank Configuration

Table 4-12 represents the estimated abatement efficiency of reducing working and breathing losses by replacing an FRT with an IFRT. The estimated abatement efficiencies were calculated based on the reduction in emissions from a FRT to an IFRT. It ranged between $\pm$ 72.05 – 99.71 % for the mixtures studied with crude oil having the lowest efficiency and JET A1 exhibiting the highest. IFRTs reduced ULP 95 and ULSD emissions considerably as the abatement efficiencies were noted as being $>$ 90 %. Studies from the European Commission (2006) suggested abatement efficiencies ranged between 60 – 90 % when implementing an IFRT. This is expected as IFRTs operate by adjusting the deck of the floating roof to accommodate for changes in liquid level of the tank thus controlling the withdrawal losses from the tank. This reduces the vapour space which further prevents the expulsion of emissions into the atmosphere.

Table 4-12: Effect of Tank Configuration of Working and Breathing Losses of the different tank mixtures

Mixture	FRT VOC emissions (ton/year)	IFRT Reduced VOC emissions (ton/year)	Abatement Efficiency (%)
Crude Oil	1.36	0.38	72.05
ULSD	85.79	4.69	94.53
ULP 95	1 486.29	8.10	99.46
JET A1	573.85	1.67	99.71
MGO	0.064	0.46	86.15

FRT – Floating Roof Tank, IFRT – Internal Floating Roof Tank, VOC – Volatile Organic Emissions, ULSD – Ultra-low Sulphur Diesel, ULP 95 – Unleaded Petrol 95, JET A1 – Jet fuel, MGO – Marine Gas Oil

The major remaining emissions from IFRTs is from the remaining liquid present on the tank walls from the raising and lowering movement of the floating roof (European Commission, 2006). The rim seal and deck fitting losses from working and breathing losses in IFRTs can also be controlled through the installation of mechanical-shoe primary seals and a welded deck to ensure minimum emissions are released. The primary seal minimizes the space between the tank wall and floating deck as the mechanical shoe seal (defined as a band of sheets) reaches the surface of the liquid and reduces the vapour space of the rim which occurs between the mechanical shoe and floating deck, thereby reducing the emissions (U.S. Environmental Protection Agency, 2006). All mixtures showed a reduction in emissions when implementing IFRTs in this range except for MGO in which emissions increased by 86.15 % in an IFRT, as seen in Table 4-12. Whilst IFRTs are usually recommended due to its reduction potential, MGO favours the use of a FRT which exhibits lower emissions from the tank. This was expected due to the low vapour pressure of 0.00048 kPa of the MGO mixture. According to the limits set out by NEMA (Molewa, 2019), the type of tank recommended for use at the mixture's true vapour pressure was noted in Table 4-13 and the specifications outlined by NEMA are presented in Appendix B.

Table 4-13: Recommendations on the tank configurations according to (Molewa, 2019)

Mixture	True Vapour Pressure (kPa)	Conditions of Tank Type	Type of Tank*
Crude Oil	17.22	Pressure: 14 – 91 kPa Throughput: > 50 000 m^3/year	3
ULSD	0.08	Pressure: ≤ 14 kPa	1
ULP 95	58.74	Pressure: 14 – 91 kPa Throughput: > 50 000 m^3/year	3
JET A1	11.32	Pressure: ≤ 14 kPa	1
MGO	0.00044	Pressure: ≤ 14 kPa	1

*1 – Fixed roof tank vented to the atmosphere, 3 – Fixed roof tank with Internal Floating Roof Tank (IFRT) or Vapour Recovery Unit (VRU)

Hence, from these suggestions, storage of crude oil and ULP 95 mixtures should occur in IFRTs or FRTs with a vapour recovery system. ULSD, JET A1 and MGO should be stored in a FRT which is minimally vented to the atmosphere. Further reduction of emissions may include an IFRT or vapour recovery systems as suggested in Chapter 2. Considering the abatement efficiencies obtained from this study and the type of configuration recommended by NEMA, it can be suggested that MGO be stored in an FRT, and the other four mixtures be stored in an IFRT.

4.4.1.2 Vapour Recovery System

The effect of vapour recovery on the emissions were determined using a FRT. An efficiency of 90 % was applied for simplicity for the vapour recovery method. This was suggested by European Commission (2006), as vapour recovery occurs through vapour treatment and consists of a complex system of units and conditions which could not be implemented into the AP-42 calculations. A vapour recovery system typically involves a two-step process: separation and liquefaction (Golder Associates, 2019b). The separation process involves the use of the following units for the separation of the hydrocarbon vapours from air: pressure-swing adsorption, absorption, and selective membrane separation (Golder Associates, 2019b). The liquefaction process involves the following units: absorption, condensation, and compression (Golder Associates, 2019b). A single process combining separation and liquefaction may be used through condensation by compression or cooling (Golder Associates, 2019b). Table 4-14 represents the total quantified reduced VOC emissions of each mixture

using a vapour treatment control method. The abatement efficiency was set at 90 % as recommended by Golder Associates, (2019b)

Table 4-14: Effect of Total VOC emissions from the Overall Vapour Recovery System on FRTs for the Five Organic Mixtures

Mixture	VOC Flashing Emissions (ton/year)	VOC Working and Breathing Emissions (ton/year)	Total Emissions (ton/year)	Reduced VOC emissions from the Vapour Recovery System (ton/year)
Crude Oil	108.25	4.36	112.61	11.26
ULSD	6 284.26	85.79	6 370.05	637.01
ULP 95	7 011 810.24	1 486.29	7 013 296.52	701 329.65
JET A1	9 634.79	573.85	10 208.64	1 020.86
MGO	1659.72	0.06	1 659.78	165.98

Considering the 90 % efficiency in emission reduction, all mixtures except for crude oil, exceeded the 100 tons/year threshold suggested by Golder Associates Africa (Pty) Ltd. (Golder Associates, 2019b). Crude oil was well below the limit by 88.74 ton/year whereas, the other mixtures were above the limits by a minimum of 65.98 ton/year for MGO and a maximum of 701 229.65 ton/year for ULP 95. This was expected as the data used in this study suggested that ULP 95 had the lowest. The extremely high emissions of ULSD, ULP 95, JET A1 and MGO, were as a result of the high volumes and throughput experienced by the tanks as well as the low operating pressure of the tank. Whereas crude oil was operated at nearly atmospheric pressure of 96.35 kPa.

Further to this, Table 4-15 represents the effect of the reduction efficiency of the individual components of a vapour recovery system.

Table 4-15: Effect of Vapour Recovery Units on the Emissions for all Mixtures

Plant type	*Recovery Rates (%)	Reduced VOC emissions (ton/year)				
		Crude oil	ULSD	ULP 95	JET A1	MGO
A	80 – 95	0.27 – 0.068	17.16 – 4.29	297.26 – 74.31	114.77 – 28.69	0.013 – 0.0032
absorption	90 – 97	0.14 – 0.041	8.58 – 2.57	148.63 – 44.56	57.38 – 17.22	0.0064 – 0.0019
C	90 – 99.5	0.14 – 0.0068	8.58 – 0.43	148.68 – 7.43	57.38 – 2.69	0.0064 – 0.00032
D	99.98	0.00027	0.017	0.3	0.11	0.000013
E	90 – 95	0.14 – 0.068	8.58 – 4.29	148.68 – 74.31	57.38 – 28.69	0.0064 – 0.0032
F	99.98	0.00027	0.017	0.3	0.11	0.000013

A – Single-stage condensation
B – Single-stage absorption
C – Single-stage absorption and membrane separation
D – Single-stage adsorption with supplementary blower
E – Compression, absorption, and membrane separation
F – Two-stages
* (European Commission, 2006)

According to the BATs by European Commission (2006), the highest efficiencies which resulted in the highest emission mitigation were observed to be from the single-stage absorption unit with a supplementary blower and the two-stage system, both having a recovery rate of 99.98 %. However, due to these significantly high efficiency rates, working and breathing emissions from most of the mixtures at each unit were significantly reduced. ULP 95 at single-stage absorption, single-stage adsorption, and membrane separation and at compression, absorption, and membrane separation, were noted to exceed the 100 tons/year threshold by $\pm$ 48.63 ton/year at its minimum efficiency of 90 %. This could be justified as BAT suggests that absorption processes are not used to recover emissions for gasoline mixtures (ULP 95) in the EU due to its minimal efficiency and an adsorption system is generally preferred (European Commission, 2006).

Hybrid systems such as the two-stage processes incorporating membrane separation and adsorption are suggested for use to ensure very low emission threshold limits are met. This is

verified as a very high efficiency of 99.98 % occurs through a two-stage system that maximizes the emission reduction (European Commission, 2006).

4.4.1.3 Nitrogen Blanketing and Pressure and Vacuum Relief Valves

Nitrogen tank blanketing is a control method implemented in FRTs to ensure the safety and environmental protection of the tank operations. Breathing losses result from either filling or emptying of the tank as well as environmental temperature changes which affect the operating temperature and hence, atmospheric pressure of the tank. Tank blanketing is therefore used to increase the storage tank pressure and reduce the vapour space of the tank, thereby reducing VOC emissions (European Commission, 2006). In this study, nitrogen blanketing was applied and then reduction of the VOC emissions from the five storage tank mixtures were determined. Calculations were performed and based on the API 2000 7^{th} Edition standards discussed in Chapter two, section 2.4.1. It was assumed that the temperature of the tank wall and the liquid mixture inside the tank were uniform. Fluctuations with atmospheric pressure were assumed negligible, venting was operated according to a set point and the tanks were assumed to be uninsulated (Moncalvo, et al., 2018). Pressure and vacuum relief valves work closely together with nitrogen blanketing to ensure adequate and controlled venting of emissions to the atmosphere. This also ensures the pressure inside the tank is maintained during rapid temperature changes caused by inconsistent weather patterns and allows for the prevention of bursting or imploding of the tank during filling or emptying respectively. To prevent this, air or vapour is required to enter or leave the tank through venting valves to ensure breathing of the tank. This accounts for daily temperature changes and hence, minimizes emissions.

The inbreathing and outbreathing rates and nitrogen required were estimated using the given throughputs and volumes of the tanks as shown in Section A.3.1 Appendix A. Table 4-16 represents the normal inbreathing and outbreathing rates obtained from performing manual calculations and Aspen Plus ® simulations.

Table 4-16: Comparison of Inbreathing and Outbreathing Rates for all Mixtures using Manual calculations and Aspen Plus ®

Mixture	Manual Calculations		Aspen Plus ®	
	Inbreathing Rate (Nm^3/h)	Outbreathing Rate (Nm^3/h)	Inbreathing Rate (Nm^3/h)	Outbreathing Rate (Nm^3/h)
Crude Oil	130 882.10	160 568.07	149.80	56.92
ULSD	176 781.73	236 267.72	7 547.00	2 796.00
ULP 95	126 194.73	153 184.35	5 972.00	2 066.00
JET A1	110 835.57	129 643.18	5 226.00	1 740.00
MGO	142 084.55	178 417.06	7 546.00	2 790.00

The manual calculations were based on applying a pressure control to maintain or adjust the nitrogen flow using the API 2000 7^{th} Edition standards. The inbreathing and outbreathing rates determined from the manual calculations were found to be considerably higher than the rates obtained from the Aspen Plus ® simulations. A decrease of $\pm$ 94.69 – 99.89 % in inbreathing rates and $\pm$ 98.44 – 99.82 % in outbreathing rates were observed from the Aspen Plus ® results from the manual calculations. A major contributing factor is attributed to the fact that the manual calculations are based on broad assumptions and estimates. Furthermore, these utilise factors based on the vapour pressure, average storage temperature and latitude of the tanks. However, the under-prediction of the rates estimated from Aspen Plus ® may be attributed to it being based on the API 620 standards instead of API 650 which includes the API 2000 standards. API 620 was used as the design pressure of the tank ranged between 17.24 – 103.42 kPa. This accounts for the large variability in the rates between the two procedures. The estimated rates obtained ensures safety considerations are met, such as overpressure or negative pressure within the tanks which may lead to explosions/implosions (European Commission, 2006).

The emergency venting requirement was also determined from Aspen Plus ® for each of the storage tank mixtures. Table 4-17 represents the flowrate of air/vapour required through the pressure relief device to ensure over pressurization does not occur and thus preventing a rupture from occurring within the tank. These flowrates ensure that the pressure of the vapour space within the tank does not exceed the set pressure designed at 20.69 kPa.

Table 4-17: Emergency Relieving Flow determined using Aspen Plus ®

Mixture	Calculated Relieving Flow (Nm^3/h)
Crude Oil	46 580
ULSD	147 800
ULP 95	180 900
JET A1	119 200
MGO	147 800

ULSD – Ultra-low Sulphur Diesel
ULP 95 – Unleaded Petrol 95
JET A1 – Jet Fuel
MGO – Marine Gas Oil

The quantity of nitrogen required for the storage tanks regulated with a nitrogen blanket were calculated according to Air Products and Chemicals Inc. (2019) and comprised of the thermal breathing and nitrogen throughput requirements. The assumed maximum and minimum ambient temperatures were based on the conditions experienced in Durban: 30 and 14 ℃. The effect of implementing this nitrogen blanket into the storage tanks were determined by calculating the working and breathing losses from the AP-42 method using the new, lowered vapour space of the tank. The efficiency of the reduced emissions using this control method were noted in Table 4-18.

The abatement efficiencies were considerably low, with a maximum efficiency of 0.019 and 0.0015 % for the crude oil storage tank and ULP 95 respectively. This was expected for crude oil and ULP 95 due to its true vapour pressure and throughput requiring a FRT with additional vapour control such as nitrogen blanketing, as discussed in section 4.3.1.1. However, the small efficiencies may be attributed to the less rigorous estimation method outlined by Air Products and Chemicals Inc. (2019), in which only a few factors such as throughput and temperature were accounted.

Table 4-18: Quantity of Nitrogen Required and its efficiency on Reducing VOC emissions

Mixture	Total volume discharged (m^3/year)	Nitrogen required (m^3/year)	Uncontrolled VOC emissions (ton/year)	Controlled VOC emissions (ton/year)	Abatement Efficiency (%)
Crude Oil	10 760.24	10 761.37	1.36	1.36	0.019
ULSD	1 602.19	1 688.77	85.79	85.79	0.00036
ULP 95	57.88	116.48	1 486.29	1 486.26	0.0017
JET A1	115.76	162.83	573.85	573.84	0.0015
MGO	141.06	227.54	0.06	0.06	0.0036

The peak nitrogen flowrate required was estimated using the method outlined in Air Products and Chemicals Inc. (2019). Table 4-19 represents the flowrates for each of the storage tank mixtures studied. This information is important and useful in determining the sizing of a nitrogen supply system. The main factor utilised was pump-out rate of the tank. In this case, ULSD had the highest peak nitrogen requirement whereas, JET A1 had the lowest as seen in Table 4-19.

Table 4-19: Calculated Peak Nitrogen Required using *Manual Calculations

Mixture	Peak nitrogen required (Nm^3/h)
Crude Oil	101 245.50
ULSD	135 101.45
ULP 95	97 718.84
JET A1	86 541.20
MGO	120 981.98

4.4.2 Operational Controls

The control methods during operation consisted of the effects of temperature, pressure, flowrates, capacity, and turnovers on the VOC emissions from flashing losses and working and breathing losses from all five organic mixture storage tanks. This section discusses the recommended conditions, focusing on temperature and pressure, when operating a storage tank of each mixture to ensure minimum emissions such that the threshold limits are adhered to.

4.4.2.1 Temperature

The temperature of the storage tank is significantly affected by its surrounding atmosphere, hence, the location and seasonal and daily changes in temperature should be considered to ensure storage tanks are operated efficiently. Based on the trends represented in section 4.1 and 4.2, it was observed that VOC emissions for flashing losses and working and breathing losses, were at a minimum at lower temperatures. The literature reviewed in this study, as seen in Chapter 2, section 2.2.3, explained the effect of temperature on the stored liquid in a tank. It suggested that ULP 95 and ULSD have higher tendencies of undergoing self-oxidation during storage, compared to the other mixtures. Therefore, tank temperatures of these mixtures, especially, should remain below 473.15 K, at which thermal oxidation occurs (Owczuk & Kotodziejczyk, 2015). Temperatures ranging between 243.15 – 323.15 K may result in polymerization, oxidation, corrosion, or even crystallisation, therefore, the tanks should be monitored closely when operating at those temperatures (Owczuk & Kotodziejczyk, 2015). The operating temperature should remain below 313.15 K as the organic liquid become reactive when higher (Owczuk & Kotodziejczyk, 2015). Hence, the optimal operating temperature of storage tanks is suggested between 293.15 and 303.15 K (Owczuk & Kotodziejczyk, 2015).

For flashing losses using Aspen Plus ® and manual flash calculations, minimum emissions were noted between the months of May – September, following atmospheric temperatures in Durban. These temperatures ranged on average between 289.65 – 292.65 K for that period. However, minimum temperatures, within these months, ranged between 283.65 – 288.45 ℃ which yielded lower emissions for all mixtures. Hence, these temperature ranges serve as ideal ranges in which the storage tanks should be operated, to release minimum emissions for flashing losses. However, due to continuously fluctuating ambient temperatures, variability in emissions occur all year round, therefore, further control methods such as the vapour recovery or nitrogen blanketing, should be implemented to account for this.

Working and breathing losses experienced similar trends with optimal operating temperatures noted at 288.15 – 293.15 K for all mixtures with both types of tanks: FRT and IFRT. However, in order to ensure emissions were below the threshold limit of 100 tons/year as proposed by Golder Associate Africa (Golder Associates, 2019b), ULSD in a FRT should maintain a maximum temperature of 294.76 K. All emissions from all mixtures were below this limit when stored in an IFRT, except for MGO. However, ULP 95 and JET A1 exceed this limit considerably when stored in a FRT, therefore, vapour recovery methods, nitrogen blanketing or an IFRT should be used instead. Therefore, it is suggested for storage tanks to operate at temperatures between 293.15 and 303.15 K to ensure the quality of the liquid remains high and emissions are minimized.

