

## Study of the Selectivity of Methane over Carbon Dioxide Using Composite Inorganic Membranes for Natural Gas Processing

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### Abstract

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. Despite this variation in the composition from source to source, the major component of natural gas is methane with inert gases and carbon dioxide. Hence, all natural gas must undergo some treatment with about 20% of total reserves requiring extensive treatment before transportation via pipelines. The question is can mesoporous membrane be highly selective for methane and be used for the treatment of natural gas? A methodology based on the use of dip-coated silica and zeolite membrane was developed. A single gas permeation test using a membrane reactor was carried out at a temperature of 293 K and a pressure range of  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  Pa. The permeance of  $\text{CH}_4$  was in the range of  $1.15 \times 10^{-6}$  to  $2.88 \times 10^{-6}$   $\text{mols}^{-1}\text{m}^2\text{Pa}^{-1}$  and a  $\text{CH}_4/\text{CO}_2$  selectivity of 1.27 at 293 K and 0.09 MPa was obtained. The pore size of the membrane was evaluated using nitrogen adsorption and was found to be 2.09 nm. The results obtained have shown that it is possible to use a mesoporous membrane to selectively remove carbon dioxide from methane to produce pipeline quality natural gas. There is a need for further study of the transport mechanism of methane through the membrane since this is essential for the separation of other hydrocarbons that could be present as impurities.

**Keywords:** Membrane; Natural gas; Permeation; Silica; Zeolite

### Introduction

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 vapor, 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 form of treatment which might involve in some cases just the removal of water. However, about 20% of natural gas currently being produced worldwide requires more extensive treatment due to an increased amount of impurities before transportation via pipelines [1]. There are regulations 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 [2]. This percentage is expected to rise as better carbon dioxide selective membranes are developed [1,2]. 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 minimize recompression cost; the membrane must selectively remove the impurities from the gas stream. This requirement determines the type of membrane that can be suitable [3].

### Dehydration of natural gas

The current technology that is being used for the removal of water vapor from natural gas is glycol absorption [4]. 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 platforms glycol units are not suitable due to space; hence the use of membranes can be competitive [5].

### 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 [5]. 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 [6], as a result there are numerous processes that have been evaluated for the removal of nitrogen. The current technology that is used now 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 to the membrane [5].

### Carbon dioxide removal

A typical plant for the removal of carbon dioxide from natural gas uses absorption technology. This consists of two towers in which the first tower contains the feed gas at high pressure and an absorbent liquid flowing counter-current to the feed gas. The absorbent liquid that contains the absorbed carbon dioxide and heavy hydrocarbons is removed from the bottom of the tower [2]. Membrane technology is competitive against absorption for the removal of carbon dioxide from natural gas [7] as the high pressure absorber tower is an expensive,

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large thick walled heavy vessel. The mass of the components absorbed is related to the size of the tower. Furthermore, these absorption units are quite difficult to maintain and corrosion is an important maintenance problem [2]. Membrane technology could offer a more competitive method for the removal of carbon dioxide from natural gas, although one of the disadvantages of using membranes is that current polymeric membrane could degrade and plastize due to the presence of components like water, carbon dioxide and  $C_{4+}$  hydrocarbons [1]. As inorganic membranes are more stable under harsh conditions than polymeric membranes, they offer a better choice of material although the cost implications of these inorganic membranes could be a limiting factor.

### Membranes for hydrocarbons recovery

Membranes can be defined as selective barriers between two components through which selective transport can occur [8]. Gas separation membranes are used for numerous applications. 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 [9]. 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 [10]. The development of inorganic membranes is riveting as they can withstand high temperatures and harsh chemical conditions. The major drawback for these membranes is their high cost, brittleness, low membrane area and low permeability in the case of highly selective dense membranes [10]. Inorganic membranes based on alumina, zeolites, carbon and silica have been used for the capture of  $CO_2$  at elevated temperatures [11]. For the separation of hydrocarbons, zeolite membranes have shown interesting separation characteristics, although their separation efficiency depends on the operating conditions like temperature, composition and total pressure [12]. 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 to get the optimal separation conditions [13-15].

