Recovery of VOC from Onshore and Offshore Shuttle Tankers using Structured Membranes

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***Abstract*— The emissions of volatile organic compounds (VOCs) from onshore offshore facilities are studied and an alternative technology for the recovery of methane, propane and butane by the use of membrane technology is explored. Permeation tests were carried out with a zeolite membrane consisting of an α – Al2O3 support. The permeance of nitrogen, carbon dioxide, helium, methane and propane through the membrane at varying pressures was determined. The permeance of CH_4 was in the range of 1.44 x 10^{-6} to 3.41 x 10^{-6} $mols^{-1}m^{-2}Pa^{-1}$ and a CH_4/C_3H_8 selectivity of 3.3 at 293 K was obtained. The molar flux of the gases was found to have an average linear regression coefficient value R^2 of 0.9892. On the basis of the results obtained it can be concluded that separation of the hydrocarbon gases can be achieved with the zeolite membrane. The main mechanism governing the flow of gases through the zeolite membrane was molecular sieving although there is evidence of deviation from this mechanism. To achieve higher selectivity of the target gas there is need for further modification of the membrane. The morphology of the membrane was determined using the scanning electron microscope, which showed the pore size of the membrane and the support layer.**

***Index Terms*— Membranes, Characterization, Separation, Volatile Organic Compounds and Zeolite.**

I. INTRODUCTION

Volatile organic compounds are chemicals that have high vapor pressure at room temperature. Due to their high vapour pressures, large numbers of molecules evaporate from the initial form of the compound and enter into the atmosphere. The chemicals in the Volatile organic compounds react in the presence of nitrogen oxides and sunlight to form smog (ground-level ozone), which affect the respiratory system of humans. VOCs are organic chemicals containing the element carbon in their molecular structure and are odourless, colourless and tasteless. Volatile organic Compounds (VOCs) are released during the storage, loading and offloading of hydrocarbon products in onshore and offshore facilities. Methane, ethane and propane are light hydrocarbons and, are considered to be the volatile organic compounds. These compounds are harmful to the environment; methane is a potent greenhouse gas, which contributes to ozone layer depletion. Other Non-methane VOCs (NMVOCS) such as ethane, butane, hexane, pentane and propane react with nitrous oxide to form ground level ozone, which affects both human and plants (1).

Apart from the VOC's being harmful to the environment, they constitute significant economic value that should not be wasted. The sources of the release of VOCs in the onshore and offshore facilities to the atmosphere mostly occur during production, transportation and storage of crude oil (1). The light hydrocarbons mostly vaporises out of the crude oil during the loading and unloading operations of shuttle tankers and also from Floating Production Storage and Offloading Units (FPSOs).

Due to the adverse effects of Volatile Organic Compounds (VOCs) in the environment and also the economic loss of these hydrocarbon compounds, some technologies are used for the abatement of VOCs that are released from both onshore and offshore facilities. Some of the commercially viable methods for treating VOCs emissions include; absorption, adsorption, thermal oxidation, membrane separation and cryogenic condensation (Howard and Nikolas2001).

VOCs Emission Sources

VOCs are emitted to the atmosphere during, production, storage and transportation of crude oil. The two main sources of light hydrocarbon emissions in oil and gas production can be found in onshore and offshore facilities.

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Onshore Facilities

The process of loading of crude oil for storage and for transport contributes to the amount of VOC emitted at onshore storage tank and terminals. The use of floating roofs on storage tanks decreases the amount of emission during the loading of crude oil into the storage tank. In order to prevent the explosive mixture of hydrocarbons and oxygen in empty storage tanks onshore, the atmosphere is usually inerted with exhaust gas. The amount of VOC emitted is dependent on the crude oil quality loaded.

In onshore oil and gas production, storage vessels contribute to a large percentage of the VOC emitted. Tanks that are expected to emit or those that emit more than 6 tons per year are referred to as affected facilities and will therefore require a reduction of 95% per Quad-O of VOC emissions according to EPA (2).