4.4.2.2 Pressure

The pressure of the storage tank is significantly affected by the atmospheric air surrounding the tank as well as the vapour pressure of the contents in the storage tank and vapour space of the tank. General trends observed in this work suggested that emissions are minimized when the tanks are maintained at higher pressures. Such as in the case of flashing losses estimated using Aspen Plus ® for the crude oil storage tank, in order to meet the 100 ton/year limit, a minimum pressure of 93.65 kPa and should be maintained at a temperature of 18 ℃, as seen in Table 4-8 to Table 4-10. However, according to Molewa (2019), storage tanks operating at a pressure of 91 kPa and above are designed as pressure vessels. Hence, the tanks were operated as low-pressure vessels and nitrogen blanketing should be implemented with pressure relief valves to ensure the pressures within the tank are maintained according to the inbreathing and outbreathing rates, as discussed in section 4.3.1.3.

4.5 Preliminary Environmental and Socio-Economic Impact Assessment

This aspect of the study was based on the Lanele Oil Terminal in which an Environmental Impact Assessment (EIA) and the socio-economic impacts were outlined by Golder Associate Africa (Pty) Ltd. Expanding the baseline data presented in the Golder Associate Africa (Pty) Ltd (Golder Associates, 2019b) study, the effects of VOC emissions on the environment and population in the Durban South Basin areas are discussed through a preliminary impact assessment.

4.5.1 Environmental Impact Assessment (EIA)

As presented and shown in the results in the earlier sections the environmental effects of VOC emissions from storage tanks are considerable. The need to minimize emissions is thus justified further by the sustainability reports released in 2020 by industries such as Sasol and BP, in which strategies for implementation are outlined to combat climate change and achieve net zero targets.

BP has set out an ambitious sustainability framework in which a net zero target is set for 2050. Of the five aims to achieve this, three relate to the reduction of emissions from storage tanks: Achieving net zero operations, net zero oil and gas and halving intensity. This means that the strategy focuses on eliminating GHG emissions and carbon emissions completely by 2050. In order to achieve this target, BP aims to achieve a 20 % reduction in these emissions by 2025 and 30 – 35 % by 2030. BP plans to do this through the implementation of energy efficiency measures, the reduction of flaring and through monitoring methane emissions. BP also aims to reduce its overall production of oil and gas through effective management of its portfolio which is inclusive of decarbonization and divestment strategies as described in detail in the company's sustainability reports. Whilst this aims to be achieved across the entire operation process system, VOC emissions are inclusive in the mitigation strategy. BP also aims to improve carbon intensity through more effective storage technology by implementing cleaner energy throughout the production process and possibly introduce advanced technologies for monitoring emissions with the effect of immediate control (BP Sustainability Report, 2020).

Sasol has faced many challenges over the past few years in meeting stringent point source standards and managing air quality. Its aim is to reduce GHG emissions by at least 10 % by 2030. The current strategies in place to ensure this and air quality management are achieved, are the following: providing detailed reports for monitoring emissions, continuous tracking of emissions and actively reducing emissions to meet compliance regulations. Specifically on VOC emissions, Sasol has managed to achieve a minimum of 30 % reduction in VOC emissions from 2009 – 2020 due to the implementation of an abatement project at the Natref tank farm which was completed between 2016 – 2020. This included the completion of a vapour recovery unit and a technical assessment methodology for implementing further reduction technologies to reduce VOC emissions from storage tanks. Currently, Sasol is in the process of finalising the identification of the specific tanks which require abatement techniques

and is finalising the gas liquor separation process for the vapour recovery system (Sasol Sustainability Report, 2020).

To further justify the need for air quality management, its effect on people and its soci-economic consequences need to be accounted for.

4.5.2 Socio-Economic and Health Impact Assessment (SHIA)

A major socio-economic issue faced in the Durban South Basin (defined from the northern Durban CBD area to the southern Umbogintwini area) is the effect of pollution on the income earning potential of the population (Smakaj, 2010). This is due to the overlapping between the dense residential area and economic-industrial hub in which there is a high concentration of economic opportunities due to the presence of a major petrochemical refinery (SAPREF) a sugar refinery, pulp and paper plant and various chemical industries. The conversion of Engen to a tank terminal is currently underway therefore, this study serves as a major contributor towards potentially limiting those emissions (Golder Associates, 2019b).

The population of the regional (Durban South Basin) and local (Project site located in ward 32) study areas, as seen in Figure 4-1514 was estimated using an annual growth rate of 1.6 % and 1.7 % respectively (Golder Associates, 2019a). The population density for 2020 was estimated to be 4 033 persons/km^2 and 1 139 persons/km^2 for the Durban South Basin and local regions respectively. According to Golder Associates Africa (Pty) Ltd. (Golder Associates, 2019a) 69 % of the population in the study area are of working age, between 15 and 40. Whilst these industries may offer a vast range of employment opportunities offering economic upliftment to the surrounding residents, the South Basin communities are prone to experience excessively high rates of respiratory illnesses, asthma, leukaemia and cancer due to the densely populated areas situated within close proximity to the industrial activity (Aylett, 2010). Globally the average population density is 25 persons/km^2, which indicates the clustered living conditions of the overpopulated Durban South Basin (Ritchie, 2019).

The deteriorating quality of air and health risks in the Durban South Basin is another contributor of pollution to the surrounding communities. This is evident from the presence of the two major oil refineries which are responsible for the production of 60 % of petrol in South Africa and approximately 50 % of Durban's emissions arise from CO_2 emissions (Aylett, 2010). As these oil refineries continue to work to meet the demands of consumers and as the population continues to rise, meeting the Sustainable Development Goals by 2030 becomes

more complex. As seen in Figure 4-15, the regional and local population is expected to increase by 16 % and 17 % respectively within the next 10 years. A significant population increase in 96 km^2 of land is representative of the rapid increase in population across South Africa in the next 10 years. This increasing population places a greater demand in petroleum products thus, higher exposures of VOC concentrations into the atmosphere are predicted. In order to meet the SDGs by 2030, the mitigation methods outlined in section 4.3 can be implemented to reduce VOC concentrations which will aid in the restoration of the air quality and minimize the health risks posed by the VOC concentrations.

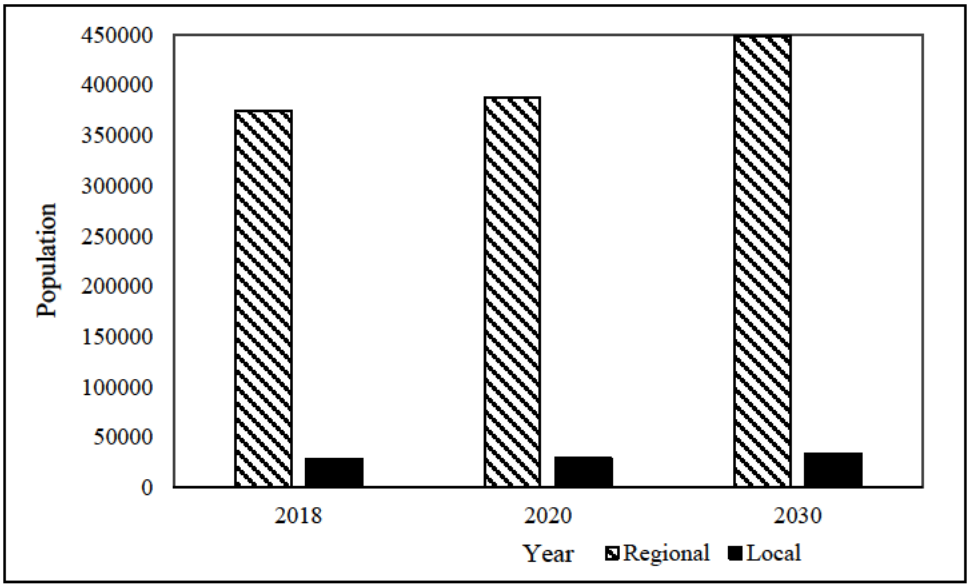


Figure 4-15: Projected Durban South Basin Regional and Local populations in 2018 2020 and 2030 (Golder Associates, 2019a).

Studies conducted by Rajabi, et al. (2020) suggested that the total average detection percentages of toluene, benzene, xylene and ethylbenzene (BTEX emissions) to the atmosphere at various locations were observed as 21, 17, 7 and 3 % respectively. This study indicated that crude oil BTEX emissions of 0.08, 0.08, 0.01 and 0.04 % from benzene, toluene, ethylbenzene and xylene, respectively. However, the long exposure to these components may lead to haematotoxicity, genotoxicity, chromosome alterations, reproductive failure, or death with benzene. Whereas long exposure to ethylbenzene may lead to severe kidney or ear damage. Rajabi. Et al. (2020) also suggested that communities within proximity to oil refineries may experience cough, wheezing, nausea, sinus, skin rashes, stomach pain and headaches to name a few. This could also be noted in the Durban South Basin as the results obtained in this study

are representative of the presence of BTEX emissions in the atmosphere. Hence a more detailed EIA and SHIA is necessary for future study.

4.6 Summary

This study aimed to contribute towards the petroleum industry by ensuring VOC emissions from storage tank emissions are maintained below the threshold values suggested by legislature. Hence, this study also contributes towards combating climate change and ensuring air quality is maintained. The monitoring of emissions, control strategies implemented and recommended, and the EIA conducted in this study may prove effective for use in the petroleum industry to monitor and control VOC emissions from storage.

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

Petroleum storage tanks have been identified as a major contributor of VOC emissions, particularly within urban areas surrounded by communities. The need to understand, monitor and control emissions is thus necessary to ensure emissions legislature and ambient air quality standards are met. This is useful to industries, such as oil refineries or tank terminals, to develop mitigation strategies which will aid in decision-making, upgrade current processes, monitoring methods and policies which will enable climate resilience.

5.1 Summary of Results

5.1.1 Crude Oil Test System

The main findings from this study suggested that the test system of crude oil using Aspen Plus ® successfully replicated the literature presented by Burr and Georgeson (2014) as a 0.54 % difference between the simulation methods of Promax and Aspen Plus ® were noted. Methane, ethane and propane showed significant recovery of crude oil emissions of 90.4 %, 58.0 % and 28.1 % respectively. This is justifiable with flashing as light hydrocarbons are vapourised. The total flashing losses of crude oil contributed to 1.1 % of the feed flowrate of 9371.5 ton/year. The operating temperature and pressure of the crude oil storage tank was suggested at 16.1 ℃ and 93.65 kPa to ensure VOC emissions, remain below the threshold of 100 ton/year as suggested by Golder Associates (Golder Associates, 2019b).

5.1.2 Flashing Losses

The analyses conducted on flashing losses using manual equilibrium flashing method for all five storage tank mixtures estimated that the highest emissions were emitted from the storage tank containing crude oil and ULP 95 and the lowest emissions were emitted from the MGO storage tank. The empirical correlations suggested that the highest emissions were emitted from the ULP 95 storage tank at 28 021.61 ton/year and the lowest at 13.33 ton/year from the crude oil storage tank. This was justified as the API gravity for the ULP 95 mixture was the highest at 79.21^{o} and lighter mixtures such as this, allows for the flashing of more hydrocarbon vapours into the atmosphere. Emissions estimated using manual calculations were notably lower than emissions estimated using Aspen Plus ® for all the organic systems. Crude oil had the greatest over-prediction and ULP 95 had the smallest over-prediction of emissions when considering

the average deviation of emissions using manual calculations with respect to Aspen Plus ® predictions. It was observed that the validity of the empirical correlations was very restrictive with only a few emissions measurements being valid due when using the VBE and VM. The empirical correlation methods under-estimated the flashing losses

5.1.3 Working and Breathing Losses

The working and breathing losses were estimated using the AP-42 method proposed by U.S. Environmental Protection Agency (2006) and focused on emissions from FRTs and IFRTs. The highest source of emissions from the FRTs were observed ULP 95 tank with an emission rate of 1486.29 tons/year and the lowest at MGO tank of 0.064 tons/year. Emissions from the IFRTs were observed to be significantly reduced for all petroleum products except for MGO which increased by 86.2 %. Jet A1 was found to have the greatest reduction in emissions levels, with an IFRT, by 99.7 % with ULP 95, ULSD and crude oil being reduced by 99.4 %, 99.5 % and 91.3 % respectively. A white painted tank with absorptance factor of 0.17 showed a 15.6 % and 10.6 % reduction in VOC emissions from FRT's and IFRT's respectively whereas a 6.1 % and 4.4 % increase in emissions were noted through using a red painted tank. The use of a lighter painted tank with a lower solar absorbance factor for emission reduction is suggested. A 10 % increase in capacity reduces the emissions by an average of: $\pm$ 1.6 % for crude oil, $\pm$ 0.12 % for ULSD, $\pm$ 0.59 % for ULP 95, $\pm$ 0.44 % for JET A1 and $\pm$ 1.7 % for MGO. It was noted that an increase in the rate of emissions is smaller with increasing turnovers. The turnovers should, therefore, be maintained at a minimum to ensure emissions are reduced. The trends analysed for working and breathing losses were similar to that of the flashing losses where it was noted that an increasing, linear trend exists for all mixtures, except for ULP 95, in both the FRT and IFRT. However, ULP 95 differs in that the emissions increase exponentially from a FRT suggesting the need to implement stricter control methods for this storage tank.

5.1.4 Control Strategies

The control strategies suggested for implementation consisted of changing the tank configuration, installing vapour recovery systems, or introducing nitrogen blanketing to reduce emissions from storage tanks. For the tank configurations, estimated efficiencies ranged between $\pm$ 72.05 – 99.71 % for the mixtures studied with crude oil having the lowest efficiency and JET A1 exhibiting the highest. IFRTs reduced ULP 95 and ULSD emissions considerable as the efficiencies were noted as $>$ 90 %. Hence, from these suggestions, storage of crude oil and ULP 95 mixtures should occur in IFRTs or FRTs with a vapour recovery system. ULSD,

JET A1 and MGO should be stored in a FRT which is vented to the atmosphere or for further reduction of emissions, an IFRT or vapour recovery systems can be implemented. Therefore, taking into account the efficiencies obtained from this study and the configuration type recommended by NEMA, MGO should be stored in a FRT, and the other four mixtures in an IFRT.

From the analysis of the vapour recovery systems, it was noted that the highest efficiencies which resulted in mitigating the emissions the most were observed to be from the single-stage absorption unit with a supplementary blower and the two-stage system, both having a recovery rate of 99.98 %. However, due to these significantly high efficiency rates, working and breathing emissions from majority of the mixtures at each unit were significantly reduced. ULP 95 at single-stage absorption, single-stage adsorption, and membrane separation and at compression, absorption, and membrane separation, were noted to exceed the 100 ton/year threshold by $\pm$ 48.63 ton/year at its minimum efficiency of 90 %. This could be justified as BAT suggests that absorption processes are not used to recover emissions for gasoline mixtures (ULP 95) in the EU due to its minimal efficiency and the adsorption system is preferred (European Commission, 2006).

The inbreathing and outbreathing rates determined from the manual calculations of implementing a nitrogen blanketing system, were found to be considerably higher than the rates obtained from Aspen Plus ®. A decrease of $\pm$ 94.69 – 99.89 % in inbreathing rates with respect to manual results and $\pm$ 98.44 – 99.82 % in outbreathing rates were noted from the Aspen Plus ® results. The under-prediction of the rates estimated from Aspen Plus ® or over-prediction from manual calculations could be attributed to assumptions and estimate factors based on the vapour pressure, average storage temperature and latitude of the tanks when using the manual calculations. The abatement efficiencies through implementing nitrogen into the tanks were considerably low, with a maximum efficiency of 0.019 % and 0.0015 % for the crude oil storage tank and ULP 95 respectively. As expected for crude oil and ULP 95 due to its true vapour pressure and throughput, a FRT is required with additional vapour control such as nitrogen blanketing. However, the small efficiencies may be attributed to the less vigorous estimation method outlined by Air Products and Chemicals Inc. (2019), in which a few factors such as throughput and temperature were accounted for.

Minimum emissions were noted between the months of May – September, following atmospheric temperatures in Durban. These temperatures ranged on average between 16.5 –

19.2 ℃. However, minimum temperatures, within these months, ranged between 10.5 – 15.3 ℃ and yielded even lower emissions for all mixtures. Hence, these temperature ranges serve as optimal ranges in which the storage tanks are operated, which release minimum emissions as flashing losses. However, to ensure emissions remain below the threshold limit of 100 ton/year as proposed by Golder Associates Africa (Pty) Ltd. (Golder Associates, 2019b), ULSD in a FRT should be maintained at a maximum temperature of 21.61 ℃. A minimum pressure of 93.65 kPa should be maintained at a temperature of 18 ℃. However, according to Molewa (2019), storage tanks operating at a pressure of 91 kPa and above are designed as pressure vessels. Hence, the tanks were operated as low-pressure vessels and nitrogen blanketing should be implemented with pressure relief valves to ensure the pressures within the tank are maintained according to the inbreathing and outbreathing rates.

5.2 Future Possibilities and Recommendations

The final objective of this study was to provide suitable recommendations for implementation in industries, to mitigate VOC emissions from organic storage tanks. This section follows the controls section of this study and suggests further possibilities of reduction strategies which were not evaluated in this study and may contribute to assisting in closing some of the gaps identified in the literature.

5.2.1 Tank Configuration

While this study contributed to analysing emissions from FRTs and IFRTs, U.S. Environmental Protection Agency (2006) suggests using External Floating Roof Tanks (EFRTs) as another effective type of floating roof tank which reduces emissions, such as the IFRT, EFRTs emit working and breathing losses. However, in this case, rim seal losses contribute the most towards loss of emissions which are mainly affected by wind. IFRTs methodology does not account for wind induced losses, making EFRTs a more desirable method of estimating emissions considering the great variability of wind experienced in Durban. Other emission sources present with EFRTs includes permeation of the material in which the rim seal is manufactured which causes a phenomenon known as the wicking effect. However, this may be reduced or eliminated with the proper material of construction. Tests performed also confirmed that wind induced losses are considerably higher than wicking losses, breathing or solubility losses. The rim seal serves to reduce evaporative emissions by reducing the annular space between the tank shell and the rim. Rim seals may consist of primary or secondary seals, however, studies by Wang, et al. (2018) have shown that implementing a double seal by

including a secondary rim seal with a primary seal to improve the tightness and effect of rim sealing. This further reduces the withdrawal losses and hence, the total working and breathing losses. Examples of secondary seals for implementation include resilient filled seals or the use of flexible wiper seals. If a mechanical shoe primary seal is used, then shoe mounted, or rim mounted secondary seals may be used in conjunction. However, U.S Environmental Protection Agency (2006) suggested that the effectiveness in reduction of emissions from rim mounted seals are greater due to its ability to shield the complete rim vapour space area. However, a downside of utilising a secondary seal is that it has the potential to limit the capacity at which the tank operates as the secondary seal is required to be contacted with the shell of the tank during filling. In future work, working and breathing emissions from EFRTs fitted with rim seals can be explored using modelled tank vessels in Aspen Plus ® and the methodology applied to IFRTs used in this work. Rim seals can be modelled with pressure fittings such a bleed valve, with sensitivities of leak rates to wind conditions.

