

An Initial Study on the Use of Membranes for Hydrocarbons Recovery from Shuttle Tankers during Crude Oil Transportation

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Abstract—There are new remote deep-water oil fields that are being discovered and this makes the use of shuttle tankers more vital for the transport of crude oil to on shore and off shore refineries. The emissions from these tankers are studied and an alternative technology for the recovery of methane, propane and butane from carbon dioxide and other inert gases that are present in the emission is being explored by the use of membrane technology. This paper looks into the transport mechanism exhibited by an inorganic ceramic membrane with an α -Al₂O₃ support. The α -Al₂O₃ support showed permeance in the range of 10^{-5} mols⁻¹m²Pa⁻¹ for CO₂, Ar, N₂ and He at 298 K.

Keywords-membrane technology; permeance; transport mechanism; lower hydrocarbons.

I. INTRODUCTION

The use of ceramic membranes has grown considerably both academically as well as industrially and they can be used for several applications. They are generally more fragile and expensive to fabricate than polymeric membranes but they can withstand more rigorous separation conditions that include high temperatures or corrosive solvents [1]. Ceramic membranes do not only have higher thermal and chemical stability but have higher permeability as well [2]. There are several types of support used for these membranes. The supports used include zeolites, silica, alumina and stainless steel [3]. The various use of ceramic membranes include hydrogen separation and purification to get ultra-pure hydrogen, recovery of CO₂ from natural gas and power station flue gases and oxygen or nitrogen enrichment of air [4,5]. Ceramic membranes can also be incorporated into chemical reactors and thus serve as a catalyst by shifting the reaction equilibrium to the product [3].

Ceramic membranes that are available commercially generally have a pore size of 5 nm or bigger [6]. With the modification of these ceramic membranes the pore size may be reduced to near molecular dimensions which enable separation of components based on the differences in adsorption or in the shape of the components [7]. There are various methods that can be used for the modification of membranes including deposition which aims at modification of an existing membrane by the formation of porous or non-porous layer on the membrane surface. Further processing by the means of annealing, carbonisation or plasma treatment can follow the deposition for further

optimisation. Examples of deposition include: chemical vapour deposition (CVD), sol-gel deposition, Langmuir-Blodgett (LB) deposition, spin coating and self-assembly [1].

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. The differences in molecular weights of the components to be separated gives rise to Knudsen diffusion which proceeds at a speed 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. Generally, diffusion of gases through porous membranes is dependent on the type of collisions occurring. At low concentrations, where there is predominantly molecule- pore wall collisions then the flow is Knudsen flow. At high concentrations where collisions are predominantly molecule –molecule then the flow is viscous flow. Knudsen flow can be achieved with membranes whose pore size is greater than 4 nm and the separation factor for a mixture of binary gases can be estimated from the square root of the ratio of the molecular weights of the gases also gas permeation by Knudsen diffusion varies inversely with the square root of the molecular weights of the gases. Hence an ideal separation for a mixture of binary gases is equal to the inverse of the square root of their molecular mass ratio [8]. The transportation equation for Knudsen and viscous flow is given by:

$$J = A\bar{P} + B \quad (1)$$

Where \bar{P} the average pressure is across a porous membrane, A and B are constants relative to the membrane structure, molecular weight and size. According to equation [1], A is the constant representing viscous flow while B is the constant representing non-viscous flow, J is the permeability of the membrane and it is calculated using the equation:

$$\frac{Q}{S} \cdot \bar{P} \quad (2)$$

Where Q is the flow rate in mols⁻¹, S is the membrane area. The pore radius of the membrane can be determined using the formula (9):

$$rp = \frac{16A\mu}{3B} \sqrt{8RT/\pi M} \quad (3)$$

Where M is the molar mass of the gas, R is the molar gas constant, T is the temperature in K and μ is the viscosity of the gas.

The Knudsen number $K = D/\lambda$ where D is the pore diameter and λ is the mean free path of the molecules determines the flow regime of the membrane. When the diameter of the pores is lower than the mean free path of the molecules then Knudsen flow is dominant [9]:

The assumptions made using this model is that there is negligible pressure drop due to the relatively small length of the capillaries used in this work [10].