Offshore Facilities

A large proportion of the VOC emission exists in offshore facilities occurs during the loading and unloading operations of Floating, Production, Storage and Offloading Units (FPSOs) and shuttle tanker (3). Some factors such as weather, crude composition, loading operation, ship stability and temperature of crude affects the variation in the amount of VOC emitted during offshore activities in various fields (4, 5). Emission occurs during the unloading of an offshore ship tank inert gas, when the inert gas is pumped at an excessive rate into the tank.

VOCs Emission Regulations

Adverse effects of volatile organic compounds (VOCs) in the environment to plants, climates, animals and humans have resulted in stringent regulations to be enforced in different countries to reduce the VOCs emission. The Environmental Protection Agency in United State of America restricted the yearly ambient air quality standards of a maximum 3-h concentration of hydrocarbon to 0.24ppm (1.6×10^{-4}kg/m^3) (6). The European Community stage restricted the emission limit to 35g total organic compounds (TOC) per cubic metre gasoline loaded which is quite similar to the 10g total organic compounds (TOC) per cubic metre gasoline loaded limit placed by the United States Environmental Protection Agency Standard (6).

Factors affecting the Rate of VOC Emission from onshore and offshore facilities

The rate of emission of Volatile Organic Compounds depends on various factors. These factors are discussed below:

Sea Condition

The blending between hydrocarbon vapour and inert gases increases as a result of the circulation in the shuttle tank between the crude oil and the atmosphere due to the ocean wave movement in offshore. Once the blending between HC vapour and Inert gases increases, the vaporisation rate of the hydrocarbon also increases which thus leads to VOC emission.

Effects of Ship movement

During loading operation, the movement of the ship can alter the emission rate and choppy water also increases the quantity of VOC emitted (7).

Nature of Hydrocarbon

A high concentration of light hydrocarbon affects the rate of VOC emitted, since the vaporization rate of the hydrocarbon is increased which thus lead to more hydrocarbon being emitted to the atmosphere. Crude oil composition with high concentration of light hydrocarbons such as methane and ethane tend to have high hydrocarbon vapour, which can mix with inert gas as a result of convection, and then cause high rate of hydrocarbon vaporization from the loading facilities (4).

Temperature of Crude Oil

The temperature of crude is a very important factor in oil and gas production. The Reid Vapour Pressure (RVP) of crude oil is determined at a specific temperature (37.8˚C), which makes RVP independent of temperature. The difference in temperature of the ship and the shore tank leads to a variation between the volumes of liquid loaded and vapour displaced. The vapour displaced into the shore tank expands and warm up when the ship's tank is colder than the shore tank (7). This leads to subsequent emission and increase in pressure inside the tank.

VOC Recovery Techniques

There are various available techniques for treating VOC emissions from onshore and offshore facilities during the loading and unloading operations. Some of these technique include; absorption, thermal oxidation, adsorption, condensation, reducing volatility and membrane separation (7).

Absorption

Absorption method for VOC recovery is a technology developed by Cool Sorption A/S. It is basically used to recover non-methane VOCs in chilled liquid or pressurized crude oil (8-11 bar) (8).

This process involves feeding the bottom of the packed column with vapour from the tank during loading operation. The vapour moves upward and is in counter current contact with the chilled liquid absorbent flowing downwards. The absorbent dissolves the hydrocarbon from the vapour/air liquid and removes it from the mixture. The residual air is vented to the atmosphere as it moves out of the top of the column. There is regeneration of the absorbent liquid in the stripping section of the absorption system (7). Methanol is injected into the absorption system to prevent the formation of hydrates in the vent gas. The process flow diagram for the absorption system is shown below.

Thermal Oxidation

Thermal oxidation method of controlling VOC emission is also called combustion method and is widely used in USA. The combustion system ranges from simple enclosed fares to catalytic oxidisers with internal heat recovery. The issue of safety and combustion emission of CO_2 are the major negative attributes of thermal oxidation. Energy recovery is used to minimise the implication of CO_2 emission while the use of enrichment dilution, detonation arrestors coupled with effective management procedures ensures safety of the system (7).