5.2.2 Vapour Destruction and Flaring

Determining the effect of vapour incineration and flaring on the reduction of VOC emissions is recommended for potential control strategies. One such system proposed by Voegel (2021) entails the implementation of fume incinerators attached to the vent of the storage tanks. These incinerators operate at a specific flowrate and controls the quantity of emissions released through the atmosphere based on compliance regulations. The efficiency of this is estimated to be 85 % (Best Available Techniques, 2006). VOC emissions from storage tanks vents can be routed to a flare or combustion device through installed piping in which the vapours undergo an oxidative combustion process and the products vented to atmosphere. This is known as Vapour Destruction (VD) and may occur through either thermal oxidation (incineration) or catalytic oxidation. A flame arrestor is necessary to prevent explosions from occurring as air that enters the storage tank may form mixtures with the volatile liquid which are explosive. Temperatures are maintained below 453 K to prevent ignition and operating temperatures of the thermal oxidation system range between 1033 – 1143 K. The catalytic oxidation system involves the use of a catalyst which allows for the process to operate at a lower temperature within the range of 593 – 813 K. However, due to this major risk and the fact that products are sent to the atmosphere, vapour incineration is not a desired control method for the reduction of VOC emissions (European Commission, 2006). This can be incorporated into the simulations from this work by employing a rigorous plug flow combustion reactor with the relevant

reaction kinetics. Using the pressure-driven simulation approach, to simulate correct flow conditions to ensure back flow and explosions are prevented in the design.

5.2.3 Tank Insulation

Tank insulation is an effective control method used to mitigate breathing losses from fixed roof storage tanks and may be inserted into the roof and sides of the tank. Tank insulation operates by reducing the varying tank temperature within the tank which relies on the surrounding ambient conditions through insulation. Hence, this reduces the extent to which the liquid in the tank volatizes. There is also a potential of complete elimination of breathing losses through tank insulation. This could only occur if the temperature of the tank, with insulation, remains constant and the surrounding air temperature of the tank would not affect the temperature of the contents within the tank (Vogel, 2021). Typical tank insulation material include spray-on insulation of approximately 3.8 cm, as external wrap insultation of fiberglass, mineral wool or ceramic fibre where thickness is dependent on the material selected and its specific thermal conductivity. Tank insulation can be incorporated into the simulated calculations by designing a thermal heating jacket with a hypothetical fluid with similar thermal properties to the selected tank insulation (Vogel, 2021).

5.2.4 Pressurized Storage Tanks

Pressurized storage tanks can be used to eliminate storage tank emissions as opposed to reducing it. These tanks operate at high pressures which allows for the vapours to be directed to nearby heaters or sent for compression through the sales gas line. The storage and transports cost of implementing pressurized tanks is high. However, the high value recovered product is suggested to compensate for this and the reduction of emissions from these tanks is estimated to be almost 100 % efficient (Hendler, et al., 2009). The costs of employing pressurized storage tanks can be determined using Aspen Plus ® Economic Analyzer and can be weighed against other mitigation strategies and penalty costs.

5.2.5 Separator Pressures

The operating pressure of the separators installed prior to the storage tanks may contribute towards reducing emissions if operated at lower pressures. Separator operating pressures higher than 40 – 50 psig require the introduction of an intermediate separator and thus adjustment of the pressure of the existing separator to 30 psig. The lowering of the separator pressure and implementing an additional separator enables the reduction of flashing losses from the storage

tanks. An added benefit of recovering liquid hydrocarbons by implementing this may also occur (Hendler, et al., 2009). The cost implications of incorporating additional separators for volatiles prior to storage can be considered by simulating the fractionation of flashing units, similar to the presented simulations. Again, these costs can be weighed against other mitigation strategies and penalty costs.

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APPENDIX A: RAW DATA AND RESULTS

Appendix A presents the raw data and results as shown in Figure 4-1 to Figure 4-7 in Chapter 4.

A.1 Crude Oil Test System Data

The crude oil mixture was modelled on Aspen Plus ® using the compositions in Table A-1 and a consistency test and RMSE was conducted to determine the interaction parameters between the binary pairs of each component.

Table A-1: Pressurized Liquid Compositions of Crude Oil Test System Mixture (extracted from (Burr & Georgeson, 2014))

Component	Composition (mol %)
Methane	0.93
Ethane	2.59
Propane	5.46
i-Butane	1.33
n-Butane	6.22
i-Pentane	2.30
n-Pentane	4.15
2-Methylpentane	2.17
n-Hexane	2.26
2,2,4-Trimethylpentane	0.12
n-Heptane	10.04
n-Octane	8.92
n-Nonane	3.71
Benzene	0.28
Toluene	0.92
Ethylbenzene	0.33
p-Xylene	1.41
C10+	46.86

Table A-2: Crude Oil Consistency and RMSE Aspen Plus ® Simulation Results

Component i	Component j	Consistency	RMSE	
			PENG-ROB	SRK
Methane	Ethane	1.00	111.63	160.27
Methane	Propane	0.50	29.81	20.07
Methane	i-butane	0.50	19.65	15.14
Methane	n-butane	1.00	14.87	11.17
Methane	i-pentane	0.35	29.74	43.89
Methane	n-pentane	1.00	15.86	17.68
Methane	n-hexane	1.00	34.06	42.39
Methane	n-heptane	0.25	695.73	774.85
Methane	n-octane	0.25	707.01	692.54
Methane	Benzene	0.25	1 14.67	808.95
Methane	Toluene	0.50	93.67	103.51
Ethane	Propane	1.00	10.60	12.12
Ethane	i-butane	0.25	68.22	67.87
Ethane	n-butane	0.25	68.43	66.83
Ethane	n-pentane	0.50	17.50	17.43
Ethane	n-hexane	0.25	57.35	38.05
Ethane	n-heptane	0.50	121.31	110.83
Ethane	n-octane	0.25	231.80	208.71
Ethane	Benzene	0.14	19.72	24.11
Propane	i-butane	0.68	13.51	13.25
Propane	n-butane	0.61	14.15	14.90
Propane	i-pentane	0.54	9.42	6.15
Propane	n-pentane	0.83	11.71	10.21
Propane	n-hexane	0.50	88.70	85.59
Propane	n-heptane	0.50	51.76	41.38
Propane	Benzene	1.00	31.64	33.76
i-butane	n-butane	0.50	3.09	2.22
n-butane	n-pentane	0.25	17.83	17.46
n-butane	n-hexane	0.50	9.29	6.08
n-butane	n-heptane	0.50	5.01	4.43
n-pentane	n-heptane	0.25	108.53	78.05

Table A-2 Crude Oil Consistency and RMSE Aspen Plus ® Simulation Results (Continued)

n-pentane	n-octane	0.35	15.17	79.97
n-pentane	Benzene	0.51	6.41	6.44
n-hexane	n-heptane	0.73	6.83	10.79
n-hexane	Benzene	1.00	5.72	9.18
n-heptane	Benzene	0.82	10.28	6.38
n-octane	Benzene	0.76	10.03	9.79

The flowrate results for each stream contributing to or from the crude oil storage tank was tabulated from Aspen Plus ®.

Table A-3: Crude Oil Mass Flowrate Stream Results from Aspen Plus ® Simulation

Component	Mass flowrate streams (ton/year)				
	Pressurized Liquid from Separator	**Feed to Tank**	**VOC Emissions**	**Product**	**Pumped Liquid Product**
Methane	8.45	8.45	7.84	0.61	0.61
Ethane	44.11	44.11	29.44	14.68	14.68
Propane	136.38	136.38	50.88	85.50	85.50
i-Butane	43.79	43.79	8.26	35.52	35.52
n-Butane	204.78	204.78	28.56	176.23	176.23
i-Pentane	94.00	94.00	5.54	88.46	88.46
n-Pentane	169.61	169.61	7.73	161.88	161.88
2-Methylpentane	105.93	105.93	2.05	103.88	103.88
n-Hexane	110.32	110.32	1.54	108.78	108.78
2,2,4-Trimethylpentane	7.76	7.76	0.04	7.73	7.73
n-Heptane	569.87	569.87	2.47	567.40	567.40
n-Octane	577.17	577.17	0.77	576.41	576.41
n-Nonane	269.53	269.53	0.11	269.42	269.42
Benzene	12.39	12.39	0.16	12.23	12.23
Toluene	48.02	48.02	0.17	47.85	47.85
Ethylbenzene	19.85	19.85	0.02	19.82	19.82
p-Xylene	84.79	84.79	0.08	84.71	84.71
C10+	6 972.97	6 972.97	0.00	6 972.97	6 972.97

A sensitivity analysis was conducted to determine the effect of varying feed flowrate on the VOC emissions and the hazardous components found in VOC emissions. This is useful in ensuring proper control methods are implemented.

Table A-4: VOC emission variations of crude oil test system tank at ± 10 – 25% of a base feed flowrate of 9479.73 tons/year.

Percent of Feed flow	Feed flow (tons/yr)	VOC (tons/yr)
-10	8 531.75	97.42
-15	8 057.77	92.01
-20	7 583.78	86.60
-25	7 109.80	81.19
0	9 479.73	108.25
10	10 427.70	119.07
15	10 901.69	124.49
20	11 375.67	129.90
25	11 849.66	135.31

Table A-5: VOC emission variation of hazardous components at ± 10 – 25% of a base feed flowrate of 9479.73 tons/year.

Percent Feed flow	Feed flow (tons/yr)	VOC (tons/yr)		
		Benzene	Toluene	P-xylene
-10	8 531.75	0.08	0.08	0.04
-15	8 057.77	0.08	0.08	0.04
-20	7 583.78	0.07	0.07	0.03
-25	7 109.80	0.07	0.07	0.03
0	9 479.73	0.09	0.09	0.04
10	10 427.70	0.10	0.10	0.05
15	10 901.69	0.10	0.11	0.05
20	11 375.67	0.11	0.11	0.05
25	11 849.66	0.11	0.11	0.05

Variations in temperature and its effects on the VOC emissions over a 12-month period were tabulated based on the minimum, maximum and average temperatures, and VOC emissions respectively. Table A-6 represents this. Variations were also conducted for summer and winter conditions, as seen in Table A-7 with its respective effect on hazardous components at varying temperatures in Table A-8.

Table A-6: VOC emissions at maximum, minimum and average temperatures of crude oil test system tank over 12 months

Month	Min Temperature (℃)	Max Temperature (℃)	Average Temperature (℃)	Min VOC (tons/yr)	Max VOC (tons/yr)	Average VOC (tons/yr)
January	21.1	27.8	24.1	124.26	162.31	140.52
February	21.1	28.0	24.3	124.26	163.54	141.65
March	20.3	27.7	23.7	120.14	161.69	138.28
April	17.4	26.1	21.6	105.94	152.06	126.88
May	13.8	24.5	19.1	89.95	142.79	114.12
June	10.6	23.0	16.6	77.25	134.42	102.23
July	10.5	22.6	16.5	76.87	132.24	101.77
August	12.5	22.8	17.7	84.62	133.32	107.35
September	15.3	23.3	19.2	96.39	136.06	114.61
October	16.8	24.0	20.1	103.15	139.96	119.12
November	18.3	25.2	21.4	110.22	146.80	125.83
December	20.0	26.9	23.1	118.61	156.83	134.96

Table A-7: VOC emission variations during winter and summer temperatures in Durban in a crude oil tank at 96.38 kPa

Season	Temperature (℃)	VOC (tons/yr)
Winter	14	90.79
	16	99.51
	18	108.78
	20	118.61
	22	129.01
Summer	24	139.96
	26	151.47
	28	163.54
	30	176.15

Table A-8: VOC emission variations of hazardous components during winter and summer temperatures in Durban in a crude oil tank at 96.38 kPa

Season	Temperature	VOC (tons/yr)		
		Benzene	Toluene	P-Xylene
Winter	14	0.06	0.06	0.03
	16	0.08	0.08	0.04
	18	0.09	0.09	0.04
	20	0.11	0.11	0.05
	22	0.12	0.13	0.06
Summer	24	0.14	0.15	0.08
	26	0.17	0.18	0.09
	28	0.19	0.21	0.11
	30	0.22	0.25	0.13

The effect of varying pressure on VOC emissions during average summer and winter conditions was tabulated in Table A-9.

Table A-9: VOC emissions at varying pressures in crude oil test system storage tank during winter (18 ℃) and summer (25 ℃) temperatures

Pressure (kPa)	VOC (tons/year)	
	Winter	Summer
18.75	523.11	608.89
37.50	324.83	391.66
56.25	221.56	276.64
75.00	157.08	202.82
93.75	113.71	151.58
96.39	108.78	145.65
112.50	83.43	114.57
131.25	61.83	87.23

A.2 Monitoring of Flashing Losses

Flashing losses were monitored through manual flash calculations, Aspen Plus ® Simulations, empirical correlations and secondar losses. This section represents the data utilized in estimating the VOC emissions using the monitoring methods for the various petroleum mixtures.

A.2.1 Manual Flashing Method

This section records the raw data and results from the manual flashing calculation method. It also records the conditions of the crude oil, ULP 95, ULSD, JET A1 and MGO storage tanks with the details of the parameters in which the calculation procedure was based.

A.2.1.1 Crude Oil

Table A-10: Components and compositions of crude oil mixture

Mixture/Component	Zi	MW	MW_{ave}
Methane	0.01	16.04	0.15
Ethane	0.03	30.07	0.78
Propane	0.05	44.10	2.41
i-Butane	0.01	58.12	0.77
n-Butane	0.06	58.12	3.62
i-Pentane	0.02	72.15	1.66
n-Pentane	0.04	72.15	2.99
2-Methylpentane	0.02	86.18	1.87
n-Hexane	0.02	86.18	1.95
2.2.4-Trimethylpentane	0.00	114.23	0.14
n-Heptane	0.10	100.21	10.06
n-Octane	0.09	114.23	10.19
n-Nonane	0.04	128.26	4.76
Benzene	0.00	78.11	0.22
Toluene	0.01	92.14	0.85
Ethylbenzene	0.00	106.17	0.35
p-Xylene	0.01	106.17	1.50
C10+	0.47	254.50	119.26
SUM	**1.00**	**1617.14**	**163.51**

Table A-11: Operating conditions of crude oil mixture

Operating Conditions	Value
Temperature (℃)	17.89
Pressure (kPa)	96,.8

Table A-12: Vapour pressure data for crude oil mixture (Golder Associates , 2019b)

Mixture/Component	A	B	C	ln(Pva)	Pva (mmHg)	Pva (Psia)
Methane	15.22	897.84	-7.16	12.06	173086.03	3346.93
Ethane	15.66	1511.42	-17.16	10.15	25466.82	492.45
Propane	15.73	1872.46	-25.16	8.68	5904.52	114.17
i-Butane	15.54	2032.73	-33.15	7.66	2113.10	40.86
n-Butane	15.68	2154.90	-34.42	7.28	1452.33	28.08
i-Pentane	15.63	2348.67	-40.05	6.28	531.73	10.28
n-Pentane	15.83	2477.07	-39.94	5.97	390.87	7.56
2-Methylpentane	15.75	2614.38	-46.58	5.05	156.50	3.03
n-Hexane	15.84	2697.55	-48.78	4.70	110.13	2.13
2.2.4-Trimethylpentane	15.69	2896.28	-52.41	3.55	34.74	0.67
n-Heptane	15.87	2911.32	-56.51	3.46	31.82	0.62
n-Octane	15.94	3120.29	-63.63	2.22	9.22	0.18
n-Nonane	15.97	3291.45	-71.33	0.99	2.68	0.05
Benzene	15.90	2788.51	-52.36	4.22	67.88	1.31
Toluene	16.01	3096.52	-53.67	2.97	19.46	0.38
Ethylbenzene	16.02	3279.47	-59.95	1.83	6.22	0.12
p-Xylene	16.10	3346.65	-57.84	1.75	5.73	0.11
C10+	16.15	4450.44	-135.60	-12.48	0.00	0.00

A, B, C – Vapour Pressure Equation Constants from the Antoine equation (Golder Associates , 2019b) used in Equation 2-55

Table A-13: Manual Flashing calculation parameters for crude oil mixture

Mixture/Component	Ptotal (mmHg)	Ki	Rachford-Rice	xi_calc	yi_calc	MW liquid	MW vapour
Methane	223.91	239.43	2.22	0.00	0.31	0.02	4.97
Ethane	19.21	35.23	0.86	0.00	0.03	0.80	0.80
Propane	322.39	8.17	0.39	0.05	0.45	19.67	19.67
i-Butane	28.10	2.92	0.03	0.01	0.04	2.26	2.26
n-Butane	90.34	2.01	0.06	0.06	0.12	7.26	7.26
i-Pentane	12.23	0.74	-0.01	0.02	0.02	1.22	1.22
n-Pentane	16.22	0.54	-0.02	0.04	0.02	1.62	1.62
2-Methylpentane	3.40	0.22	-0.02	0.02	0.00	0.40	0.40
n-Hexane	2.49	0.15	-0.02	0.02	0.00	0.30	0.30
2.2.4-Trimethylpentane	0.04	0.05	0.00	0.00	0.00	0.01	0.01
n-Heptane	3.20	0.04	-0.10	0.10	0.00	0.44	0.44
n-Octane	0.82	0.01	-0.09	0.09	0.00	0.13	0.13
n-Nonane	0.10	0.00	-0.04	0.04	0.00	0.02	0.02
Benzene	0.19	0.09	0.00	0.00	0.00	0.02	0.02
Toluene	0.18	0.03	-0.01	0.01	0.00	0.02	0.02
Ethylbenzene	0.02	0.01	0.00	0.00	0.00	0.00	0.00
p-Xylene	0.08	0.01	-0.01	0.01	0.00	0.01	0.01
C10+	0.00	0.00	-0.47	0.47	0.00	0.00	0.00
	722.91	**289.65**	**2.78**	**0.97**	**1.00**	**34.20**	**39.15**