### Gas transport through inorganic membranes

The separation of gases in membranes is possible due to the difference in the rate of movement of the different species through the membrane. For membranes having large pore sizes of 0.1 to 10  $\mu m$ , the gases permeate via convective flow and there is not much separation of the gases observed because flow depends on the viscosity of the gases. For mesoporous membranes, separation is based on the collision between the gas molecule and the membrane pore wall and hence the mean free path of the gas molecules is greater than the pore size. The diffusion here is governed by Knudsen mechanism and the rate of transport of any gas is inversely proportional to the square root of its molecular weight. However, for a microporous membrane with pore size less than 2 nm, separation of gases is based mostly on molecular sieving. The transport mechanism in these membranes is often complex and involves surface diffusion that occurs when the permeating species exhibit a strong affinity for the membrane surface and thus adsorbed on the walls of the pores [8].

The permeation of gases through a membrane is dependent on both the diffusion and the concentration gradient of the species along the membrane. The selective transport of a gas molecule through a

membrane is often associated with the pressure, temperature, electric potential and concentration gradient. The permeability and selectivity are some of the parameters that are used to determine a membrane's performance. The permeance  $P$  ( $mol m^{-2} s^{-1} Pa^{-1}$ ) represents the proportionality coefficient with the flux at steady state of a particular gas through a membrane:

$$P = \frac{Q}{A \times \Delta p} \quad (1)$$

Where  $Q$  is the molar gas flow rate through the membrane ( $mol s^{-1}$ ),  $A$  is the membrane surface area ( $m^2$ ) and  $\Delta p$  is the pressure difference across the membrane (Pa). The permeance is therefore a measure of the quantity of a component that permeates through the membrane.

The calculated gas selectivity is the ratio of the permeability coefficients of two different gases as they permeate independently through the membrane is given by:

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (2)$$

where  $P_i$  and  $P_j$  is the permeance of the single gases through the membrane ( $mol m^{-2} s^{-1} Pa$ ).

The selectivity is the measure of the ability of a membrane to separate two gases and it is used to determine the purity of the permeate gas as well as determine the quantity of product that is lost.

## Experimental

### Membrane modification

Two types of membranes (silica and zeolite) were prepared on  $\alpha$ -alumina support and tested for the flux of methane, propane, nitrogen, helium, argon and carbon dioxide at varying feed pressures and in the case of the silica membrane the temperature was varied. The membranes were fabricated using the dip coating method as illustrated in Figure 1.

**Silica membrane preparation:** As depicted in Figure 1, the membrane was prepared by the dip-coating method. The support outside surface was exposed into a solution that comprises of silicone elastomer, curing agent and isopentane in the ratio 10:1:100 respectively and the volumes used are given in Table 1. The mixture was first homogenised with magnetic stirring for 2 hours before the support was dipped for 1 hour with constant stirring to prevent the

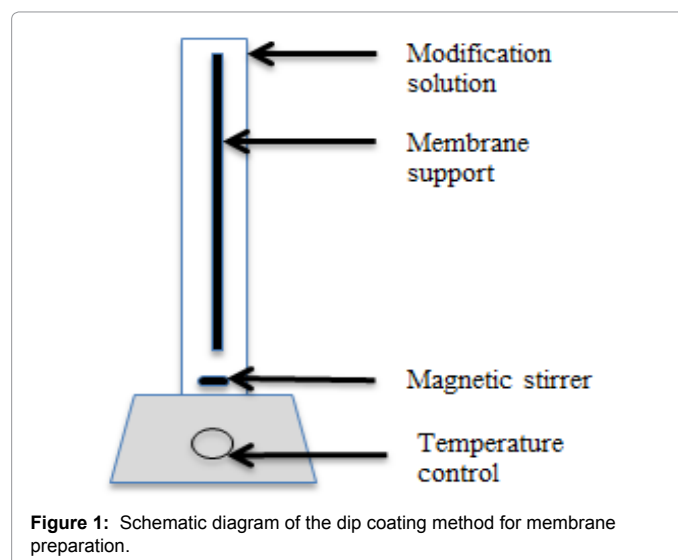


Figure 1: Schematic diagram of the dip coating method for membrane preparation.

mixture from coagulating. The membrane was air dried for 30 minutes and thermally treated at 333 K for 2 hours prior to permeation test.

**Zeolite membrane preparation:** The zeolite membrane was prepared also by the dip-coating method. Here, however 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 2. Zeolite crystals were deposited on the outside surface of the alumina support which was then dipped into the solution and maintained for 20 hours at 343 K. The membrane was withdrawn and 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 tests.