Adsorption

Adsorption system is mainly used to separate inert gas from hydrocarbon fractions. There are various adsorption system, one of which is the use of activated carbon. In this type of adsorption technique, the carbon absorbs the organic molecules and the gases like CO_2 and air move through the bed unadsorbed and are emitted to the atmosphere (7). Before the bed becomes saturated, regeneration is carried out either by vacuum steam stripping, but once the bed becomes saturated, the adsorption process stops and the vapour moves through the bed directly without being absorbed.

The use of two beds increases the efficiency of the adsorption process. This continuous operation process involves the use of one bed for the operation, while the other bed is being regenerated.

Cryogenic Condensation

This is method of VOC reduction involving the passing a mixture of VOC- containing gas through a liquid nitrogen cooled condenser (7). This technology is often used in pharmaceutical industry. It is a cost-effective technique of VOCs emission control when compared with the other technologies already discussed (9). A mathematical description of the process can be developed in order to design a counter current single tube condenser using nitrogen vapour as coolant (10).

Reducing Volatility

This is one of the simplest ways to reduce VOC emissions. It entails the reduction of the volatility of shuttle tanks and cargos. Although the vapour pressure of pure substances cannot be altered, changing the composition of the crude to include more of heavier molecular weight compounds and less of lighter molecular weight ones can reduce the gasoline vapour pressure. The volatility of the crude is reduced before loading and storage.

Membrane Separation

This is a new technology that has been adopted for the separation of hydrocarbon and inert gases. This involves the dissolving of vapour molecules in the membrane, which moves by the principle of diffusion to the other end and desorb into the membrane support material (11). The principle of pressure differential drives the diffusion process. Gas separation can be used for various applications such as pollution control, photochemical process, oxygen enrichment, pharmaceutical process and many more (12). Polymeric membrane and inorganic membranes are the two major classifications of membranes. The Organic membrane is mostly used for gas separation are non-porous. Polymeric membrane is not effective in petrochemical plants because they can’t withstand high temperature and pressure. To this effect, the polymer membrane plasticized and become swollen when heavy hydrocarbons is used as the feed gas stream (13).
Inorganic membrane can withstand high temperatures but they are expensive. Alumina, silica, carbon and zeolite can all be used for inorganic membrane (13).

This research adapts the use of Y-type Zeolite membrane for the separation and subsequent recovery of hydrocarbon gases under varying conditions of temperature and pressure since zeolites have the ability to withstand high temperature and pressure as well as fine pore size distribution that is highly selective to hydrocarbon gases.

II. EXPERIMENTAL

A solution containing Silicone oxide, aluminium oxide, sodium oxide and deionised water was prepared and homogenised at room temperature for 20 hours, the amount of each substance used is given in Table 1. Zeolite crystals were deposited on alumina support, which is subsequently dipped into the solution and kept for 20 hours at 343 K. The membrane was washed with deionised water and the pH of the rinse water was monitored. When the rinse water pH was neutral the membrane was air dried for 20 minutes and thermally treated in the oven at 338 K for 2 hours prior to permeation test.

Table 1: Composition of the modification solution for zeolite membrane

Chemical	Amount (ml)
Aluminium oxide	10
Sodium hydroxide	14
Deionised water	798
Silicone oxide	1

The morphology of the membrane was determined by the use of the Zeiss EVO LS10 scanning electron Microscope. Nitrogen physisorption measurements were carried out at 77.35 K using a Quantachrome adsorption gas analyser. The operating conditions of the instrument in given in table 2.

Table 2: Optimum operating conditions of the Quantachrome Gas Analyser

Parameter	Value
Area (A^2mol_{-1})	16.2
Non-Ideality (1/mmHg)	6.58 x 10 -5
Sample cell type (mm)	
Analysis time (mins)	12 237
Mol weight ($gmol^{-1}$)	28.0134
Ambient temperature (K)	300
Bath temperature (K)	77

The experimental rig (fig. 1) was used to determine the permeance of the gases. The gases were fed to the zeolite membrane from the gas cylinder through the gas inlet; the pressure was controlled at the inlet port by a pressure gauge. The permeate flow rate of the individual gases was measured by a flow meter in liters per minute.