Table A-14: Manual Flashing calculation results for crude oil mixture

Mixture/Component	Feed flowrate (kmol/hr)	Vapour Flowrate (kmol/hr)	Liquid Flowrate (kmol/hr)
Methane	0.06	0.00	0.06
Ethane	0.17	0.00	0.17
Propane	0.36	0.01	0.35
i-Butane	0.09	0.00	0.09
n-Butane	0.41	0.01	0.40
i-Pentane	0.15	0.00	0.15
n-Pentane	0.27	0.01	0.27
2-Methylpentane	0.14	0.00	0.14
n-Hexane	0.15	0.00	0.15
2.2.4-Trimethylpentane	0.01	0.00	0.01
n-Heptane	0.66	0.02	0.65
n-Octane	0.59	0.02	0.57
n-Nonane	0.25	0.01	0.24
Benzene	0.02	0.00	0.02
Toluene	0.06	0.00	0.06
Ethylbenzene	0.02	0.00	0.02
p-Xylene	0.09	0.00	0.09
C10+	3.10	0.08	3.02
	6.55	**0.17**	**6.38**

Table A-15: Manual Flashing excel calculation results for crude oil mixture

Solver Results	Value
ABS	4.55E-10
SUM	2.78
PACTUAL (mmHg)	722.91
PINPUT (mmHg)	722.91
V/F	0.04
L/F	0.96

ABS – Absolute value
SUM – Total Pressure
PACTUAL – Actual pressure value
PINPUT – Input pressure value
V/F – Vapour fraction
Liquid fraction

Table A-16: Manual Flashing calculation flowrate results for crude oil mixture

Mixture/Component	Feed flowrate (tons/year)	Vapour Flowrate (tons/year)	Liquid Flowrate (tons/year)
Methane	8.64	0.22	8.42
Ethane	45.12	1.17	43.95
Propane	139.49	3.62	135.87
i-Butane	44.79	1.16	43.62
n-Butane	209.45	5.44	204.02
i-Pentane	96.14	2.50	93.65
n-Pentane	173.47	4.50	168.97
2-Methylpentane	108.34	2.81	105.53
n-Hexane	112.84	2.93	109.91
2.2.4-Trimethylpentane	7.94	0.21	7.74
n-Heptane	582.86	15.13	567.73
n-Octane	590.33	15.32	575.00
n-Nonane	275.68	7.16	268.52
Benzene	12.67	0.33	12.34
Toluene	49.11	1.27	47.84
Ethylbenzene	20.30	0.53	19.77

Table A-17: Manual Flashing calculation flowrate results for crude oil mixture

p-Xylene	86.73	2.25	84.48
C10+	6909.30	179.35	6729.95
	9473.20	**245.90**	**9227.30**

A.2.1.2 ULP 95 Data

Table A-18: Data Specifications used in the Manual Flashing Method for ULP 95

Mixture/Component	Average Vapor Pressure (psia)	Vapor Molecular Weight (lb/lbmol)	Liquid Mass Fraction	Vapor Mass Fraction	Molecular Weight (lb/lbmol)
Gasoline (RVP 10)	**6.80**	**66.00**			**92.00**
1,2,4-Trimethylbenzene	0.04	120.19	0.03	0.00	120.19
Benzene	1.72	78.11	0.02	0.01	78.11
Cyclohexane	1.76	84.16	0.00	0.00	84.16
Ethylbenzene	0.18	106.17	0.01	0.00	106.17
Hexane (-n)	2.74	86.17	0.01	0.01	86.17
Isooctane	0.93	114.22	0.04	0.00	114.22
Isopropyl benzene	0.08	120.20	0.01	0.00	120.20
Toluene	0.51	92.13	0.07	0.01	92.13
Unidentified Components	8.70	65.62	0.75	0.98	89.36
Xylene (-m)	0.15	106.17	0.07	0.00	106.17

Table A-19: Operating conditions used in the Manual Flashing Method for ULP 95

Operating Conditions	Value
Temperature (℃)	23.51
Pressure (kPa)	58.09

Table A-20: Vapour pressure data used in the Manual Flashing Method for ULP 95

Mixture/Component	A	B	C	log(Pva)	Pva (mmHg)	Pva (Psia)
Gasoline (RVP 10)	16.22	3 622.58	-64.59	0.61	1.84	0.04
1,2,4-Trimethylbenzene	6.91	1 211.03	220.79	1.95	88.68	1.71
Benzene	6.84	1 201.53	222.65	1.96	91.18	1.76
Cyclohexane	6.98	1 424.26	213.21	0.96	9.09	0.18
Ethylbenzene	6.88	1 171.17	224.41	2.15	141.91	2.74
Hexane (-n)					48.27	0.93
Isooctane	6.96	1 460.79	207.78	0.65	4.44	0.09
Isopropyl benzene	6.95	1 344.80	219.48	1.42	26.28	0.51
Toluene					449.87	8.70
Unidentified Components	7.01	1 462.27	215.11	0.88	7.60	0.15
Xylene (-m)						

A, B, C – Vapour Pressure Equation Constants (Golder Associates, 2019b) used in Equation 2-55

Table A-21: Data used in the Manual Flashing Method for ULP 95

Mixture/Component	Ki	Density (kg/m^3)	Feed density (kg/m^3)	Liquid density	Zi
Gasoline (RVP 10)			671.03		
1,2,4-Trimethylbenzene	0.01	880.00		22.00	0.0014
Benzene	0.35	885.00		15.93	0.0069
Cyclohexane	0.38	779.00		1.87	0.00097
Ethylbenzene	0.04	867.00		12.14	0.0012
Hexane (-n)	0.56	659.00		6.59	0.0058
Isooctane	0.00	692.00		27.68	0.0019
Isopropyl benzene	0.02	862.00		4.31	0.00034
Toluene	0.10	867.00		60.69	0.010
Unidentified Components	1.31	666.00		496.57	0.97
Xylene (-m)	0.03	864.00		60.48	0.0054

Table A-22: Data used in the Manual Flashing Method for ULP 95 compositions

Mixture/Component	Rachford-Rice	Ptotal (mmHg)	Ki	xi_calc	yi_calc
Gasoline (RVP 10)	0.33	0.61	0.00	0.33	0.00
1,2,4-Trimethylbenzene	0.02	2.99	0.20	0.03	0.01
Benzene	0.00	0.42	0.21	0.00	0.00
Cyclohexane	0.05	0.50	0.02	0.06	0.00
Ethylbenzene	0.01	2.53	0.33	0.02	0.01
Hexane (-n)	0.01	0.84	0.11	0.02	0.00
Isooctane	0.03	0.15	0.01	0.03	0.00
Isopropyl benzene	0.15	4.50	0.06	0.17	0.01
Toluene	0.00	420.83	1.03	0.94	0.97
Unidentified Components	0.30	2.34	0.02	0.31	0.01
Xylene (-m)	0.91	435.71	1.99	1.91	1.00

Table A-23: Results of the Manual Flashing Method for ULP 95

Solver Results	Value
ABS	0.02
SUM	-8.86E-11
PACTUAL (mmHg)	435.71
PINPUT (mmHg)	435.71
V/F	0.01
L/F	0.99

ABS – Absolute value
SUM – Total Pressure
PACTUAL – Actual pressure value
PINPUT – Input pressure value
V/F – Vapour fraction
Liquid fraction

Table A-24: Flow Results of the Manual Flashing Method for ULP 95

Component	Feed flowrate (tons/yr)	Vapour Flowrate (tons/yr)	Liquid Flowrate (tons/yr)
Gasoline (RVP 10)			
1,2,4-Trimethylbenzene	11 071.51	669.48	10 402.02
Benzene	54 468.61	3 293.66	51 174.95
Cyclohexane	7 715.67	466.56	7 249.11
Ethylbenzene	9 130.66	552.12	8 578.54
n-Hexane	46 121.93	2 788.94	43 332.99
Isooctane/2,2,4-Trimethylpentane	15 297.40	925.02	14 372.39
Isopropylbenzene	2 667.49	161.30	2 506.19
Toluene	81 908.37	4 952.91	76 955.47
unidentified	7 664 560.62	463 467.36	7 201 093.26
m-xylene	42 632.05	2 577.91	40 054.14
Average	**7 935 574.31**	**479 855.25**	**7 455 719.06**

A.2.1.3 ULSD Data

Table A-25: Data Specifications used in the Manual Flashing Method for ULSD

Mixture/Component	Vapor Pressure (psia)			Vapor Molecular Weight (lb/lbmol)	Liquid Mass Fraction	Vapor Mass Fraction	Molecular Weight (lb/lbmol)
	Average	Minimum	Maximum				
Distillate fuel oil no. 2	**0.01**	**0.01**	**0.01**	**130.00**			**18.00**
1,2,4-Trimethylbenzene	0.04	0.03	0.04	120.19	0.01	0.05	120.19
Benzene	1.72	1.49	1.97	78.11	0.00	0.00	78.11
Ethylbenzene	0.18	0.15	0.21	106.17	0.00	0.00	106.17
Hexane (-n)	2.74	2.40	3.13	86.17	0.00	0.00	86.17
Toluene	0.51	0.43	0.60	92.13	0.00	0.02	92.13
Unidentified Components	0.01	0.01	0.01	134.54	0.99	0.86	189.60
Xylene (-m)	0.15	0.12	0.18	106.17	0.00	0.06	106.17

Table A-26: Operating conditions used in the Manual Flashing Method for ULSD

Operating Conditions	Value
Temperature (℃)	25
Pressure (kPa)	106.70

Table A-27: Vapour pressure data used in the Manual Flashing Method for ULSD

Mixture/Component	A	B	C	log(Pva)	Pva (mmHg)	Pva (Psia)
Distillate fuel oil no. 2						
1,2,4-Trimethylbenzene	16.22	3622.58	-64.59	0.71	2.03	0.04
Benzene	6.91	1211.03	220.79	1.98	95.04	1.84
Ethylbenzene	6.98	1424.26	213.21	1.00	9.91	0.19
Hexane (-n)	6.88	1171.17	224.41	2.18	151.44	2.93
Toluene	6.95	1344.80	219.48	1.45	28.40	0.55
Unidentified Components					0.46	0.01
Xylene (-m)	7.01	1462.27	215.11	0.92	8.30	0.16

A, B, C – Vapour Pressure Equation Constants (Golder Associates, 2019b) used in Equation 2-55

Table A-28: Data used in the Manual Flashing Method for ULSD

Mixture/Component	Ki	Density (kg/m^3)	Feed density (kg/m^3)	Liquid density (kg/m^3)	Zi
Distillate fuel oil no. 2			850.77		
1,2,4-Trimethylbenzene	4.99	880.00		8.80	0.000018
Benzene	0.00	885.00		0.00	0.00000060
Ethylbenzene	32.00	867.00		0.09	0.0000010
Hexane (-n)	0.00	659.00		0.00	0.00000013
Toluene	76.00	867.00		0.26	0.0000073
Unidentified Components	0.87	850.70		839.30	0.00058
Xylene (-m)	20.66	864.00		2.51	0.000020
Air					0.99

Table A-29: Data used in the Manual Flashing Method for ULSD compositions

Mixture/Component	Rachford-Rice	Ptotal (mmHg)	Ki	xi_calc	yi_calc
Distillate fuel oil no. 2					
1,2,4-Trimethylbenzene	-0.000019	0.000038	0.0025	0.000019	0.000000048
Benzene	-0.00000070	0.000057	0.12	0.00000060	0.000000071
Ethylbenzene	-0.0000010	0.000010	0.012	0.0000010	0.000000013
Hexane (-n)	-0.00000020	0.000019	0.19	0.00000013	0.000000024
Toluene	-0.0000075	0.00021	0.036	0.0000073	0.00000026
Unidentified Components	-0.00058	0.00026	0.00057	0.00058	0.00000033
Xylene (-m)	-0.000020	0.00016	0.010	0.000019	0.00000021
Air	1.00	799.30	0.99	0.99	0.99

Table A-30: Results of the Manual Flashing Method for ULSD

Solver Results	Value
ABS	1.0044
SUM	2.0044
PACTUAL (mmHg)	800.31
PINPUT	800.31
V/F	0.00063
L/F	0.99

ABS – Absolute value
SUM – Total Pressure
PACTUAL – Actual pressure value
PINPUT – Input pressure value
V/F – Vapour fraction
Liquid fraction

Table A-31: Flow Results of the Manual Flashing Method for ULSD

Component	Feed flowrate (tons/yr)	Vapour Flowrate (tons/yr)	Liquid Flowrate (tons/yr)
1,2,4-Trimethylbenzene	252.46	0.16	252.30
Benzene	8.01	0.0050	8.00
Ethylbenzene	13.91	0.0087	13.90
n-hexane	1.69	0.0011	1.68
Toluene	97.36	0.061	97.30
Unidentified	7 790.47	4.90	7 785.57
m-xylene	264.68	0.17	264.52
Average	**8 428.57**	**5.30**	**8 423.27**

A.2.1.4 JET A1 Data

Table A-32: Data Specifications used in the Manual Flashing Method for JET A1

Mixture/Component	Vapor Pressure (psia)			Vapor Molecular Weight (lb/lbmol)	Liquid Mass Fraction	Vapor Mass Fraction	Molecular Weight (lb/lbmol)
	Average	Minimum	Maximum				
Jet kerosene	**0.01**	**0.01**	**0.01**	**130.00**			**162.00**
Benzene	1.72	1.49	1.97	78.11	0.00	0.01	78.11
Ethylbenzene	0.18	0.15	0.21	106.17	0.00	0.02	106.17
Hexane (-n)	2.74	2.40	3.13	86.17	0.00	0.01	86.17
Toluene	0.51	0.43	0.60	92.13	0.00	0.07	92.13
Unidentified Components	0.01	0.01	0.01	138.75	0.99	0.85	162.55
Xylene (-m)	0.15	0.12	0.18	106.17	0.00	0.04	106.17

Table A-33: Operating conditions used in the Manual Flashing Method for JET A1

Operating Conditions	Value
Temperature (°C)	30.00
Pressure (mmHg)	881.00

Table A-34: Vapour pressure data used in the Manual Flashing Method for JET A1

Mixture/Component	A	B	C	log(Pva)	Pva (mmHg)	Pva (Psia)
Jet kerosene						
Benzene	6.91	1 211.03	220.79	1.95	88.68	1.71
Ethylbenzene	6.98	1 424.26	213.21	0.96	9.09	0.18
Hexane (-n)	6.88	1 171.17	224.41	2.15	141.91	2.74
Toluene	6.95	1 344.80	219.48	1.42	26.28	0.51
Unidentified Components					0.53	0.01
Xylene (-m)	7.01	1 462.27	215.11	0.88	7.60	0.15

A, B, C – Vapour Pressure Equation Constants (Golder Associates, 2019b) used in Equation 2-55

Table A-35: Data used in the Manual Flashing Method for JET A1

Mixture/Component	Ki	Density (kg/m^3)	Feed density (kg/m^3)	Liquid density (kg/m^3)	Zi
Jet kerosene			838.78		
Benzene	0.18	885.00		0.00	0.0000033
Ethylbenzene	0.020	867.00		1.13	0.0000112
Hexane (-n)	0.28	659.00		0.07	0.0000066
Toluene	0.055	867.00		1.13	0.0000328
Unidentified Components	0.00080	843.00		838.11	0.0008944
Xylene (-m)	0.017	864.00		2.68	0.0000232
Air	0.99				0.9990286

Table A-36: Data used in the Manual Flashing Method for JET A1 compositions

Mixture/Component	Rachford-Rice	Ptotal (mmHg)	Ki	xi_calc	yi_calc
Jet kerosene					
Benzene	-0.0000040	0.00039	0.18	0.0000033	0.00000059
Ethylbenzene	-0.000011	0.00015	0.020	0.000011	0.00000022
Hexane (-n)	-0.0000091	0.0012	0.28	0.0000066	0.00000189
Toluene	-0.000035	0.0012	0.055	0.000033	0.0000018
Unidentified Components	-0.00090	0.00047	0.0010	0.00090	0.00000071
Xylene (-m)	-0.000024	0.00026	0.017	0.000023	0.00000039
Air	1.00	659.75	0.99	0.99	1.00

Table A-37: Results of the Manual Flashing Method for JET A1

Solver Results	Value
ABS	1.25
SUM	2.25
PACTUAL (mmHg)	661.00
PINPUT (mmHg)	661.00
V/F	0.00092
L/F	0.99

ABS – Absolute value
SUM – Total Pressure
PACTUAL – Actual pressure value
PINPUT – Input pressure value
V/F – Vapour fraction
Liquid fraction

Table A-38: Flow Results of the Manual Flashing Method for JET A1

Component	Feed flowrate (tons/yr)	Vapour Flowrate (tons/yr)	Liquid Flowrate (tons/yr)
Benzene	32.28	0.030	32.25
Ethylbenzene	111.29	0.10	111.19
n-Hexane	65.041	0.060	64.98
Toluene	325.21	0.30	324.91
Unidentified	8871.64	8.17	8863.47
m-xylene	229.81	0.21	229.60
Average	**9 635.27**	**8.87**	**9 626.40**

A.2.1.5 MGO Data

Table A-39: Data Specifications used in the Manual Flashing Method for MGO

Mixture/Component	Vapor Pressure (psia)			Vapor Molecular Weight	Liquid Mass Fraction	Vapor Mass Fraction	Molecular Weight
	Average	Minimum	Maximum				
Distillate fuel oil no. 2	**0.01**	**0.01**	**0.01**	**130.00**			**188.00**
1,2,4-Trimethylbenzene	0.04	0.03	0.04	120.19	0.01	0.05	120.19
Benzene	1.72	1.49	1.97	78.11	0.00	0.00	78.11
Ethylbenzene	0.18	0.15	0.21	106.17	0.00	0.00	106.17
Hexane (-n)	2.74	2.40	3.13	86.17	0.00	0.00	86.17
Toluene	0.51	0.43	0.60	92.13	0.00	0.02	92.13
Unidentified Components	0.01	0.01	0.01	134.54	0.99	0.86	189.60
Xylene (-m)	0.15	0.12	0.18	106.17	0.00	0.06	106.17

