Effect of Temperature on Gas Separations Using Porous Alumina Membranes

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Abstract
Critical issues in present technologies used for the recovery of emissions of volatile organic compounds (VOCs) from shuttle tankers arise due to the presence of inert gases, which serve as blanket during loading and offloading operations of crude oil. A contribution to the body of knowledge in this field is aimed at concisely researching into the transport mechanism of membranes for the effective recovery of the VOCs.

A methodology based on the modification of inorganic membranes using different types of support with the aim to achieving high selectivity for the hydrocarbons was employed. The feasibility of using these modified membranes in natural gas processing was also presented. A permeation test was carried out using an inorganic ceramic membrane with an α – Al₂O₃ support. The permeance of nitrogen, carbon dioxide, helium, methane and argon through the membrane at a temperature of up to 450 °C and varying pressures was determined. The selectivity of hydrogen over methane was found to be optimum for the membrane at 200 °C and at a pressure of 0.9 barg. The type of flow exhibited by helium, nitrogen and carbon dioxide was found to be Knudsen flow.

Keywords: Volatile Organic compounds, Natural Gas Processing and Membrane Technology.

1. INTRODUCTION:

The production of crude oil from wells that tap into sub-sea reservoirs is facilitated by large systems of offshore production units that are located close to one or more sub-sea wells in an oil field. At these production units, the removal of contaminants from the crude oil is carried out. After which the crude is transported from the offshore production units to onshore storage facilities or refineries via pipelines. However, new wells are being drilled at more remote locations and where the sea bottom has uneven terrain; hence the use of pipelines becomes complex and relatively more expensive. There is apparently the need for a cost effective and environmentally safe system for the effective transportation of crude oil from remote offshore facilities to onshore refineries.

Although the transport system does not appear complicated, each segment has its challenges. The major complexity for crude oil transportation is the location of the oil well. With increasing distance there is no real competitive choice to the shuttle tanker. The advantages of shuttle tanker transportation of crude oil over pipelines include:

- Avoidance of hurricanes
- Flow assurance
- Flexibility of destination

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The global increase in remote oil fields has increased the need for the use of shuttle tankers as well as motivated research into the use of membrane technology as a viable option for the recovery of hydrocarbons during shuttle tanker loading and offloading operations as well as to further investigate the use of membrane technology for natural gas processing.

In the last few years, the potentialities of membrane operations have been widely recognized. The attention to the process intensification strategy as the best approach for an appropriate sustainable industrial growth confirmed that membrane engineering is a powerful tool for this strategy.

The factors considered for the selection of membranes for a given application are strongly related to several factors like the separation efficiency, productivity, durability and mechanical integrity. Different aspects need to be investigated in-depth in order to maintain good separation process including:

- Structure and material of the membrane
- Membrane transport properties (which include permeability and selectivity)
- Module and process design.

The membranes that are more permeable to lighter hydrocarbons are the polyacetylene polymers, the micro porous absorbent carbon and the silicon rubber.

This research work will look at optimising the conditions of membranes to enhance their permeability and selectivity to separate binary mixtures of gases. Volatile organic compounds (VOCs) consist of a mixture of light hydrocarbons and the main component is methane which is considered as a greenhouse gas. The other components of VOCs consist mainly of propane and butane and are commonly referred to as non-methane volatile organic compound (NMVOCs). They react chemically with NO\textsubscript{x} which results in the formation of ground level ozone. Emission of VOCs to the atmosphere from shuttle tankers worldwide has not been systematically measured and observed. The emission has great impact on the environment as well as causing great monetary loss. There are various measures in place for the control of VOCs emitted from shuttle tankers. However, the main problem in the recovery of VOCs from tankers is that the evaporated hydrocarbons are diluted in vast amounts of inert gasses when the gas mixture is displaced by the inflow of oil during loading of the cargo tanks.

Natural gas is an important fuel gas that can be used as a power generation fuel and as a basic raw material in petrochemical industries. Its composition varies extensively from one gas field to another; a particular field might have about 95% methane, with small quantities of other hydrocarbons, nitrogen, carbon dioxide, hydrogen sulphide and water vapour, while another field may have about 10% of lower hydrocarbons like propane, butane or ethane as well as high carbon dioxide contents. Although there is variation in the composition from source to source, the major component of natural gas is methane with other hydrocarbons and unwanted impurities. Hence, all natural gas must undergo some treatment with about 20% requiring extensive treatment before transportation via pipelines as regulations are in place to tightly regulate the composition of the natural gas transported to the pipelines. Membrane technology has only about 5% of the market for processing natural gas in the United States. This percentage is expected to rise as better carbon dioxide selective membranes are developed. High pressures in the range of 500 – 1500 psi are usually required to transport natural gas to a gas processing plant and for a membrane to be used to remove impurities and to minimise recompression cost, the membrane must remove the impurities from the gas into the permeate stream. This requirement determines the type of membrane that can be suitable.
1.3.1 Dehydration of Natural Gas

The current technology that is being used for the removal of water vapour from natural gas is glycol absorption\textsuperscript{14}. Water is an easily condensable compound hence; there are many membranes with high water permeability as well as high water/methane selectivity. The use of glycol absorption is quite prominent and it has a low operational cost. For membrane technology to be competitive, it must cut down the rate of loss of methane with the permeate water. Offshore platform glycol units are not suitable due to space hence the use of membranes can be competitive\textsuperscript{15}.