III. RESULTS AND DISCUSSION

The zeolite membrane showed permeance in the range of 10^{-6} $molm^{-2}s^{-1}Pa^{-1}$ for CO_2, CH_4, He and N_2, but in the range of 10^{-7} for propane. These permeances are relatively high when compared to literature values (14). The maximum selectivity for this membrane was calculated and presented in Table 3:

Table 3: Maximum selectivity of methane through a zeolite membrane at 293 K

Gas mixture	CH_4/CO_2	CH_4/C_3H_8	CH_4/N_2	CH_4/He
Selectivity	2.9	3.3	1.4	1.2

The selectivity of methane over propane (Table 3) is higher than the values ranging from 1.42 to 2.56 obtained from the work of Tirouni, Sadeghi and Pakizeh (2015) (15).

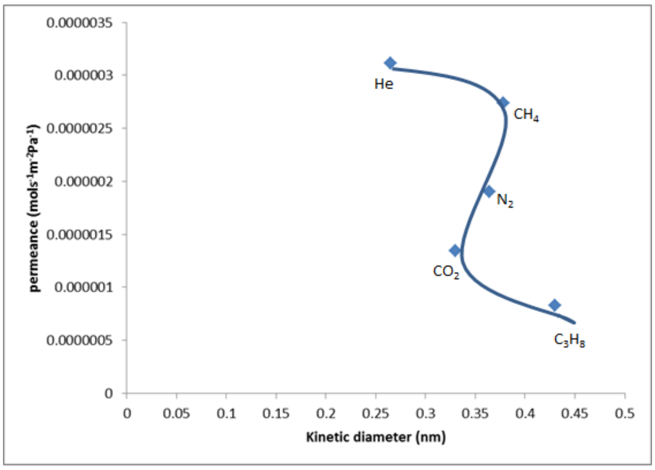

Fig. 1: Effect of kinetic diameter on gas permeance at 293 K and 10^4 Pa

The order of the kinetic diameter of the gases in Figure 1 is given as He<CO_2<N_2<CH_4<C_3H_8. The separation of helium, nitrogen and propane as observed in Fig. 2 was based on molecular sieving properties of zeolite. Carbon dioxide and methane deviated from the expected pattern. This could indicate the presence of inter-crystalline defects in the zeolite membrane (16).

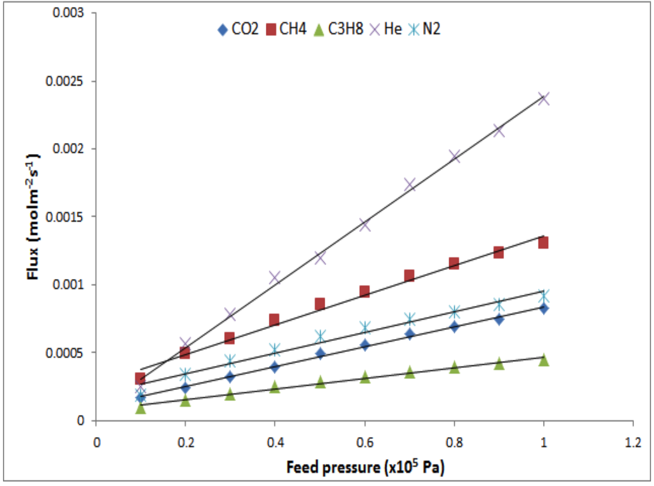

Fig. 2: Molar flux of the gases through zeolite membrane at 293K

The molar fluxes are linear functions of the pressure drop across the zeolite membrane (16). Figure 2 shows the molar fluxes of the gases increase linearly with the increase in pressure. Pressure has significant effect on the gas flux (Fig. 2). The difference between the fluxes of the gases increases with increase in pressure, rate of increase of the flux of carbon dioxide, propane, methane, oxygen and nitrogen was observed to have slightly reduced at a higher of pressure of about 1.0×10^5 Pa and higher. The contribution of viscous flux to the overall mass transfer at higher pressure for zeolite membrane might have caused this. A good linear regression value in the range of $R^2 = 0.99$ was observed.