Table A-40: Operating conditions used in the Manual Flashing Method for MGO

Operating Conditions	Value
Temperature (°C)	23.80
Pressure (kPa)	870.00

Table A-41: Vapour pressure data used in the Manual Flashing Method for MGO

Mixture/Component	A	B	C	log(Pva)	Pva (mmHg)	Pva (Psia)
Distillate fuel oil no. 2						
1,2,4-Trimethylbenzene	16.22	3 622.58	(64.59)	0.56	1.75	0.03
Benzene	6.91	1 211.03	220.79	1.93	85.78	1.66
Ethylbenzene	6.98	1 424.26	213.21	0.94	8.72	0.17
Hexane (-n)	6.88	1 171.17	224.41	2.14	137.55	2.66
Toluene	6.95	1 344.80	219.48	1.40	25.32	0.49
Unidentified Components					0.46	0.01
Xylene (-m)	7.01	1 462.27	215.11	0.86	7.29	0.14

A, B, C – Vapour Pressure Equation Constants (Golder Associates, 2019b) used in Equation 2-55

Table A-42: Data used in the Manual Flashing Method for MGO

Mixture/Component	Ki	Density (kg/m^3)	Feed density (kg/m^3)	Liquid density (kg/m^3)	Zi
Distillate fuel oil no. 2			850.77		
1,2,4-Trimethylbenzene	4.99	880.00		8.80	0.000017
Benzene	0.00	885.00		0.00	0.00000054
Ethylbenzene	32.00	867.00		0.09	0.00000094
Hexane (-n)	0.00	659.00		0.00	0.00000011
Toluene	76.00	867.00		0.26	0.0000066
Unidentified Components	0.87	850.00		838.61	0.00053
Xylene (-m)	20.66	864.00		2.51	0.000018
Air	4.99				0.99

Table A-43: Data used in the Manual Flashing Method for MGO compositions

Mixture/Component	Rachford-Rice	Ptotal (mmHg)	Ki	xi_calc	yi_calc
Distillate fuel oil no. 2					
1,2,4-Trimethylbenzene	-0.000017	0.000030	0.0020	0.000017	0.000000034
Benzene	-0.00000060	0.000046	0.099	0.00000050	0.000000053
Ethylbenzene	-0.00000095	0.0000080	0.010	0.00000090	0.000000009
Hexane (-n)	-0.00000014	0.000016	0.16	0.00000010	0.000000018
Toluene	-0.0000068	0.00017	0.029	0.0000066	0.00000019
Unidentified Components	-0.00053	0.00024	0.00050	0.00053	0.00000028
Xylene (-m)	-0.000018	0.00013	0.0084	0.000010	0.00000015
Air	1.00	869.00	0.99	0.99	0.99

Table A-44: Results of the Manual Flashing Method for MGO

Solver Results	Value
ABS	0.99
SUM	1.99
PACTUAL (mmHg)	870.00
PINPUT (mmHg)	870.00
V/F	0.00060
L/F	0.99

ABS – Absolute value
SUM – Total Pressure
PACTUAL – Actual pressure value
PINPUT – Input pressure value
V/F – Vapour fraction
Liquid fraction

Table A-45: Flow Results of the Manual Flashing Method for MGO

Mixture/Component	Feed flowrate (tons/yr)	Vapour Flowrate (tons/yr)	Liquid Flowrate (tons/yr)
Distillate fuel oil no. 2			
1,2,4-Trimethylbenzene	76.37	0.044	76.33
Benzene	2.42	0.0014	2.42
Ethylbenzene	4.21	0.0024	4.21
Hexane (-n)	0.51	0.00030	0.51
Toluene	29.45	0.017	29.44
Unidentified Components	2 356.71	1.34	2 355.36
Xylene (-m)	80.07	0.046	80.02
Average	**2 549.74**	**1.45**	**2 548.29**

A.2.2 Aspen Plus ® Simulations

This section records the raw data and results obtained from performing the Aspen Plus ® Simulations of ULP 95, ULSD, JET A1 and MGO mixtures. It outlines the required storage tank conditions, parameters used in the calculation procedure and consistency test results.

A.2.2.1 ULP 95

Table A-46: ULP 95 Input Parameters for Aspen Plus ® Simulation

Input Parameter	Value
Feed Flowrate (ton/year)	7 838 306.34
Separator Temperature (K)	298.15
Separator Pressure (kPa)	200.00
Storage Tank Temperature (K)	296.66
Storage Tank Pressure (kPa)	14.67
Valve Pressure Drop (kPa)	100.00
Unidentified Density (kg/m^3)	666.00
Unidentified Molecular Weight	89.36

Table A-47: Pressurized Liquid Compositions of ULP 95 Mixture

Component	Mass Fraction
1,2,4-Trimethylbenzene	0.0014
Benzene	0.0069
Cyclohexane	0.00097
Ethylbenzene	0.0012
Hexane (-n)	0.0058
Isooctane	0.0019
Isopropyl benzene	0.00034
Toluene	0.010
Unidentified Components	0.97
Xylene (-m)	0.0054

Table A-48: ULP 95 Consistency and Aspen Plus ® Simulation Results

Component i	Component j	Consistency	RMSE	
			PENG-ROB	SRK
Benzene	n-hexane	0.38	20.30	25.45
Benzene	Toluene	0.25	8.35	4.23
Cyclohexane	n-hexane	0.50	3.06	6.94
1,2,4-trimethylbenzene	Ethylbenzene	0.50	1.93	7.37
Benzene	2,2,4-trimethylpentane	0.50	16.23	15.37
Benzene	Isopropylbenzene	0.43	22.40	21.33
cyclohexane	ethylbenzene	0.16	11.79	10.65
cyclohexane	2,2,4-trimethylpentane	0.50	3.25	3.00
cyclohexane	m-xylene	0.25	13.22	13.30
ethylbenzene	n-hexane	0.54	2.48	2.81
ethylbenzene	2,2,4-trimethylpentane	0.50	12.23	12.12
ethylbenzene	Isopropylbenzene	0.50	3.45	2.47
ethylbenzene	m-xylene	0.89	2.38	4.25
n-hexane	2,2,4-trimethylpentane	0.50	6.14	6.22
n-hexane	Toluene	0.50	13.65	15.36
2,2,4-trimethylpentane	Toluene	0.50	15.60	17.21
2,2,4-trimethylpentane	m-xylene	0.51	14.82	15.35

Table A-49: ULP 95 Mass Flowrate Stream Results from Aspen Plus ® Simulation

Component	Mass Flowrate Streams (ton/year)			
	Pressurized Liquid from Separator	Feed to Tank	VOC Emissions	Product
1,2,4-Trimethylbenzene	10 935.80	10 935.80	3 417.19	7 518.61
Benzene	53 800.97	53 800.97	49 086.52	4 714.45
Cyclohexane	7 621.10	7 621.10	6 813.00	808.10
Ethylbenzene	9 018.75	9 018.75	4 430.33	4 588.42
Hexane (-n)	45 556.60	45 556.60	41 797.94	3 758.66

Table A-50: ULP 95 Mass Flowrate Stream Results from Aspen Plus ® Simulation (continued)

Isooctane	15 109.90	15 109.90	11 924.89	3 185.01
Isopropyl benzene	2 634.79	2 634.79	823.31	1 811.48
Toluene	80 904.40	80 904.40	59 367.67	21 536.73
Unidentified Components	7 570 614.51	7 570 614.51	6 815 316.39	755 298.12
Xylene (-m)	42 109.50	42 109.50	18 832.99	23 276.51

A.2.2.2 ULSD

Table A-51: ULSD Input Parameters for Aspen Plus ® Simulation

Input Parameter	Value
Feed Flowrate (ton/year)	8 428.57
Separator Temperature (K)	308.15
Separator Pressure (kPa)	200.00
Storage Tank Temperature (K)	298.15
Storage Tank Pressure (kPa)	106.70
Valve Pressure Drop (kPa)	100.00
Unidentified Density (kg/m^3)	850.70
Unidentified Molecular Weight	189.60

Table A-52: Pressurized Liquid Compositions of ULSD Mixture

Component	Mass Fraction
1,2,4-Trimethylbenzene	0.000019
Benzene	0.00000060
Ethylbenzene	0.0000010
Hexane (-n)	0.00000013
Toluene	0.0000073
Unidentified Components	0.00058
Xylene (-m)	0.000020

Table A-53: ULSD Consistency and Aspen Plus ® Simulation Results

Component i	Component j	Consistency	RMSE	
			PENG-ROB	SRK
Benzene	n-hexane	0.38	20.30	25.45
Benzene	Toluene	0.57	4.28	3.74
1,2,4-Trimethylbenzene	Ethylbenzene	0.50	1.93	7.37
Ethylbenzene	n-hexane	0.50	2.48	2.81
Ethylbenzene	m-xylene	0.89	2.38	4.25
n-hexane	Toluene	0.50	13.65	15.36

Table A-54: ULSD Mass Flowrate Stream Results from Aspen Plus ® Simulation

Component	Mass Flowrate Streams (ton/year)			
	Pressurized Liquid from Separator	Feed to Tank	VOC Emissions	Product
1,2,4-Trimethylbenzene	252.44	252.44	250.61	1.82
Benzene	8.01	8.01	8.01	0.00
Ethylbenzene	13.91	13.91	13.89	0.02
Hexane (-n)	1.69	1.69	1.69	0.00
Toluene	97.35	97.35	97.30	0.05
Unidentified Components	7 789.68	7 789.68	5 648.65	2 141.03
Xylene (-m)	264.66	264.66	264.18	0.48

A.2.2.3 JET A1

Table A-55: JET A1 Input Parameters for Aspen Plus ® Simulation

Input Parameter	Value
Feed Flowrate (ton/year)	9 635.27
Separator Temperature (K)	308.15
Separator Pressure (kPa)	200.00
Storage Tank Temperature (K)	303.15
Storage Tank Pressure (kPa)	88.13
Valve Pressure Drop (kPa)	100.00
Unidentified Density (kg/m^3)	843.00
Unidentified Molecular Weight	162.55

Table A-56: Pressurized Liquid Compositions of JET A1 Mixture

Component	Mass Fraction
Benzene	0.0000031
Ethylbenzene	0.000011
Hexane (-n)	0.0000062
Toluene	0.000031
Unidentified Components	0.000847
Xylene (-m)	0.000022

Table A-57: JET A1 Consistency and Aspen Plus ® Simulation Results

Component i	Component j	Consistency	RMSE	
			PENG-ROB	SRK
Benzene	n-hexane	0.34	20.30	25.45
Benzene	Toluene	0.25	4.17	3.50
Ethylbenzene	m-xylene	0.89	2.38	4.25
n-hexane	toluene	0.50	13.65	15.36
Ethylbenzene	n-hexane	0.54	2.48	2.81

Table A-58: JET A1 Mass Flowrate Stream Results from Aspen Plus ® Simulation

Component	Mass Flowrate Streams (ton/year)			
	Pressurized Liquid from Separator	Feed to Tank	VOC Emissions	Product
Benzene	32.28	32.28	32.28	0.00
Ethylbenzene	111.29	111.29	111.29	0.00
Hexane (-n)	65.04	65.04	65.04	0.00
Toluene	325.19	325.19	325.19	0.00
Unidentified Components	8 871.20	8 871.20	8 871.20	0.00
Xylene (-m)	229.80	229.80	229.80	0.00

A.2.2.4 MGO

Table A-59: MGO Input Parameters for Aspen Plus ® Simulation

Input Parameter	Value
Feed Flowrate (ton/year)	2 549.74
Separator Temperature (K)	308.15
Separator Pressure (kPa)	200.00
Storage Tank Temperature (K)	295.95
Storage Tank Pressure (kPa)	115.99
Valve Pressure Drop (kPa)	100.00
Unidentified Density (kg/m^3)	850.00
Unidentified Molecular Weight	189.6

Table A-60: Pressurized Liquid Compositions of MGO Mixture

Component	Mass Fraction
1,2,4-Trimethylbenzene	0.000017
Benzene	0.00000054
Ethylbenzene	0.00000094
Hexane (-n)	0.00000011
Toluene	0.0000066
Unidentified Components	0.00053
Xylene (-m)	0.000018

Table A-61: MGO Consistency and Aspen Plus ® Simulation Results

Component i	Component j	Consistency	RMSE	
			PENG-ROB	SRK
Benzene	n-hexane	0.34	20.30	25.45
1,2,4-trimethylbenzene	ethylbenzene	0.50	1.93	7.37
ethylbenzene	n-hexane	0.54	2.48	2.81
ethylbenzene	m-xylene	0.89	2.38	4.25
n-hexane	Toluene	0.50	13.65	15.36
Benzene	Toluene	0.57	4.28	3.74

Table A-62: MGO Mass Flowrate Stream Results from Aspen Plus ® Simulation

Component	Mass Flowrate Streams (ton/year)			
	Pressurized Liquid from Separator	Feed to Tank	VOC Emissions	Product
1,2,4-Trimethylbenzene	76.40	76.37	75.55	0.00
Benzene	2.42	2.42	2.42	0.00
Ethylbenzene	4.21	4.21	4.20	0.00
Hexane (-n)	0.51	0.51	0.51	0.00
Toluene	29.46	29.46	29.44	0.00
Unidentified Components	2 357.55	2 323.52	1 467.76	0.00
Xylene (-m)	80.10	80.09	79.88	0.00

A.2.3 Empirical Correlations

The following section records the input and output parameters for the calculation procedures of the Vasquez-Beggs and Valko-McCain empirical correlations. The effect of varying conditions on the VOC emissions were also investigated and tabulated.

A.2.3.1 VBE

Table A-63: Input and Output Parameters of the VBE at varying feed flowrates for the different mixtures

Mixture	Percent of Feed Flow	Input parameters					Output parameters					
		API (ºAPI)	P_S (Psia)	T_S (ºF)	SG_S	Q (bbl/d)	SGc	Rs (scf/bbl)	MW_{TV}	Xvoc (lb-voc/lb)	E_{Tot} (ton/year)	E_{VOC} (ton/year)
Crude Oil	-10.00	45.00	56.70	66.00	0.81	171.20	0.76	12.70	41.40	0.06	43.15	2.40
	-15.00	45.00	56.70	66.00	0.81	161.69	0.76	12.70	41.40	0.06	40.75	2.26
	-20.00	45.00	56.70	66.00	0.81	152.18	0.76	12.70	41.40	0.06	38.35	2.13
	-25.00	45.00	56.70	66.00	0.81	142.67	0.76	12.70	41.40	0.06	35.96	2.00
	0.00	45.00	56.70	66.00	0.81	190.22	0.76	12.70	41.40	0.06	47.94	2.66
	10.00	45.00	56.70	66.00	0.81	209.25	0.76	12.70	41.40	0.06	52.74	2.93
	15.00	45.00	56.70	66.00	0.81	218.76	0.76	12.70	41.40	0.06	55.13	3.06
	20.00	45.00	56.70	66.00	0.81	228.27	0.76	12.70	41.40	0.06	57.53	2.55
	25.00	45.00	56.70	66.00	0.81	237.78	0.76	12.70	41.40	0.06	59.93	3.33
ULP 95	-10.00	79.21	29.01	77.00	0.67	143 413.99	0.53	17.43	66.00	0.10	79 053.80	7 905.38
	-15.00	79.21	29.01	77.00	0.67	135 446.55	0.53	17.43	66.00	0.10	74 661.92	7 466.19

Table A-61: Input and Output Parameters of the VBE at varying feed flowrates for the different mixtures (Continued)

	-20.00	79.21	29.01	77.00	0.67	127 479.11	0.53	17.43	66.00	0.10	70 270.04	7 027.00
	-25.00	79.21	29.01	77.00	0.67	119 511.66	0.53	17.43	66.00	0.10	65 878.17	6 587.82
	0.00	79.21	29.01	77.00	0.67	159 348.88	0.53	17.43	66.00	0.10	87 837.55	2 898.64
	10.00	79.21	29.01	77.00	0.67	175 283.77	0.53	17.43	66.00	0.10	96 621.31	9 662.13
	15.00	79.21	29.01	77.00	0.67	183 251.21	0.53	17.43	66.00	0.10	101 013.19	10 101.32
	20.00	79.21	29.01	77.00	0.67	191 218.66	0.53	17.43	66.00	0.10	105 405.06	10 540.51
	25.00	79.21	29.01	77.00	0.67	199 186.10	0.53	17.43	66.00	0.10	109 796.94	10 979.69
	-10.00	34.40	29.01	77.00	0.85	242 384.79	0.77	3.47	130.00	0.16	52 426.52	8 213.49
	-15.00	34.40	29.01	77.00	0.85	228 918.97	0.77	3.47	130.00	0.16	49 513.94	7 757.18
	-20.00	34.40	29.01	77.00	0.85	215 453.14	0.77	3.47	130.00	0.16	46 601.35	7 300.88
	-25.00	34.40	29.01	77.00	0.85	201 987.32	0.77	3.47	130.00	0.16	43 688.77	6 844.57
ULSD	0.00	34.40	29.01	77.00	0.85	269 316.43	0.77	3.47	130.00	0.16	58 251.69	9 126.10
	10.00	34.40	29.01	77.00	0.85	296 248.07	0.77	3.47	130.00	0.16	64 076.86	10 038.71
	15.00	34.40	29.01	77.00	0.85	309 713.89	0.77	3.47	130.00	0.16	66 989.45	10 495.01
	20.00	34.40	29.01	77.00	0.85	323 179.72	0.77	3.47	130.00	0.16	69 902.03	10 951.32
	25.00	34.40	29.01	77.00	0.85	336 645.54	0.77	3.47	130.00	0.16	72 814.62	11 407.62
	-10.00	35.96	29.01	77.00	0.84	178 160.37	0.76	3.67	130.00	0.17	40 724.58	6 786.75
	-15.00	35.96	29.01	77.00	0.84	168 262.57	0.76	3.67	130.00	0.17	38 462.10	6 409.71
JET A1	-20.00	35.96	29.01	77.00	0.84	158 364.78	0.76	3.67	130.00	0.17	36 199.62	6 032.67
	-25.00	35.96	29.01	77.00	0.84	148 466.98	0.76	3.67	130.00	0.17	33 937.15	5 655.63

Table A-61: Input and Output Parameters of the VBE at varying feed flowrates for the different mixtures (Continued)