1.3.2 Removal of Nitrogen

The specification of inert gases in the natural gas pipelines is less than 4%, gas reserves having higher contents are of low quality, although gas containing about 10% inert gases can be blended with low nitrogen content gas to achieve pipeline quality gas\textsuperscript{15}. The economic importance of the content of nitrogen in natural gas is high. In the United States, the value of shut-in gas containing 10 to 15% nitrogen is about $30 billion\textsuperscript{16}, as a result there are numerous processes that have been evaluated for the removal of nitrogen. The current technology that is used in large scale is the cryogenic plants. Membranes can be used to achieve these separations, the challenge being to develop membranes with high methane/nitrogen separation efficiency. The membrane system as compared to the cryogenic plant reduces the concentrations of water, hydrocarbons like propane and butane to a very low level as these components permeate preferentially through a membrane\textsuperscript{15}.

1.3.3 Carbon dioxide Removal

A typical plant for the removal of carbon dioxide from natural gas uses adsorption technology. This consist of two towers where the first tower contains the feed gas at high pressure and an absorbent liquid flowing counter current to each other. The absorbent liquid that contains the absorbed carbon dioxide and heavy hydrocarbons is removed from the bottom of the tower\textsuperscript{12}. Membrane technology is competitive against absorption for the removal of carbon dioxide from natural gas\textsuperscript{17} as the high-pressure absorber tower is an expensive, large thick walled heavy vessel. The mass of the components absorbed is related to the size of the tower. Furthermore, these absorbance units are quite difficult to maintain and corrosion is an important maintenance problem\textsuperscript{12}. Membrane technology could offer a more competitive method for the removal of carbon dioxide from natural gas.

1.4 Membranes for Hydrocarbons Recovery

Membranes can be defined as selective barriers between two components through which differential transport can occur\textsuperscript{18}. Gas separation membranes are used for numerous applications which include: oxygen enrichment, refinery hydrogen recovery, helium separation, pollution control and recovery of hydrocarbons\textsuperscript{18}, air humidification and so many more uses.

Membranes used for gas separations can be generally classified into organic polymeric membranes and inorganic membranes. The organic polymeric membranes that are used for gas separations are hollow asymmetric and nonporous. An important feature in the preparation of polymer membrane for gas separations is the process of spinning them into hollow fibre membranes, which due to its large area is suitable for large-scale industrial applications\textsuperscript{19}. The major drawback for the use of these polymeric membranes is that they can’t stand high temperatures and harsh chemical conditions. In petrochemical plants, natural gas treatment plants and refineries, feed gas streams of heavy hydrocarbons can be a problem as the polymer membranes can be plasticised or become swollen\textsuperscript{20}. The development of inorganic membranes is riveting as they can stand high temperatures and harsh chemical conditions. The major drawback for these ceramic membranes is their high cost,
brittleness, low membrane area and low permeability in the case of highly selective dense membranes. Inorganic membranes based on alumina, zeolites, carbon and silica have been used for the capture of CO$_2$ at elevated temperatures. For the separation of hydrocarbons, zeolite membranes have shown interesting separation characteristics, although their separation efficiency is depended on the operating conditions like temperature, composition and total pressure. In a membrane separation unit, the temperature and pressure are usually kept constant; hence a study of the separation features of the membrane is needed for optimal separation conditions.

Transport properties of ceramic membranes can be explained as the movement of components through the membrane. There are various mechanisms that govern these transport properties, which are:

1.4.1 Knudsen diffusion

Knudsen diffusion arises due to the differences in molecular weights of the components to be separated and it proceeds at a speed that is inversely proportional to the square root of the molecular weight of the component. However, separation by Knudsen diffusion requires that the pore diameter of the membrane to be smaller than the mean free path of the components.

1.4.2 Poiseulle flow

This is also called viscous flow and at high concentrations where collisions are predominantly molecule – molecule then the flow is viscous flow. Hence when the pore radius $r_p$ is greater than the mean free path $\lambda$, the mechanism governing the transport of materials across the membranes is Poiseulle flow.

1.4.3 Slip flow

When the pore radius and the mean free path are approximately equal, slip flow occurs. This is an intermediate range between Knudsen and poiseuille flow.

1.4.3 Sieving action

Molecular sieving effect to separate gases occurs when the pores of a membrane decreases to the 5 Å to 10 Å range. If the gases to be separated have different atomic diameters then the smaller molecules will permeate through the membrane while the larger molecules will be retained. Here very high separation could be achieved.