Gas transport through $\alpha\text{-Al}_2\text{O}_3$ support can involve both Knudsen and viscous flow when the interaction between the gas and the pore walls of a porous membrane is negligible. [11]. A plot of gas permeability against the mean pressure drop is depicted in Fig. 1; this is for a membrane that is free of defects.

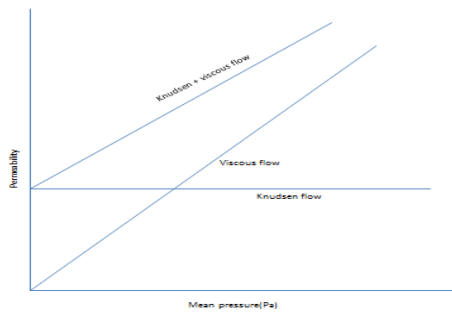


Figure 1. The contributions of Knudsen diffusion and viscous flow. (Adopted from Li, Zhao and Xiong[11])

Another way to explain transport mechanism in membranes is that when the membranes have pore diameters that are in between the sizes of the gas molecules to be separated in this case the membrane acts as a molecular sieve. These membranes are porous and their pore sizes are usually about 0.5 nm or bigger. 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 selectivity could be achieved [8]. Surface diffusion is a transport mechanism where the diffusing species adsorbs on the walls of the membrane pore and then rapidly moves across the surface to be permeated on the other side. Capillary condensation occurs when a porous membrane is in contact with a vapour; the saturation vapour pressure in the pores is different from the saturation vapour pressure of the components [12].

The contributions of the different transport mechanisms rely on the gases to be separated, the properties of the membrane as well as the operating conditions like temperature and pressure. For a commercial ceramic membrane, at elevated temperatures and low pressures the most likely transport mechanism employed is the Knudsen flow. Molecular sieving does not take place due to pore sizes being larger than the gas molecules [8]. The transport of gases through only Knudsen diffusion has been found to be inhibitive on the selectivity of a separating system. To

overcome this difficulty, various efforts to promote other modes of transport have been made by surface modification [4].

This work looks at the transport mechanism exhibited by single gases through a ceramic porous membrane that have an α -alumina support.

II. EXPERIMENTAL

The schematic diagram of a membrane reactor used for the permeation test for the gases is given in Fig. 2. Four different gases: carbon dioxide, helium, nitrogen and argon were used to test for their permeability through a porous ceramic membrane at various pressures.

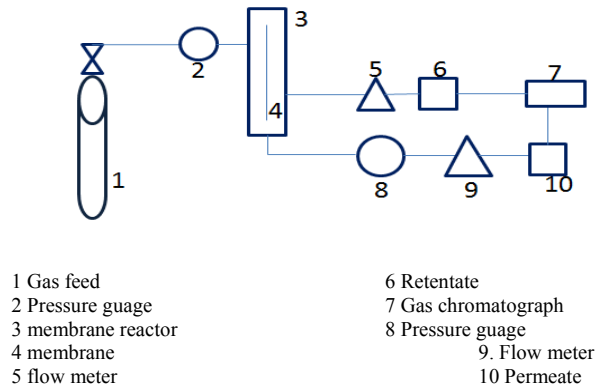


Figure 2. Schematic diagram of a membrane reactor

The morphology of the membrane was determined by the use of the scanning electron Microscope (SEM) and the elemental composition of the membrane was confirmed using Energy Dispersive X-Ray Analysis (EDAX).