	0.00	35.96	29.01	77.00	0.84	197 955.97	0.76	3.67	130.00	0.17	45 249.53	7 540.83
	10.00	35.96	29.01	77.00	0.84	217 751.57	0.76	3.67	130.00	0.17	49 774.48	8 294.92
	15.00	35.96	29.01	77.00	0.84	227 649.37	0.76	3.67	130.00	0.17	52 036.96	8 671.96
	20.00	35.96	29.01	77.00	0.84	237 547.16	0.76	3.67	130.00	0.17	54 299.44	9 049.00
	25.00	35.96	29.01	77.00	0.84	247 444.96	0.76	3.67	130.00	0.17	56 561.91	9 426.04
	-10.00	34.19	29.01	77.00	0.85	80 665.21	0.77	3.45	130.00	0.16	17 314.67	2 712.63
	-15.00	34.19	29.01	77.00	0.85	76 183.81	0.77	3.45	130.00	0.16	16 352.75	2 561.93
	-20.00	34.19	29.01	77.00	0.85	71 702.41	0.77	3.45	130.00	0.16	15 390.82	2 411.23
	-25.00	34.19	29.01	77.00	0.85	67 221.01	0.77	3.45	130.00	0.16	14 428.90	2 260.53
MGO	0.00	34.19	29.01	77.00	0.85	89 628.01	0.77	3.45	130.00	0.16	19 238.53	3 014.04
	10.00	34.19	29.01	77.00	0.85	98 590.81	0.77	3.45	130.00	0.16	21 162.38	3 315.44
	15.00	34.19	29.01	77.00	0.85	103 072.21	0.77	3.45	130.00	0.16	22 124.31	3 466.14
	20.00	34.19	29.01	77.00	0.85	107 553.61	0.77	3.45	130.00	0.16	23 086.23	3 616.84
	25.00	34.19	29.01	77.00	0.85	112 035.01	0.77	3.45	130.00	0.16	24 048.16	3 767.55

Table A-64: Input and Output Parameters of the VBE at varying feed pressure for the different mixtures

Mixture	P_S (Psia)	Input parameters				Output parameters					
		API (ºAPI)	T_S (ºF)	SG_S	Q (bbl/d)	SG_C	R_S (scf/bbl)	MW_{TV}	X_{VOC} (lbvoc/lb)	E_{Tot} (ton/year)	E_{VOC} (ton/year)
Crude Oil	29.01	45.00	66.00	0.81	190.22	0.72	5.42	41.40	0.06	20.47	1.14
	58.02	45.00	66.00	0.81	190.22	0.76	13.08	41.40	0.06	49.36	2.74
	87.02	45.00	66.00	0.81	190.22	0.79	21.85	41.40	0.06	82.47	4.58
	116.03	45.00	66.00	0.81	190.22	0.81	31.43	41.40	0.06	118.64	6.59
	145.04	45.00	66.00	0.81	190.22	0.82	41.66	41.40	0.06	157.25	8.74
ULP 95	29.01	79.21	77.00	0.67	159 348.88	0.53	17.43	66.00	0.10	87 839.65	8 783.97
	58.02	79.21	77.00	0.67	159 348.88	0.60	45.17	66.00	0.10	227 656.03	22 765.60
	87.02	79.21	77.00	0.67	159 348.88	0.64	78.28	66.00	0.10	394 568.32	39 456.83
	116.03	79.21	77.00	0.67	159 348.88	0.67	115.33	66.00	0.10	581 309.02	58 130.90
	145.04	79.21	77.00	0.67	159 348.88	0.70	155.55	66.00	0.10	784 024.34	78 402.43
ULSD	29.01	34.40	77.00	0.85	269 316.43	0.77	3.47	130.00	0.16	58 252.96	9 126.30
	58.02	34.40	77.00	0.85	269 316.43	0.81	8.32	130.00	0.16	139 527.57	21 859.32
	87.02	34.40	77.00	0.85	269 316.43	0.84	13.84	130.00	0.16	232 306.66	36 394.71
	116.03	34.40	77.00	0.85	269 316.43	0.85	19.87	130.00	0.16	333 379.84	52 229.51
	145.04	34.40	77.00	0.85	269 316.43	0.87	26.29	130.00	0.16	441 070.92	69 101.11
JET A1	29.01	35.96	77.00	0.84	197 955.97	0.76	3.67	130.00	0.17	45 250.52	7 541.00

Table A-62: Input and Output Parameters of the VBE at varying feed pressure for the different mixtures (Continued)

	58.02	35.96	77.00	0.84	197 955.97	0.80	8.81	130.00	0.17	108 652.35	18 106.91
	87.02	35.96	77.00	0.84	197 955.97	0.83	14.69	130.00	0.17	181 142.26	30 187.36
	116.03	35.96	77.00	0.84	197 955.97	0.85	21.10	130.00	0.17	260 188.75	43 360.46
	145.04	35.96	77.00	0.84	197 955.97	0.86	27.93	130.00	0.17	344 469.15	57 405.78
	29.01	34.19	77.00	0.85	89 628.01	0.77	3.45	130.00	0.16	19 238.95	3 014.10
	58.02	34.19	77.00	0.85	89 628.01	0.81	8.25	130.00	0.16	46 065.47	7 216.92
MGO	87.02	34.19	77.00	0.85	89 628.01	0.84	13.73	130.00	0.16	76 682.66	12 013.62
	116.03	34.19	77.00	0.85	89 628.01	0.85	19.70	130.00	0.16	110 032.46	17 238.42
	145.04	34.19	77.00	0.85	89 628.01	0.87	26.07	130.00	0.16	145 562.47	22 804.79

Table A-65: Input and Output Parameters of the VBE at varying pressure for the different mixtures

Mixture	Ps (Psia)	Input parameters				Output parameters					
		API (oAPI)	Ts (F)	SGs	Q (bbl/d)	SGc	Rs (scf/bbl)	MWTV	Xvoc (lbvoc/lb)	Etot (ton/year)	Evoc (ton/year)
Crude Oil	56.70	45.00	70.00	0.81	190.22	0.76	12.66	41.40	0.06	47.78	2.65
	56.70	45.00	100.00	0.81	190.22	0.74	12.33	41.40	0.06	46.54	2.59
	56.70	45.00	150.00	0.81	190.22	0.71	11.78	41.40	0.06	44.48	2.47
	56.70	45.00	200.00	0.81	190.22	0.68	11.24	41.40	0.06	42.42	2.36
	56.70	45.00	250.00	0.81	190.22	0.64	10.69	41.40	0.06	40.35	2.24
	56.70	45.00	295.00	0.81	190.22	0.61	10.20	41.40	0.06	38.50	2.14
ULP 95	29.01	79.21	70.00	0.67	159 348.88	0.54	18.71	66.00	0.10	94 324.91	9 432.49
	29.01	79.21	100.00	0.67	159 348.88	0.48	13.84	66.00	0.10	69 756.42	6 975.64
	29.01	79.21	150.00	0.67	159 348.88	0.39	8.45	66.00	0.10	42 598.64	4 259.86
	29.01	79.21	200.00	0.67	159 348.88	0.30	5.07	66.00	0.10	25 558.10	2 555.81
	29.01	79.21	250.00	0.67	159 348.88	0.20	2.83	66.00	0.10	14 257.01	1 425.70
	29.01	79.21	295.00	0.67	159 348.88	0.12	1.40	66.00	0.10	7 077.35	707.73
ULSD	29.01	34.40	70.00	0.85	269 316.43	0.78	3.58	130.00	0.16	60 000.72	9 400.11
	29.01	34.40	100.00	0.85	269 316.43	0.75	3.16	130.00	0.16	53 011.37	8 305.11
	29.01	34.40	150.00	0.85	269 316.43	0.70	2.61	130.00	0.16	43 745.15	6 853.41
	29.01	34.40	200.00	0.85	269 316.43	0.65	2.18	130.00	0.16	36 561.17	5 727.92

Table A-63: Input and Output Parameters of the VBE at varying pressure for the different mixtures (Continued)

	29.01	34.40	250.00	0.85	269 316.43	0.59	1.84	130.00	0.16	30 800.84	4 825.47
	29.01	34.40	295.00	0.85	269 316.43	0.55	1.58	130.00	0.16	26 488.38	4 149.85
JET A1	29.01	35.96	70.00	0.84	197 955.97	0.77	3.78	130.00	0.17	46 672.51	7 777.97
	29.01	35.96	100.00	0.84	197 955.97	0.74	3.32	130.00	0.17	40 996.57	6 832.08
	29.01	35.96	150.00	0.84	197 955.97	0.68	2.72	130.00	0.17	33 517.61	5 585.71
	29.01	35.96	200.00	0.84	197 955.97	0.63	2.25	130.00	0.17	27 759.39	4 626.10
	29.01	35.96	250.00	0.84	197 955.97	0.58	1.88	130.00	0.17	23 170.25	3 861.32
	29.01	35.96	295.00	0.84	197 955.97	0.53	1.60	130.00	0.17	19 752.12	3 291.69
MGO	29.01	34.19	70.00	0.85	89 628.01	0.78	3.55	130.00	0.16	19 812.40	3 103.94
	29.01	34.19	100.00	0.85	89 628.01	0.75	3.14	130.00	0.16	17 518.55	2 744.57
	29.01	34.19	150.00	0.85	89 628.01	0.70	2.59	130.00	0.16	14 474.87	2 267.73
	29.01	34.19	200.00	0.85	89 628.01	0.65	2.17	130.00	0.16	12 112.89	1 897.69
	29.01	34.19	250.00	0.85	89 628.01	0.60	1.83	130.00	0.16	10 217.39	1 600.72
	29.01	34.19	295.00	0.85	89 628.01	0.55	1.58	130.00	0.16	8 797.33	1 378.25

Table A-66: Input and Output Parameters of the VBE at varying Temperature for the different mixtures

Mixture	Input parameters					Output parameters					
	Ps (Psia)	API (oAPI)	Ts (ºF)	SGs	Q (bbl/d)	SGc	Rs (scf/bbl)	MWTV	Xvoc (lbvoc/lb)	Etot (ton/year)	Evoc (ton/year)
Crude Oil	56.70	45.00	70.00	0.81	190.22	0.76	12.66	41.40	0.06	47.78	2.65
	56.70	45.00	100.00	0.81	190.22	0.74	12.33	41.40	0.06	46.54	2.59
	56.70	45.00	150.00	0.81	190.22	0.71	11.78	41.40	0.06	44.48	2.47
	56.70	45.00	200.00	0.81	190.22	0.68	11.24	41.40	0.06	42.42	2.36
	56.70	45.00	250.00	0.81	190.22	0.64	10.69	41.40	0.06	40.35	2.24
	56.70	45.00	295.00	0.81	190.22	0.61	10.20	41.40	0.06	38.50	2.14
ULP 95	29.01	79.21	70.00	0.67	159 348.88	0.54	18.71	66.00	0.10	94 324.91	94 324.91
	29.01	79.21	100.00	0.67	159 348.88	0.48	13.84	66.00	0.10	69 756.42	69 756.42
	29.01	79.21	150.00	0.67	159 348.88	0.39	8.45	66.00	0.10	42 598.64	42 598.64
	29.01	79.21	200.00	0.67	159 348.88	0.30	5.07	66.00	0.10	25 558.10	25 558.10
	29.01	79.21	250.00	0.67	159 348.88	0.20	2.83	66.00	0.10	14 257.01	14 257.01
	29.01	79.21	295.00	0.67	159 348.88	0.12	1.40	66.00	0.10	7 077.35	7 077.35
ULSD	29.01	34.40	70.00	0.85	269 316.43	0.78	3.58	130.00	0.16	60 000.72	9 400.11
	29.01	34.40	100.00	0.85	269 316.43	0.75	3.16	130.00	0.16	53 011.37	8 305.11
	29.01	34.40	150.00	0.85	269 316.43	0.70	2.61	130.00	0.16	43 745.15	6 853.41
	29.01	34.40	200.00	0.85	269 316.43	0.65	2.18	130.00	0.16	36 561.17	5 727.92

Table A-64: Input and Output Parameters of the VBE at varying Temperature for the different mixtures (Continued)

	29.01	34.40	250.00	0.85	269 316.43	0.59	1.84	130.00	0.16	30 800.84	4 825.47
	29.01	34.40	295.00	0.85	269 316.43	0.55	1.58	130.00	0.16	26 488.38	4 149.85
JET A1	29.01	35.96	70.00	0.84	197 955.97	0.77	3.78	130.00	0.17	46 672.51	7 777.97
	29.01	35.96	100.00	0.84	197 955.97	0.74	3.32	130.00	0.17	40 996.57	6 832.08
	29.01	35.96	150.00	0.84	197 955.97	0.68	2.72	130.00	0.17	33 517.61	5 585.71
	29.01	35.96	200.00	0.84	197 955.97	0.63	2.25	130.00	0.17	27 759.39	4 626.10
	29.01	35.96	250.00	0.84	197 955.97	0.58	1.88	130.00	0.17	23 170.25	3 861.32
	29.01	35.96	295.00	0.84	197 955.97	0.53	1.60	130.00	0.17	19 752.12	3 291.69
MGO	29.01	34.19	70.00	0.85	89 628.01	0.78	3.55	130.00	0.16	19 812.40	3 103.94
	29.01	34.19	100.00	0.85	89 628.01	0.75	3.14	130.00	0.16	17 518.55	2 744.57
	29.01	34.19	150.00	0.85	89 628.01	0.70	2.59	130.00	0.16	14 474.87	2 267.73
	29.01	34.19	200.00	0.85	89 628.01	0.65	2.17	130.00	0.16	12 112.89	1 897.69
	29.01	34.19	250.00	0.85	89 628.01	0.60	1.83	130.00	0.16	10 217.39	1 600.72
	29.01	34.19	295.00	0.85	89 628.01	0.55	1.58	130.00	0.16	8 797.33	1 378.25

A.2.3.2 VME

Table A-67: Input and Output Parameters of the VME at varying feed flowrates for the different mixtures

Mixture	Input parameters						Output parameters						
	Ps (Psia)	API (°API)	Ts (°F)	Q (bbl/d)	MWtv	Xvoc	z_1	z_2	z_3	z	Rs (Rs/bbl)	Etot (ton/year)	Evoc (ton/year)
Crude Oil	43.00	45.00	66.00	171.20	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	215.97	12.00
	43.00	45.00	66.00	161.69	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	203.98	11.33
	43.00	45.00	66.00	152.18	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	191.98	10.67
	43.00	45.00	66.00	142.67	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	179.98	10.00
	43.00	45.00	66.00	190.22	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	239.97	13.33
	43.00	45.00	66.00	209.25	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	263.97	14.66
	43.00	45.00	66.00	218.76	66.00	0.06	-0.16	-0.87	0.35	-0.68	28.61	275.97	15.33

Table A-65: Input and Output Parameters of the VME at varying feed flowrates for the different mixtures (Continued)

	43.00	45.00	66.00	228.27	66.00	0.06	-	0.16	-	0.87	0.35	-0.68	28.61	287.97	16.00
	43.00	45.00	66.00	237.78	66.00	0.06	-	0.16	-	0.87	0.35	-0.68	28.61	299.96	16.66
ULP 95	14.31	79.21	77.00	143 413.99	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	252 194.50	25 219.45
	14.31	79.21	77.00	135 446.55	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	238 183.70	23 818.37
	14.31	79.21	77.00	127 479.11	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	224 172.89	22 417.29
	14.31	79.21	77.00	119 511.66	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	210 162.09	21 016.21
	14.31	79.21	77.00	159 348.88	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	280 216.12	28 021.61
	14.31	79.21	77.00	175 283.77	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	308 237.73	30 823.77
	14.31	79.21	77.00	183 251.21	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	322 248.53	32 224.85
	14.31	79.21	77.00	191 218.66	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	336 259.34	33 625.93
	14.31	79.21	77.00	199 186.10	66.00	0.10	-	0.74	-	0.95	1.76	0.08	55.59	350 270.14	35 027.01
ULSD	14.31	34.40	77.00	242 384.79	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	108 650.25	17 021.87
	14.31	34.40	77.00	228 918.97	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	102 614.13	16 076.21
	14.31	34.40	77.00	215 453.14	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	96 578.00	15 130.55

Table A-*65*: Input and Output Parameters of the VME at varying feed flowrates for the different mixtures (Continued)

	14.31	34.40	77.00	201 987.32	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	90 541.88	14 184.89
	14.31	34.40	77.00	269 316.43	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	120 722.50	18 913.19
	14.31	34.40	77.00	296 248.07	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	132 794.75	20 804.51
	14.31	34.40	77.00	309 713.89	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	138 830.88	21 750.17
	14.31	34.40	77.00	323 179.72	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	144 867.00	22 695.83
	14.31	34.40	77.00	336 645.54	130.00	0.16	-	0.74	-	0.95	-0.10	-1.78	7.19	150 903.13	23 641.49
JET A1	14.31	35.96	77.00	178 160.37	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	88 779.39	14 795.08
	14.31	35.96	77.00	168 262.57	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	83 847.20	13 973.14
	14.31	35.96	77.00	158 364.78	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	78 915.01	13 151.19
	14.31	35.96	77.00	148 466.98	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	73 982.82	12 329.24
	14.31	35.96	77.00	197 955.97	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	98 643.76	16 438.98
	14.31	35.96	77.00	217 751.57	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	108 508.14	18 082.88

Table A-65: Input and Output Parameters of the VME at varying feed flowrates for the different mixtures (Continued)

	14.31	35.96	77.00	227 649.37	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	113 440.33	18 904.83
	14.31	35.96	77.00	237 547.16	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	118 372.52	19 726.78
	14.31	35.96	77.00	247 444.96	130.00	0.17	-	0.74	-	0.95	-0.03	-1.72	8.00	123 304.70	20 548.73
MGO	14.31	34.19	77.00	80 665.21	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	35 622.46	5 580.85
	14.31	34.19	77.00	76 183.81	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	33 643.43	5 270.80
	14.31	34.19	77.00	71 702.41	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	31 664.41	4 960.76
	14.31	34.19	77.00	67 221.01	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	29 685.38	4 650.71
	14.31	34.19	77.00	89 628.01	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	39 580.51	6 200.95
	14.31	34.19	77.00	98 590.81	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	43 538.56	6 821.04
	14.31	34.19	77.00	103 072.21	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	45 517.58	7 131.09
	14.31	34.19	77.00	107 553.61	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	47 496.61	7 441.14
	14.31	34.19	77.00	112 035.01	130.00	0.16	-	0.74	-	0.95	-0.11	-1.79	7.09	49 475.64	7 751.18

Table A-68: Input and Output Parameters of the VME at varying pressures for the different mixtures