### Characterization

The membranes were characterized using nitrogen physisorption measurements carried out by a nitrogen physisorption Quantachrome gas analyzer.

### Permeation set up

The permeance of carbon dioxide, oxygen, methane nitrogen and propane were each determined at various pressures ranging from  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  Pa using the gas permeation set up in Figure 2. This pressure range was selected as a scale down experimental value to determine the effect of pressure on gas permeance. The single gases used for this work were obtained from BOC, UK and have a purity assay of 99.9%. The permeate side was maintained at atmospheric pressure. The flux of the permeate gas was measured with a Cole-Palmer volumetric digital flow meter ( $L \text{ min}^{-1}$ ).

## Results and Discussion

### Characterisation using nitrogen physisorption

One of the most important techniques for the characterisation of nano- sized porous materials in terms of surface area, pore volume and pore size distribution is the physical adsorption of gas on the surface of the material. Different types of physisorption isotherms (Figure 3) are observed for different materials. Type I: microporous, type II: non-porous or macro-porous, type III: non-porous or macro-porous with weak interaction, type IV: mesoporous, type V: mesoporous with weak interaction and type VI: layer-by-layer adsorption.

The specific surface area of the silica and zeolite membrane was determined from the adsorption of nitrogen on the external and internal surface of the membranes at 77.35 K using a quantachrome adsorption gas analyser. The operating conditions of the instrument in given in Table 3.

The adsorption and desorption isotherm of the zeolite membrane is presented in Figure 4 and it corresponds to type III isotherm from Figure 2. This indicates that the zeolite may be macro porous or non-porous adsorbent with weak adsorbent-adsorbate interaction (1). In theory, zeolites and silica are highly porous and have very large surface area.

The physisorption isotherm for the silica membrane is presented in Figure 5 and it shows the adsorption and desorption isotherms which corresponds to type IV or V which indicates the membrane is a mesoporous adsorbent, the pore sizes and specific surface area of the membrane is given in Table 4.

Substance	Amount (ml)
Curing agent	5
Isopentane	500
Silicone elastomer	50

Table 1: Composition of the modification solution for silica membrane.

The adsorption behaviour of mesoporous materials is determined by the adsorbent-adsorbate interactions. Hence the Kelvin equation (equation 3) which is based on cylindrical pores is used for the evaluation of the pore size distribution of the membrane layer by the

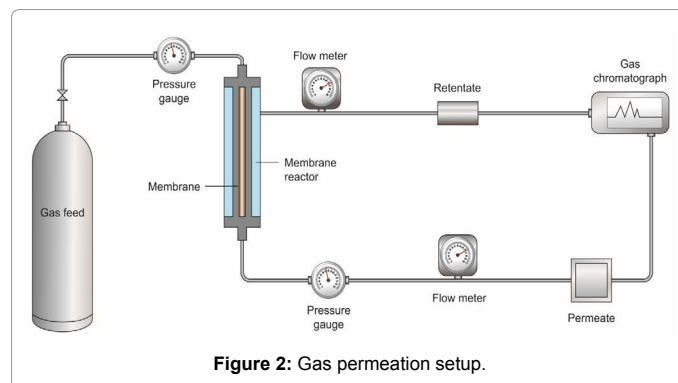


Figure 2: Gas permeation setup.

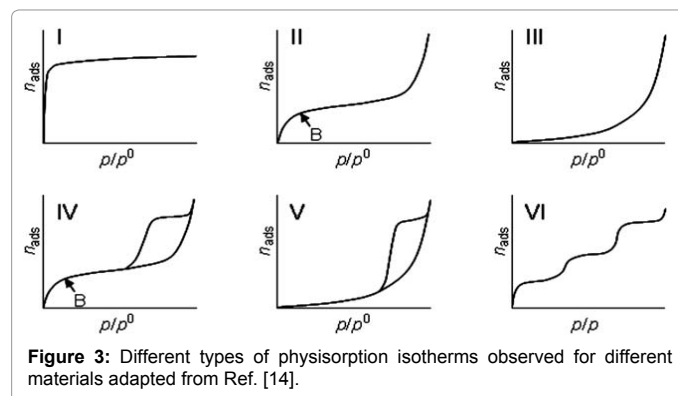


Figure 3: Different types of physisorption isotherms observed for different materials adapted from Ref. [14].