Figure 3 (a) and (b) shows the cross sectional view and outer surface of the zeolite membrane. The surface of the membrane is covered with a dense layer of zeolite crystals.

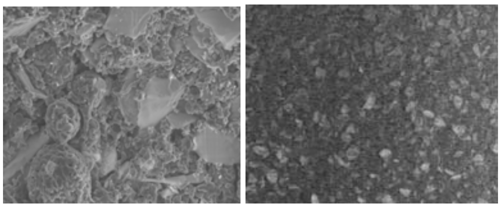
(a) (b)

Fig. 3: SEM images of the cross sectional view (a) and outer surface (b) of zeolite membrane

Fig. 3 clearly shows the zeolite crystals that are deposited on the alumina support. The cross sectional and outer images show a good bonding of the zeolite to the support. The cross sectional view showed the formation of an intermediate layer on the support. This might have led to an improvement in the affinity amidst the zeolite top layer and the alumina support. The zeolite crystals deposited on the surface of the alumina support is visible from the micrograph in the outer surface image in figure 3(b). The pore sizes seen on the outer image was observed to be larger, this could have been caused by the result of interaction of the solution used to coat the membrane surface.

It can be observed that the pore diameter is not uniformly distributed.

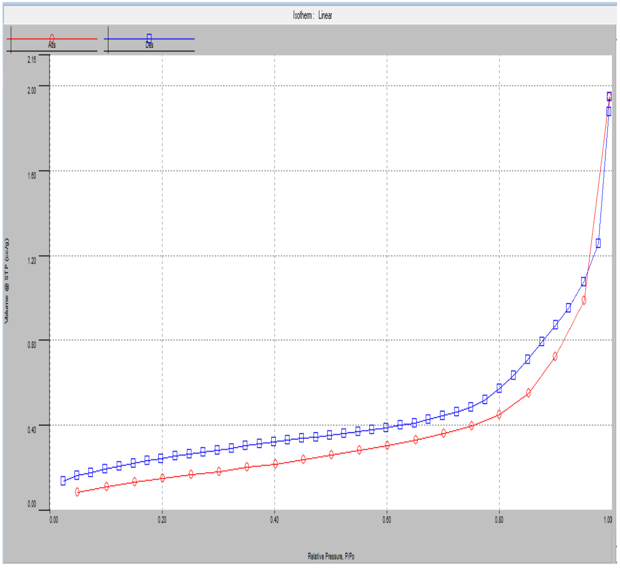

Fig. 4: Physisorption isotherm of the zeolite membrane

The hysteresis isotherms in Figure 4 corresponds to type IV and V; this implies the membrane is mesoporous and could undergo capillary condensation as well during hysteresis. Table 4 shows the desorption summary of the membrane.

Table 4: Desorption summary of the zeolite membrane

Parameter	Value
Pore Volume (cc/g)	0.003
Pore Diameter Dv(d) (nm)	3.94
Surface Area (m^2g^{-1})	0.520

IV. CONCLUSION

The emission of volatile organic compounds from shuttle tankers does not only cause harmful effects to the environment but also causes huge monetary loss. The use of membrane technology is one of the emerging technologies that can be used for the recovery of volatile organic compounds. This recovery is based on the permeances and separation factor of the gases through the membrane. Previous studies have shown that membrane material used for gas separation affects the separation factor of that membrane. Zeolites (from literature and preliminary experiments and this work) have shown to be a better choice of membrane material for the possible use on offshore and offshore storage facilities. Further work needs to be done for the synthesis of a defect-free membrane that is reproducible and can be introduced into the petroleum and gas industries for the separation of lower hydrocarbons at a competitive cost.

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