III. RESULTS AND DISCUSSIONS

A. Gas permeation

Fig. 3 shows the plot of permeance of the gases against the pressure drop across the membrane. The $\alpha\text{-Al}_2\text{O}_3$ support showed permeance in the range of 10^{-5} $\text{molm}^{-2}\text{Pa}^{-1}$ for CO_2 , Ar, N_2 and He at room temperature

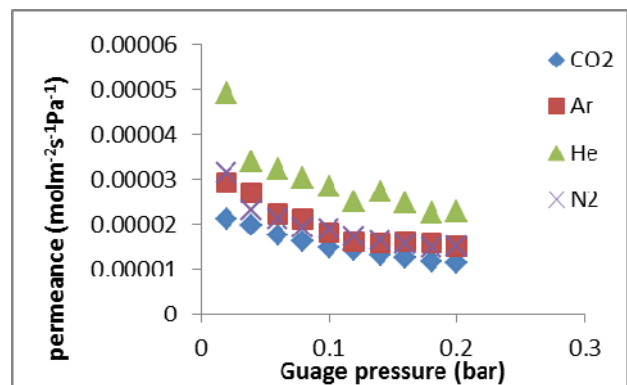


Figure 3. Effect of pressure on gas permeance of $\alpha\text{-Al}_2\text{O}_3$ ceramic membrane at room temperature.

The permeance decreased with increase in feed pressure, CO₂ has the lowest permeance but the highest molecular weight and He has the lowest molecular weight but highest permeance, hence this follows an inverse relationship between molecular weight and permeance which follows the flow mechanism of Knudsen flow [8]. At pressures higher than 0.1 bar the graph indicates a flow that is consistent with Knudsen flow for a membrane that is free from defects as shown in Fig. 1. The order of molecular weights is CO₂ > Ar > N₂ > He nitrogen and argon have close permeance as can be observed in Fig. 3 but their molecular weights are not close. This could imply that a different flow mechanism was responsible for the transport of these gases across the membrane.

Fig. 4 shows the plot of the permeability against the mean pressure.

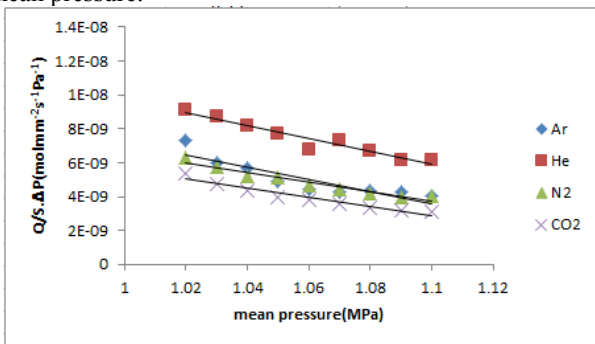


Figure 4. Effect of mean pressure on the permeability of the gases

From the equation;

$$y = mx + c \quad (4)$$

The slope (m) of the graph is the viscous contribution, while the intercept (c) is the contribution due non-viscous flow. From the graph the pore radius and the mean free path of the molecules was calculated and represented in Table 1 below.

TABLE I. PORE RADIUS OF THE MEMBRANE AND MEAN FREE PATH OF THE GASES

	rp(m)	λ(m)
Ar	0.037*10 ⁻¹⁰	1.48*10 ⁻⁴
He	0.312*10 ⁻¹⁰	6.24*10 ⁻⁴
N ₂	0.044*10 ⁻¹⁰	2.93*10 ⁻⁴
CO ₂	0.029*10 ⁻¹⁰	1.99*10 ⁻⁴

Theoretically the pore radius of the membrane is supposed to be the same. From Table 1, it can be seen that the pore radius is much lower than the mean free path which implies that the dominant flow of the gases is Knudsen flow.

The Knudsen selectivity was calculated using the ratios of the molecular weights of the gases [8].

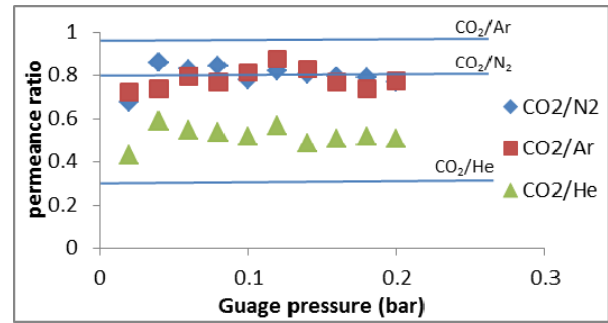


Figure 5. Permselectivity with CO₂ at room temperature.