Mixture	Input parameters						Output parameters						
	Ps (Psig)	API (oAPI)	Ts (ºF)	Q (bbl/d)	MWtv	Xvoc	z_1	z_2	z_3	z	Rs (Rs/bbl)	Etot (ton/year)	Evoc (ton/year)
Crude Oil	29.01	45.00	66.00	190.22	66.00	0.06	-0.74	-0.87	0.35	-1.26	15.23	127.76	7.10
	58.02	45.00	66.00	190.22	66.00	0.06	0.30	-0.87	0.35	-0.22	43.56	365.38	20.30
	87.02	45.00	66.00	190.22	66.00	0.06	0.84	-0.87	0.35	0.32	68.22	572.19	31.79
	116.03	45.00	66.00	190.22	66.00	0.06	1.19	-0.87	0.35	0.67	92.29	774.05	43.00
	145.04	45.00	66.00	190.22	66.00	0.06	1.44	-0.87	0.35	0.93	116.95	980.87	54.49
ULP 95	29.01	79.21	77.00	159 348.88	66.00	0.10	-0.74	-0.95	1.76	0.08	55.60	280 222.57	28 022.26
	58.02	79.21	77.00	159 348.88	66.00	0.10	0.30	-0.95	1.76	1.12	142.38	717 628.02	71 762.80
	87.02	79.21	77.00	159 348.88	66.00	0.10	0.84	-0.95	1.76	1.66	271.88	1 370 382.29	137 038.23

Table A-66: Input and Output Parameters of the VME at varying pressures for the different mixtures (Continued)

	116.03	79.21	77.00	159 348.88	66.00	0.10	1.19	-0.95	1.76	2.01	459.28	2 314 915.15	231 491.52
	145.04	79.21	77.00	159 348.88	66.00	0.10	1.44	-0.95	1.76	2.26	715.40	3 605 861.97	360 586.20
ULSD	29.01	34.40	77.00	269 316.43	130.00	0.16	-0.74	-0.95	-0.10	-1.78	7.20	120 727.98	18 914.05
	58.02	34.40	77.00	269 316.43	130.00	0.16	0.30	-0.95	-0.10	-0.74	27.02	453 394.16	71 031.75
	87.02	34.40	77.00	269 316.43	130.00	0.16	0.84	-0.95	-0.10	-0.20	44.05	739 099.36	115 792.23
	116.03	34.40	77.00	269 316.43	130.00	0.16	1.19	-0.95	-0.10	0.15	58.96	989 310.99	154 992.05
	145.04	34.40	77.00	269 316.43	130.00	0.16	1.44	-0.95	-0.10	0.40	72.82	1 221 889.11	191 429.29
JET A1	29.01	35.96	77.00	197 955.97	130.00	0.17	-0.74	-0.95	-0.03	-1.72	8.00	98 648.09	16 439.70
	58.02	35.96	77.00	197 955.97	130.00	0.17	0.30	-0.95	-0.03	-0.67	28.82	355 459.08	59 237.26

Table A-66: Input and Output Parameters of the VME at varying pressures for the different mixtures (Continued)

	87.02	35.96	77.00	197 955.97	130.00	0.17	0.84	-0.95	-0.03	-0.14	46.57	574 421.09	95 727.28
	116.03	35.96	77.00	197 955.97	130.00	0.17	1.19	-0.95	-0.03	-0.21	62.28	768 074.07	127 999.54
	145.04	35.96	77.00	197 955.97	130.00	0.17	1.44	-0.95	-0.03	-0.47	77.03	950 067.82	158 328.80
MGO	29.01	34.19	77.00	89 628.01	130.00	0.16	-0.74	-0.95	-0.11	-1.79	7.09	39 582.31	6 201.23
	58.02	34.19	77.00	89 628.01	130.00	0.16	0.30	-0.95	-0.11	-0.75	26.78	149 529.00	23 426.21
	87.02	34.19	77.00	89 628.01	130.00	0.16	0.84	-0.95	-0.11	-0.21	43.71	244 068.87	38 237.46
	116.03	34.19	77.00	89 628.01	130.00	0.16	1.19	-0.95	-0.11	-0.14	58.52	326 760.19	51 192.43
	145.04	34.19	77.00	89 628.01	130.00	0.16	1.44	-0.95	-0.11	-0.39	72.26	403 510.44	63 216.64

Table A-69: Input and Output Parameters of the VME at varying temperatures for the different mixtures

Mixture	Input parameters						Output parameters						
	Ps (Psig)	API (oAPI)	Ts (°F)	Q (bbl/d)	MWtv	Xvoc	z_1	z_2	z_3	z	Rs (Rs/bbl)	Etot (ton/year)	Evoc (ton/year)
Crude Oil	43.00	45.00	70.00	190.22	66.00	0.06	-0.16	-0.90	0.35	-0.71	27.80	233.20	12.96
	43.00	45.00	100.00	190.22	66.00	0.06	-0.16	-1.08	0.35	-0.89	23.21	194.65	10.81
	43.00	45.00	150.00	190.22	66.00	0.06	-0.16	-1.28	0.35	-1.09	18.57	155.76	8.65
	43.00	45.00	200.00	190.22	66.00	0.06	-0.16	-1.43	0.35	-1.24	15.65	131.22	7.29
	43.00	45.00	250.00	190.22	66.00	0.06	-0.16	-1.54	0.35	-1.35	13.58	113.91	6.33
	43.00	45.00	295.00	190.22	66.00	0.06	-0.16	-1.62	0.35	-1.43	12.16	102.03	5.67
ULP 95	14.31	79.21	70.00	159 348.88	66.00	0.10	-0.74	-0.90	1.76	-0.12	57.83	291 493.71	29 149.37
	14.31	79.21	100.00	159 348.88	66.00	0.10	-0.74	-1.08	1.76	-0.05	49.88	251 423.92	25 142.39
	14.31	79.21	150.00	159 348.88	66.00	0.10	-0.74	-1.28	1.76	-0.26	42.04	211 895.00	21 189.50
	14.31	79.21	200.00	159 348.88	66.00	0.10	-0.74	-1.43	1.76	-0.40	37.09	186 954.94	18 695.49
	14.31	79.21	250.00	159 348.88	66.00	0.10	-0.74	-1.54	1.76	-0.51	33.55	169 110.14	16 911.01
	14.31	79.21	295.00	159 348.88	66.00	0.10	-0.74	-1.62	1.76	-0.60	31.08	156 637.56	15 663.76
ULSD	14.31	34.40	70.00	269 316.43	130.00	0.16	-0.74	-0.90	-0.10	-1.74	7.77	130 361.23	20 423.26

Table A-67: Input and Output Parameters of the VME at varying temperatures for the different mixtures (Continued)

	14.31	34.40	100.00	269 316.43	130.00	0.16	-0.74	-1.08	-0.10	-1.91	5.77	96 830.68	15 170.14
	14.31	34.40	150.00	269 316.43	130.00	0.16	-0.74	-1.28	-0.10	-2.12	3.97	66 665.06	10 444.19
	14.31	34.40	200.00	269 316.43	130.00	0.16	-0.74	-1.43	-0.10	-2.26	2.97	49 904.71	7 818.40
	14.31	34.40	250.00	269 316.43	130.00	0.16	-0.74	-1.54	-0.10	-2.37	2.34	39 267.71	6 151.94
	14.31	34.40	295.00	269 316.43	130.00	0.16	-0.74	-1.62	-0.10	-2.45	1.94	32 578.86	5 104.02
JET A1	14.31	35.96	70.00	197 955.97	130.00	0.17	-0.74	-0.90	-0.03	-1.67	8.61	106 243.41	17 705.46
	14.31	35.96	100.00	197 955.97	130.00	0.17	-0.74	-1.08	-0.03	-1.85	6.46	79 714.10	13 284.35
	14.31	35.96	150.00	197 955.97	130.00	0.17	-0.74	-1.28	-0.03	-2.05	4.51	55 575.72	9 261.69
	14.31	35.96	200.00	197 955.97	130.00	0.17	-0.74	-1.43	-0.03	-2.19	3.41	42 007.53	7 000.56
	14.31	35.96	250.00	197 955.97	130.00	0.17	-0.74	-1.54	-0.03	-2.31	2.70	33 316.70	5 552.23
	14.31	35.96	295.00	197 955.97	130.00	0.17	-0.74	-1.62	-0.03	-2.39	2.25	27 811.10	4 634.72
MGO	34.19	14.31	70.00	89 628.01	130.00	0.16	-0.74	-0.90	-0.11	-1.74	7.66	42 756.37	6 698.50
	34.19	14.31	100.00	89 628.01	130.00	0.16	-0.74	-1.08	-0.11	-1.92	5.68	31 713.84	4 968.50
	34.19	14.31	150.00	89 628.01	130.00	0.16	-0.74	-1.28	-0.11	-2.13	3.90	21 795.38	3 414.61

Table A-67: Input and Output Parameters of the VME at varying temperatures for the different mixtures (Continued)

34.19	14.31	200.00	89 628.01	130.00	0.16	-0.74	-1.43	-0.11	-2.27	2.92	16 293.60	2 552.66
34.19	14.31	250.00	89 628.01	130.00	0.16	-0.74	-1.54	-0.11	-2.38	2.29	12 806.41	2 006.34
34.19	14.31	295.00	89 628.01	130.00	0.16	-0.74	-1.62	-0.11	-2.46	1.90	10 615.84	1 663.15

A.2.4 Working and Breathing Losses

This section summarises the raw data and results obtained from performing manual calculations to determine the secondary losses from the various storage tanks. VOC emissions were estimated at varying conditions and calculations were based on the AP-42 method.

A.2.4.1 Floating Roof Tanks

Table A-70: Input and Output Parameters of the Working and Breathing Losses of different mixtures from a FRT

Area	Parameter	Units	Crude Oil	ULP 95	ULSD	JET A1	MGO
Tank Vapour Space Volume	Vv	Ft^3	1 425.03	219 300.39	323 634.27	176 110.20	323 634.27
	D	ft	12.00	108.27	127.95	98.43	127.95
	Hvo	ft	12.60	23.82	25.17	23.15	25.17
	Hvo	ft	12.60	23.82	25.17	23.15	25.17
	Hs	ft	25.00	65.62	65.62	65.62	65.62
	HL	ft	12.50	49.21	49.21	49.21	49.21
	HRO	ft	0.10	7.42	8.76	6.74	8.76

Table A-68: Input and Output Parameters of the Working and Breathing Losses of different mixtures from a FRT (Continued)

	HRO	ft	0.10	14.51	17.15	13.19	17.15
	SR	ft/ft	0.05	108.27	127.95	98.43	127.95
	RS	ft	6.00	54.13	63.98	49.21	63.98
Vapour Density	Wv	lb/ft^3	0.02	0.09	(0.00)	0.02	0.00
	Mv	lb/lb-mole	50.00	62.00	130.00	80.00	190.00
	PVA	psia	2.50	8.52	(0.08)	1.64	0.00
	R	$(psia.ft^3)/(lb\text{-}mole.R)$	10.73	10.73	10.73	10.73	10.73
	TLA	R	513.95	531.37	309.20	531.37	533.21
	TLA	R	513.95	531.37	309.20	531.37	533.21
	TAA	R	505.30	529.53	307.36	529.53	529.53
	TB	R	508.38	529.55	307.38	529.55	530.33
	alpha	-	0.68	0.17	0.17	0.17	0.30
	I	$Btu/ft^2.d$	1 290.00	1 365.00	1 365.00	1 365.00	1 365.00
	TAA	R	505.30	529.53	307.36	529.53	529.53
	TAX	F	56.70	77.36	77.36	77.36	77.36
	TAN	F	33.90	61.70	61.70	61.70	61.70
	TAX	R	516.70	537.36	537.36	537.36	537.36
	TAN	R	493.90	521.70	521.70	521.70	521.70

Table A-68: Input and Output Parameters of the Working and Breathing Losses of different mixtures from a FRT (Continued)

	PVA @ T	psia	2.50	8.52	(0.08)	1.64	0.00
	T	F	53.95	71.37	(150.80)	71.37	73.21
	T1	F	50.00	70.00	70.00	70.00	70.00
	T2	F	60.00	80.00	80.00	80.00	80.00
	P1	psi	2.30	8.30	0.01	1.60	0.00
	P2	psi	2.80	9.90	0.02	1.90	0.00
Vapour Space Expansion Factor	KE		0.28	1.40	0.05	0.15	0.04
	Delta TV	R	40.98	17.77	17.77	17.77	22.74
	TLA	R	513.95	531.37	309.20	531.37	533.21
	Delta PV	psia	2.50	8.52	(0.08)	1.64	0.00
	Delta PB	psia	0.06	0.06	0.06	0.06	0.06
	PA	psia	14.70	14.70	14.70	14.70	14.70
	PVA	psia	2.50	8.52	(0.08)	1.64	0.00
	Delta TV	R	40.98	17.77	17.77	17.77	22.74
	Delta TA	R	22.80	15.66	15.66	15.66	15.66
	TAX	R	516.70	537.36	537.36	537.36	537.36
	TAN	R	493.90	521.70	521.70	521.70	521.70
	alpha	-	0.68	0.17	0.17	0.17	0.30
	I	$Btu/ft^2.d$	1 290.00	1 365.00	1 365.00	1 365.00	1 365.00

Table A-68: Input and Output Parameters of the Working and Breathing Losses of different mixtures from a FRT (Continued)

	Delta PB	psig	0.06	0.06	0.06	0.06	0.06
	PBP	psig	0.03	0.03	0.03	0.03	0.03
	PBV	psig	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)
Vented Vapour Space Saturation Factor	Ks		0.37	0.09	1.12	0.33	1.00
	PVA	psia	2.50	8.52	(0.08)	1.64	0.00
	Hvo	ft	12.60	23.82	25.17	23.15	25.17
Standing Losses	Total standing losses	lb/yr	1 233.89	884 507.74	(19 225.71)	75 903.27	10.54
	Total standing losses	ton/yr	0.56	401.21	(8.72)	34.43	0.00
Working Losses	Total working losses	lb/yr	11 254.49	2 392 194.16	(1 259 973.72)	1 189 213.95	146.03
	Total working losses	ton/yr	5.10	1 085.08	(571.51)	539.42	0.07
	Mv	lb/lb-mole	50.00	62.00	130.00	80.00	190.00
	PVA	psia	2.50	8.52	(0.08)	1.64	0.00
	Q	bbl/yr	257 478.81	4 528 663.75	125 353412.72	9 057 327.51	11 036 521.30
	KN	-	0.47	1.00	1.00	1.00	1.00

Table A-68: Input and Output Parameters of the Working and Breathing Losses of different mixtures from a FRT (Continued)

KP (for crude oil)	-	0.75	1.00	1.00	1.00	1.00
Q	bbl/yr	257 478.81	4 528 663.75	125 353 412.72	9 057 327.51	11 036 521.30
Q	bbl/day	185.50	4 528 663.75	125 353 412.72	9 057 327.51	11 036 521.30
N	bbl/yr.ft^3	100.00	6.00	24.00	9.00	7.00
Q	bbl/yr	67 707.50	4 528 663.75	125 353 412.72	9 057 327.51	11 036 521.30
VLX	Ft^3	5 654.87	1 812 275.10	2 531 194.15	1 497 748.02	2 531 194.15
	bbl	14 454.86				
VLX	Ft^3	5 654.87	1 812 275.10	2 531 194.15	1 497 748.02	2 531 194.15
D	ft	12.00	108.27	127.95	98.43	127.95
HLX	ft	12.50	49.21	49.21	49.21	49.21

Table A-71: Input and Output Parameters of the Working and Breathing Losses of different mixtures from an IFRT

Area	Parameter	Units	Crude Oil	ULP 95	ULSD	JET A1	MGO
Withdrawl Losses	LWD	lb/yr	933.78	352.75	10,306.85	883.84	1,024.12
	LWD	ton/yr	0.42	0.16	4.68	0.40	0.46
	Q	bbl/yr	257,478.81	4,528,663.75	125,353,412.72	9,057,327.51	11,036,521.30
	C	$bbl/10^3.ft^3$	0.01	0.00	0.00	0.00	0.00
	WL		7.10	5.60	7.00	6.40	7.90
	D	ft	12.00	108.27	127.95	98.43	127.95
	NC		1.00	7.00	8.00	6.00	8.00
	FC		1.00	1.00	1.00	1.00	1.00
Rim Seal Losses	LR	lb/yr	161.90	8,304.51	(126.53)	1,351.28	0.17
	LR	ton/yr	0.07	3.77	(0.06)	0.61	0.00
	KRA	lb-mole/ft-yr	5.80	5.80	5.80	5.80	5.80
	P*	-	0.05	0.21	(0.00)	0.03	0.00
	P* Numerator	-	0.17	0.58	(0.01)	0.11	0.00
	P* Denominator	-	3.65	2.72	4.01	3.77	4.00
	KC (for volatile organic liquids)	-	1.00	1.00	1.00	1.00	1.00
	Mv	lb/lb-mole	50.00	62.00	130.00	80.00	190.00
	LR	lb/yr	430.77	9,200.18	(139.71)	1,453.66	0.18

Table A-69: Input and Output Parameters of the Working and Breathing Losses of different mixtures from an IFRT (Continued)

	LR	ton/yr	0.20	4.17	(0.06)	0.66	0.00
	FF	lb-mole/yr	185.19	695.68	819.46	614.12	819.46
	P*	-	0.05	0.21	(0.00)	0.03	0.00
	MV	lb/lb-mole	50.00	62.00	130.00	80.00	190.00
	KC	-	1.00	1.00	1.00	1.00	1.00
	FF		185.19	695.68	819.46	614.12	819.46
Deck Fitting Losses	Access Hatch (Bolted cover, gasketed)		1.60	1.60	1.60	1.60	1.60
	NF	-	1.00	1.00	1.00	1.00	1.00
	Kfa	lb-mole/yr	1.60	1.60	1.60	1.60	1.60
	Fixed Roof Support column well		47.00	329.00	376.00	282.00	376.00
	NF	-	1.00	7.00	8.00	6.00	8.00
	Kfa	lb-mole/yr	47.00	47.00	47.00	47.00	47.00
	Gauge Float Well (Bolted cover, gasketed)		2.80	2.80	2.80	2.80	2.80
	NF	-	1.00	1.00	1.00	1.00	1.00
	Kfa	lb-mole/yr	2.80	2.80	2.80	2.80	2.80

Table A-69: Input and Output Parameters of the Working and Breathing Losses of different mixtures from an IFRT (Continued)