1.4.4 Surface diffusion

Surface diffusion and adsorption are another mechanism that governs the permeation of gases through membranes that have small pore sizes. When the pore diameter of the membrane is in the range of 50 to 100 Å then adsorption on the walls of the membrane is observed. It is often noted that the amount of gas that is absorbed on the membrane pore walls is greater than the amount of gas that is not absorbed. The absorbed gas molecules then move by surface diffusion through the membrane with the flow rate obeying Fick’s law.

1.4.5 Capillary condensation

Capillary condensation occurs when a porous membrane is in contact with a vapour and the saturation vapour pressure in the pores is different from the saturation vapour pressure of the
components. Also with increasing gas pressures at temperatures below the critical temperature, capillary condensations can occur. The condensed gas molecules will be transported across the membrane pores.

The pore size of the membrane and the mean free path of the molecules determine the flow mechanism that will determine the separation of the components. A membrane can use a combination of transport mechanism for the separation of components.

2. MATERIALS AND METHODS:

The dip-coating solution was prepared by mixing 50 ml of silicon elastomer (Sylgard®) and nine parts of isopentane contained in a glass tube to obtain a clear and colourless solution. A curing agent (Sylgard®) equivalent to one-tenth of the elastomer was added and the resulting solution was mixed at room temperature. The solution was then allowed to age for 30 minutes after which the ceramic support was immersed for 30 minutes. The membrane was then oven dried at 65°C for 24 hours to form an ultra-thin layer on the support.

Permeation Test

The permeation test was carried out using a membrane reactor permeation test set up. The schematic diagram of the permeation test for the gases is given in Fig. 1:

It consists of membrane that is placed inside the membrane reactor and the gas inlet where the gas is being fed into the membrane. The pressure is controlled by the pressure gauge at the inlet port. The flow rate of the permeate gas is measured by the flow meter.

3. RESULTS AND DISCUSSION:

The membrane showed an increasing flow rate with increase in feed pressure. This is in the range of 0.6 to 4.5 Lmin⁻¹ for CO₂, Ar, N₂, CH₄ and He at 285°C. Fig. 2 shows the plot of flow rate of the gases against the feed pressure.
It can be seen in Table 1 that the selectivity of methane over nitrogen and methane over argon showed similar values with the ideal selectivity which was estimated by Knudsen diffusion mechanism. The selectivity of CH₄/N₂ obtained in this experiment is similar with the Knudsen selectivity value which is 1.32. Also, CH₄/Ar is 1.54 (this work) was close to the expected ideal Knudsen selectivity implying that the gas transport were mainly influenced by Knudsen diffusion transport mechanism. However, the selectivity of CH₄/H₂ is higher when compared to the ideal selectivity. This suggests that the membrane could be applied to recover hydrocarbons from other gases.

Fig. 3 shows the relationship between gas permeance and molecular weight in γ-alumina membrane at 450 °C. The measured permeances of the gas species (He, N₂ and CO₂) are inversely proportional to the square root of molecular weight as expected for a process attributed to Knudsen flow mechanism.
Fig. 4 shows CO$_2$ flow rates and temperature relationship at different feed pressures. In the case of 0.05 and 0.15 barg a slight decrease of flow rate was observed at a temperature ranging from 165 to 450 °C. Also, for 0.45 to 0.85 barg the flow rate is almost constant for the entire temperature increase which is in good agreement with the expected Knudsen diffusion. In general, flow rate increases as the pressure increases.

Fig. 4: CO$_2$ flow rates and temperature relationship in γ-alumina membrane at different feed pressures.

4. CONCLUSION:

From these results, it can be concluded that hydrogen separation from methane could be possible. As the temperature increases, residence time on the surface of the membrane is suspected to decrease and thus the facilitated flow mechanism becomes dominant which results in the observed behaviour (Fig. 2). The permeances of CO$_2$, N$_2$ and He have an inverse relationship with the square root of their molecular weights, which indicates the flow mechanism responsible for the transport of these gases across the membrane is the Knudsen flow mechanism. Argon and methane showed that there is another mechanism that is responsible for their transport across the membrane. To fully understand the separation and selectivity of methane from inert gases, there is need for further modification of the nano-composite membrane to achieve good separation of methane from the other gases. Mixed gas separations experiments are planned in the near future.

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6. REFERENCES:


**AUTHOR'S BRIEF BIOGRAPHY:**

The authors Habiba Shehu (left) and Mohammed Nasir Kajama (Right) are research student in the Institute of Design Innovation & Sustainability and undertaking research at the Center for Process Integration and Membrane Technology, Robert Gordon University. They have published more than 10 papers. Professor Edward Gobina is a pioneer in membrane reactor-separators for chemical conversion and gas separations. He has over 150 publications including 20 awarded patents and 25 books. He is currently the Director of the Centre for Process Integration & Membrane Technology at Robert Gordon University at Aberdeen, UK.