The values of the knudsen selectivity calculated for the gases are shown in Table 2.

TABLE II. KNUDSEN SELECTIVITY CALCULATED USING THE MOLECULAR WEIGHTS OF THE GASES.

Gases	Knudsen selectivity
CO ₂ /N ₂	0.799
CO ₂ /Ar	0.952
CO ₂ /He	0.302

The Knudsen selectivity calculated has shown higher values for CO₂/Ar at all the pressures used than the experimental Knudsen selectivity calculated using the ratio of the gas permeability. This could indicate another flow mechanism should be employed for the separation of these gases. For CO₂/He, the Knudsen selectivity calculated is lower than the experimental value which could indicate a good separation.

A plot of the permeance against the inverse of the square root of the molecular weights of the gases is given in Fig. 6 below.

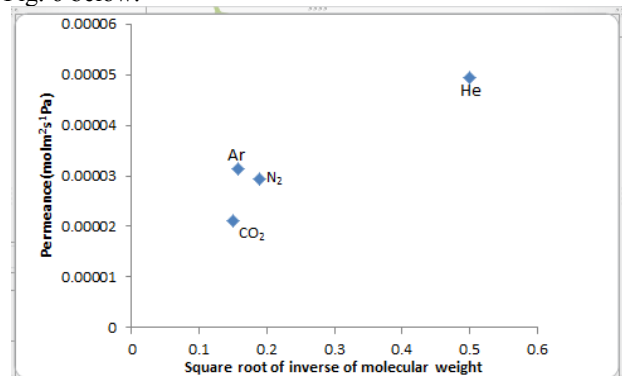


Figure 6. Permeance against inverse of the square root of the molecular weights of the gases.

The graph is not linear as expected for Knudsen flow mechanism.

To further explain the flow mechanism that the membrane exhibited, Fig. 7 is a plot of gas permeance at room temperature against the kinetic diameter of the gas molecules to see if the mechanism could be molecular sieving. According to Pandey and Chauhan [8] the smaller

molecules will permeate while the larger molecules will be retained.

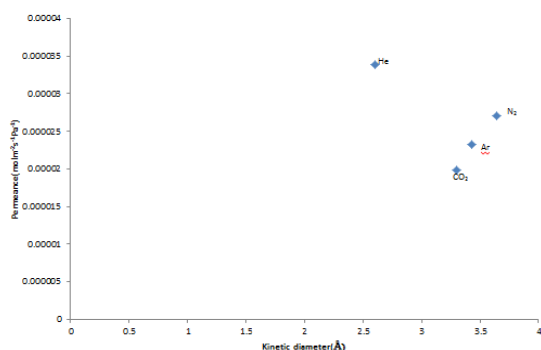


Figure 7. Permeance at 298 K and 2 kPa against kinetic diameter

The order of the kinetic diameter of the gases starting from the largest is $N_2 > Ar > CO_2 > He$. It can be seen that nitrogen having the highest kinetic diameter is permeating at a rate that is higher than argon and carbon dioxide which both have lower kinetic diameters. It can be seen from Fig. 7 that the membrane did not exhibit molecular sieving flow mechanism.

Nitrogen and argon have similar permeance although having different molecular weights. This could indicate there is a different flow mechanism that is responsible for the flow of these gases.

IV. CONCLUSION

To investigate gas separations efficiency of inorganic membranes, the support was modified and the flow mechanism employed by the membrane was determined. On the basis of the results obtained it can be concluded that the main mechanism governing the flow of gases through the modified ceramic membrane was Knudsen flow although there is evidence that another flow mechanism come to play. Further work should be carried out to determine how to modify a membrane support to get a specific flow mechanism. Studies from literature have

shown that for the separation of lower hydrocarbons, zeolite membranes have more efficacy than the silica or alumina ones. Hence modification with zeolite will be explored as well.

V. REFERENCES

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