	Vacuum Breaker		6.20	6.20	6.20	6.20	6.20
	NF	-	1.00	1.00	1.00	1.00	1.00
	Kfa	lb-mole/yr	6.20	6.20	6.20	6.20	6.20
	Deck Leg		50.88	279.37	356.15	244.81	356.15
	NF	-	6.44	35.36	45.08	30.99	45.08
	Kfa	lb-mole/yr	7.90	7.90	7.90	7.90	7.90
	Ladder Well		76.00	76.00	76.00	76.00	76.00
	NF	-	1.00	1.00	1.00	1.00	1.00
	Kfa	lb-mole/yr	76.00	76.00	76.00	76.00	76.00
	Rim Vent		0.71	0.71	0.71	0.71	0.71
	NF	-	1.00	1.00	1.00	1.00	1.00
	Kfa	lb-mole/yr	0.71	0.71	0.71	0.71	0.71
Deck Seam Losses	LD	lb/yr	-	-	-	-	-
	LD	ton/yr	-	-	-	-	-
	KD (for welded decks)		-	-	-	-	-
Total Losses	LT	lb/yr	1 526.45	17 857.44	10 040.61	3 688.78	1 024.47
	LT	ton/yr	0.69	8.10	4.55	1.67	0.46

Table A-72: Input and Output Parameters of the variations in paint colour for the Working and Breathing Losses of different mixtures

Paint colour	Paint shade/type	Paint factors	condition	Crude Oil		ULP 95		ULSD		JET A1		MGO	
				FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)
White	N/A	0.17	Good	3.68	0.34	1 486.29	8.10	85.79	4.69	573.85	1.67	0.06	0.46
Aluminum	Specular	0.36	Good	3.93	0.35	1 595.13	8.74	93.98	4.69	605.30	1.74	0.07	0.46
Gray	Light	0.54	Good	4.17	0.37	1 705.47	9.38	101.76	4.70	635.14	1.80	0.08	0.46
Aluminum	Diffuse	0.60	Good	4.25	0.37	1 744.10	9.61	104.36	4.70	645.09	1.82	0.09	0.46
Gray	Medium	0.68	Good	4.36	0.38	1 797.27	9.91	107.83	4.70	658.37	1.85	0.09	0.46
Red	Primer	0.89	Good	4.64	0.40	1 947.37	10.77	116.96	4.70	693.23	1.93	0.10	0.46

Table A-73: Input and Output Parameters of the variations in Capacity for the Working and Breathing Losses of different mixtures

Capacity (%)	Crude Oil	ULP 95	ULSD	JET A1	MGO
0	4.49	1,510.68	86.57	583.88	0.08
10	4.47	1,509.45	86.47	583.28	0.08
20	4.45	1,507.96	86.37	582.57	0.08
30	4.42	1,506.11	86.27	581.72	0.08
40	4.40	1,503.77	86.16	580.66	0.08
50	4.36	1,500.70	86.06	579.34	0.07
60	4.31	1,496.52	85.95	577.63	0.07
70	4.25	1,490.46	85.85	575.33	0.07
80	4.16	1,480.91	85.74	572.06	0.07
90	4.03	1,463.61	85.63	567.06	0.07
100	3.81	1,422.75	85.52	558.47	0.07

Table A-74: Input and Output Parameters of the variations in production rate for the Working and Breathing Losses of different mixtures

Production Rate (bbd)	Crude Oil		ULP 95		ULSD		JET A1		MGO	
	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)
0	0.56	0.27	401.21	7.94	0.42	0.02	34.43	1.27	0.00	0.00
100	2.61	0.33	409.95	7.94	0.44	0.02	36.60	1.27	0.00	0.00
200	4.66	0.39	418.70	7.94	0.47	0.02	38.78	1.28	0.01	0.00
300	6.70	0.45	427.44	7.94	0.49	0.02	40.95	1.28	0.01	0.00
400	8.75	0.51	436.19	7.95	0.52	0.02	43.12	1.28	0.01	0.01
500	10.80	0.57	444.93	7.95	0.54	0.02	45.30	1.28	0.01	0.01
600	12.85	0.63	453.68	7.95	0.57	0.03	47.47	1.28	0.01	0.01
700	14.89	0.69	462.42	7.95	0.59	0.03	49.65	1.28	0.01	0.01
800	16.94	0.75	471.17	7.95	0.62	0.03	51.82	1.29	0.01	0.01
900	18.99	0.81	479.92	7.95	0.64	0.03	53.99	1.29	0.01	0.01
1000	21.04	0.87	488.66	7.95	0.67	0.03	56.17	1.29	0.01	0.02
5000	102.95	3.27	838.48	8.00	1.66	0.09	143.12	1.35	0.02	0.08
10000	205.34	6.27	1 275.76	8.07	2.90	0.15	251.81	1.43	0.03	0.15
15000	307.72	9.28	1 713.03	8.13	4.15	0.22	360.50	1.51	0.04	0.23
20000	410.11	12.28	2 150.31	8.20	5.39	0.29	469.19	1.60	0.05	0.31
25000	512.50	15.28	2 587.58	8.26	6.63	0.36	577.88	1.68	0.06	0.38
30000	614.89	18.28	3 024.86	8.33	7.88	0.43	686.57	1.76	0.07	0.46

Table A-75: Input and Output Parameters of the variations in turnovers for the Working and Breathing Losses of different mixtures

Turnovers (1/yr)	Crude Oil		ULP 95		ULSD		JET A1		MGO	
	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)	FRT (ton/yr)	IFRT (ton/yr)
0	0.56	0.27	401.21	7.94	0.42	0.02	34.43	1.27	0.00	0.00
10	1.65	0.31	2 209.67	8.21	35.99	1.97	633.78	1.72	0.10	0.66
20	2.75	0.35	4 018.14	8.47	71.56	3.91	1 233.14	2.16	0.19	1.33
30	3.84	0.40	5 826.61	8.74	107.13	5.86	1 832.49	2.61	0.29	1.99
40	4.57	0.44	7 032.26	9.01	130.85	7.81	2 232.06	3.05	0.35	2.65
50	4.75	0.48	7 333.67	9.27	136.78	9.76	2 331.95	3.50	0.37	3.32
60	4.94	0.52	7 635.08	9.54	142.71	11.71	2 431.84	3.94	0.38	3.98
70	5.12	0.57	7 936.49	9.81	148.64	13.65	2 531.74	4.39	0.40	4.65
80	5.30	0.61	8 237.90	10.07	154.56	15.60	2 631.63	4.84	0.41	5.31
90	5.48	0.65	8 539.31	10.34	160.49	17.55	2 731.52	5.28	0.43	5.97
100	5.66	0.69	8 840.73	10.61	166.42	19.50	2 831.41	5.73	0.45	6.64

A.3 Controls

Nitrogen blanketing was utilised as a control method to determine its effect on reducing VOC emissions from the various petroleum storage tank mixtures. This section presents the data utilised in the nitrogen blanketing calculation procedure.

A.3.1 Nitrogen Blanketing

Table A-76: Inbreathing parameters for Nitrogen Blanketing requirement of different mixtures

Inbreathing Parameter	Units	Crude Oil	ULP 95	ULSD	JET A1	MGO
Latitude	Degrees	30.99	30.99	30.99	30.99	30.99
Vapour Pressure	psia	6.80	6.80	0.01	0.01	0.01
Ave. storage temp	F	74.32	74.32	74.32	74.32	74.32
Tank Volume	barrels	143 457.77	136 279.23	220 562.70	113 216.59	161 438.48
Insulation	None	1.00	1.00	1.00	1.00	1.00
Max pump in/out rate	gallons/min	5.48	0.03	0.82	0.06	0.07
C-factor		6.50	6.50	6.50	6.50	6.50
Max pump out rate	gpm	43.98	0.24	6.55	0.47	0.58
Temperature drop		81 502.50	78 625.76	110 137.83	69 055.95	88 525.63
Tank blanketing regulator flow	scfh	81 546.48	78 626.00	110 144.38	69 056.43	88 526.20
	Nm3/h	130 882.10	126 194.73	176 781.73	110 835.57	142 084.55
hexane vp	psia	2.40	2.40	2.40	2.40	2.40

Table A-77: Outbreathing parameters for Nitrogen Blanketing requirement of different mixtures

Outbreathing Parameter	Units	Crude Oil	ULP 95	ULSD	JET A1	MGO
Max pump in rate		87.95	0.47	13.10	0.95	1.15
Temperature rise		99 954.45	95 441.49	147 207.30	80 773.62	111 162.12
Y-factor		0.32	0.32	0.32	0.32	0.32
Vapour recovery regulator flow	scfh	100 042.41	95 441.96	147 220.40	80 774.57	111 163.28
	Nm3/h	160 568.07	153 184.35	236 267.72	129 643.18	178 417.06

Table A-78: Total Nitrogen Required input and output parameters of different mixtures

Parameter	Units	Crude Oil	ULP 95	ULSD	JET A1	MGO
NT	Ft^3/month	31 669.57	342.79	4 969.86	479.18	669.63
	M^3/year	13 420 930.24	145 266.97	2 106 128.97	162.83	283 776.03
NW	Ft^3/month	31 668.45	170.35	4 715.39	340.71	415.16
VT	gal/month	236 880.00	1 274.25	35 271.13	2 548.49	3 105.38
NTB	F^3/month	1.12	172.43	254.47	138.47	254.47
VHS	gal	10 659.94	1 640 480.84	2 420 952.42	1 317,395.81	2 420 952.42
Thigh	F	86.00	86.00	86.00	86.00	86.00
Tlow	F	57.20	57.20	57.20	57.20	57.20
F		66.00	66.00	66.00	66.00	66.00

Table A-79: Total Peak Nitrogen Required input and output parameters of different mixtures

Parameter	Units	Crude Oil	ULP 95	ULSD	JET A1	MGO
Vol	Gallons	4 518 919.73	4 292 795.90	6 947 725.00	3 566 322.70	5 085 312.00
NM	scfh	63 081.31	63 081.31	84 175.36	53 919.75	75 378.18
P	gpm	5.48	5.48	0.82	0.06	0.07
G	scfh	63 037.33	63 037.33	84 168.81	53 919.28	75 377.60

Table A-80: Normal Venting requirement input parameters of different mixtures for Aspen Plus ® Simulation

Parameter	Crude Oil	ULP 95	ULSD	JET A1	MGO
Set Pressure [mbarG]	206.85	206.68	206.85	206.80	206.85
Vacuum Set Pressure [mbarG]	(206.85)	(206.85)	(206.85)	(206.84)	(206.80)
Maximum Liquid Inflow [m³/h]	20.20	0.11	3.01	0.22	0.26
Maximum Liquid Outflow [m³/h]	10.10	0.05	1.50	0.11	0.13
Tank Vapor Molecular Weight	28.80	28.80	28.00	28.80	28.80
Volatile Liquid	TRUE	TRUE	TRUE	TRUE	TRUE

Table A-81: Normal Venting results of different mixtures for Aspen Plus ® Simulation

Parameter	Crude Oil		ULP 95		ULSD		JET A1		MGO	
	Inbreathing	Outbreathing	Inbreathing	Outbreathing	Inbreathing	Outbreathing	Inbreathing	Outbreathing	Inbreathing	Outbreathing
Liquid Movement [Nm³/h]	10.10	40.39	0.05	0.22	1.50	6.02	0.11	0.44	0.13	0.52
Thermal [Nm³/h]	139.70	16.53	5,972.00	2,065.00	7,545.00	2,790.00	5,226.00	1,740.00	7,545.00	2,790.00
Total [Nm³/h]	149.80	56.92	5,972.00	2,066.00	7,547.00	2,796.00	5,226.00	1,740.00	7,546.00	2,790.00
Preliminary Device Area [cm²]	6.26	2.07	249.30	74.96	310.70	100.00	218.20	63.13	315.00	101.20
Preliminary Calculated Size [cm]	2.82	1.62	17.82	9.77	19.89	11.28	16.67	8.97	20.03	11.35

Table A-82: Emergency Venting input parameters of different mixtures for Aspen Plus ® Simulation

Parameter	Crude Oil	ULP 95	ULSD	JET A1	MGO
Set Pressure [mbarG]	206.85	206.85	206.85	206.84	206.85
Bottom Tan Above Grade [m]	0.91	0.91	0.91	0.91	0.91
Flame Height from Grade [m]	9.14	9.14	9.14	9.14	9.14
Calculate Environment Factor?	FALSE	FALSE	FALSE	FALSE	FALSE
Environment Factor F	1.00	1.00	1.00	1.00	1.00
Relieving Gas Temperature [ºC]	23.51	23.51	23.51	23.51	23.51
Relieving Gas Molecular Weight	66.00	66.00	130.00	130.00	130.00
Fluid Latent Heat [kJ/kg]	116.30	116.30	116.30	116.30	116.30

Table A-83: Emergency Venting results of different mixtures for Aspen Plus ® Simulation

Parameter	Crude Oil	ULP 95	ULSD	JET A1	MGO
Calculated Exposed Area [m²]	87.56	853.60	1 009.00	776.00	1 009.00
Calculated Heat Input [Kcal/h]	2 423 000.00	9 409 000.00	10 790 000.00	8 702 000.00	10 790 000.00
Calculated Relieving Flow [Nm³/h]	46 580.00	180 900.00	147 800.00	119 200.00	147 800.00
Preliminary Device Area [cm²]	2 530.00	9 825.00	11 270.00	9 086.00	11 270.00
Preliminary Calculated Size [cm]	56.76	111.80	119.80	107.60	119.80

APPENDIX B: REGULATIONS AND LEGISLATURE

B.1 Regulatory Framework

There are various regulatory requirements implemented locally and nationally to ensure proper environmental management and responsibility (Shell and BP Refineries , 2018). The key Acts and Regulations pertaining to VOC emissions from petroleum storage tanks and its effects on the environment are outlined below and should be considered during an Environmental Impact Assessment (EIA).

B.1.1 The Constitution of the Republic of South Africa

South African legislation has seen significant changes since 1994, placing emphasis on the sustainable development and responsible environmental management practices (Shell and BP Refineries , 2018). The Constitution of the Republic of South Africa, in accordance to chapter 2 and section 24 of the Constitution (Act No. 108 of 1996), states that: "Everyone has the right to an environment that is not harmful to their health or well-being and to have the environment protected, for benefit of present and future generations, through reasonable legislation and other measures that prevent pollution and ecological degradation, promote conservation and secure ecologically sustainable development and use of natural resources while prompting justifiable economic and social development" (Caddick, 2019).

The constitution is not the only regulation which promotes sustainable development and cannot serve as a means to combat adverse environmental effects alone. Therefore, other regulatory policies exist and have been implemented to ensure that focus is given to specific industries and sectors of the environment for complete environmental management (Shell and BP Refineries , 2018).

B.1.2 The National Environmental Management Act (NEMA)

The National Environmental Management Act (NEMA) (Amended Act No. 107 of 1998) is a regulative framework used to describe the principles required to act upon by authoritative figures to ensure protection of the environment and sustainable development in South Africa (Caddick, 2019).

According to section 4b of the NEMA, action must be carried out to satisfy the principles outlined by the NEMA to ensure all people within an environment and all aspects of an

environment are taken care off. This means that industrial practices or any practice related to production, service or projects, which may cause adverse effects to the environment in terms of waste or pollution, must be minimised, re-used or recycled. Thus, ensuring that actions are taken to promote development which is sustainable (Shell and BP Refineries , 2018).

According to section 28 of the NEMA, any action taken to purposefully cause significant harm to the environment is regarded as a criminal offense with serious consequences. This act stipulates that preventative and control measures should be implemented to ensure minimal pollution of, or waste into the environment. If it is impossible to prevent this, rehabilitation of the environment should occur (Caddick, 2019).

Rectification of pollution or environmental degradation can occur through the following means: conducting an environmental impact assessment (EIA), training employees through education to work with minimal risk, monitoring and controlling certain actions taken towards initiating environmental harm, preventing or eliminating the dispersion of pollutants as much as possible and alleviating the negative effects of pollution (Shell and BP Refineries , 2018).

B.1.2.1 Environmental Impact Assessment (EIA) Regulations

The NEMA regulations (Amended, 2014 and 2017), dictates the methods, processes and requirements of conducting an EIA in support of sections 24 and 44 of the NEMA. This regulation outlines activities forbidden from occurring without consent or approval from an EIA. It also specifies that activities in accordance with GNR. 983, 984 or 985 requires an independent EAP to conduct the EIA process. The EA is responsible for ensuring environmental management practices are adhered to thereby, assisting with promoting good environmental practices and decisions. Two categories of EIA regulations may exist namely: basic assessment as well as scoping and EIA. Basic assessments are typically required by smaller projects with easy control and management of activities and environmental impacts (Caddick, 2019).

B.1.3 National Environmental Management: Air Quality Act

The National Environmental Management: Air Quality Act (Act No. 39 of 2009) and amended as (NEM: AQA), is a regulatory means to provide protection of the environment through controlling the external environment exposed to the pollutants. Sections 24a and 24b of Constitution of the Republic of South Africa are in correspondence to this act, in which the promotion of social and economic development through environmental protection should be

adhered to. Conservation of the environment and the prevention of environmental degradation and the release of air pollutants are also key driving factors with this act (Golder Associates , 2019).

This act is also responsible for permitting standards with regards to emission control and ambient air quality. These standards are adapted to the needs of various environmental sectors in which provincial or local sectors may have a personalised regulation whereby leniency or stringency is considered depending on the needs of area. The NEM: AQA also aids with the processing and issuing of the Atmospheric Emissions Licences (AELs) in which listed activities are provided with guidelines to control and monitor emissions (Golder Associates , 2019).

B.1.4 National Ambient Air Quality Standards (NAAQS)

The National Ambient Air Quality Standards (NAAQS) provides a criteria of threshold values of common ambient concentration pollutants for South Africa. This aids in the prevention of developing negative human health problems (Golder Associates , 2019).

B.1.5 Carbon Tax Act

The Carbon Tax Act (Act No. 15 of 2019) is a recently implemented means to promote environmental protection and sustainable development. This act operates on the principle of implementing a tax levied and sent to the National Revenue Fund, to people or industries conducting activities related to the emission of greenhouse gases in terms of carbon dioxide equivalent. Sources of emissions from combustion of fuel, fugitive emissions or chemical process (including VOCs) related to the release of carbon emissions are implied to accord with the act and minimum thresholds for certain activities are set out to serve as guidelines to ensure proper environmental management. The rate of carbon tax on the greenhouse gas emissions are set to a value of R120 per ton of carbon dioxide equivalent. Paying a carbon tax also implies the offsetting of carbon emissions from emission sources (Government Gazette: Republic of South Africa, 2019).