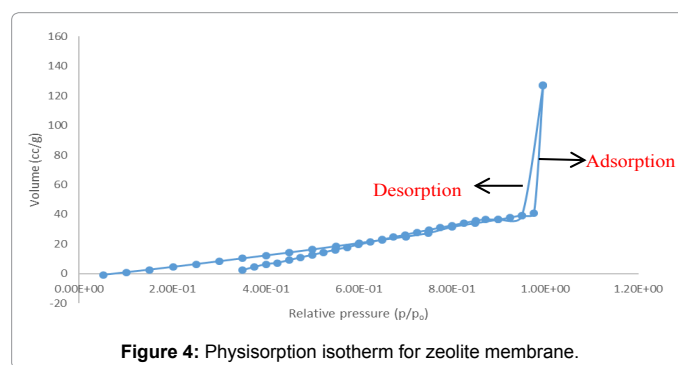


Figure 4: Physisorption isotherm for zeolite membrane.

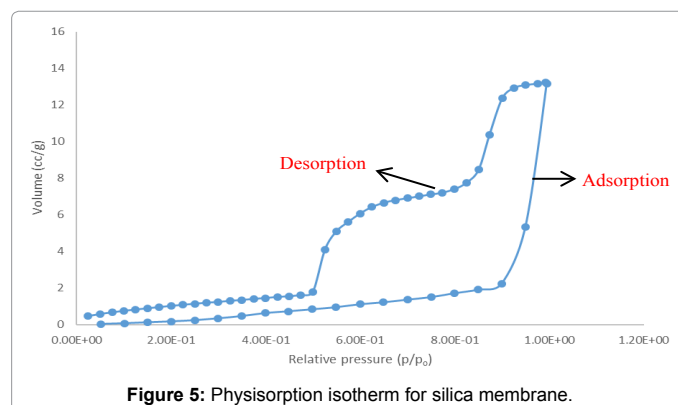


Figure 5: Physisorption isotherm for silica membrane.

Barrett-Joyner-Halenda (BJH) method. The BJH graph (Figure 6 (a) and (b)) shows the adsorption and desorption branches which are used to determine the pore sizes of the membrane.

$$r_p = r_k + t \quad (3)$$

where  $r_p$  is the pore radius of the membrane layer,  $r_k$  is the kelvin radius and  $t$  is the thickness of the membrane layer.

The silica membrane has smaller pore size than the zeolite membrane, although the surface area of the silica is much larger than the zeolite membrane. This is supposed to affect the flow and separation of gases through these materials.

### Single gas permeation tests

The main parameters that determine the efficiency of a membrane performance are the separation factor and the permeation flux [15]. At only gas phase conditions in the feed and the permeate sides, single

gases  $\text{CH}_4$  and  $\text{CO}_2$  were fed into the membrane reactor at a pressure range of 0.1 to  $1 \times 10^5$  Pa and a temperature of 298 K.

Carbon dioxide has a much higher permeation flux through the silica membrane than the zeolite membrane (Figure 7 (a)). The maximum flux of  $\text{CO}_2$  through the zeolite membrane at 1 bar was  $9.9 \times 10^{-2} \text{ mol s}^{-1} \text{ m}^{-2}$  while through the silica membrane it was  $2.3 \times 10^{-1} \text{ mol s}^{-1} \text{ m}^{-2}$ . This could be as the result of the diffusion of  $\text{CO}_2$  through the silica layer by adsorptive surface flow. The pore size of the silica membrane ( $4.183 \times 10^{-9} \text{ m}$ ) is smaller than the pore size of the zeolite membrane ( $11.394 \times 10^{-9} \text{ m}$ ) as observed in Table 4. In the case of methane, the permeation flux is higher at  $2.0 \times 10^{-1} \text{ mol s}^{-1} \text{ m}^{-2}$  at 1 bar through the zeolite membrane (Figure 7 (b)) than  $1.2 \times 10^{-1} \text{ mol s}^{-1} \text{ m}^{-2}$  for the silica membrane at  $1 \times 10^5$  Pa. The molecular sieving abilities as well as selective sorption properties of zeolites that make some specie to absorb on the surface of the membrane at a greater rate than another. The selectivity  $\alpha$  of  $\text{CH}_4/\text{CO}_2$  as determined from equation (2) is expressed in Figure 8.

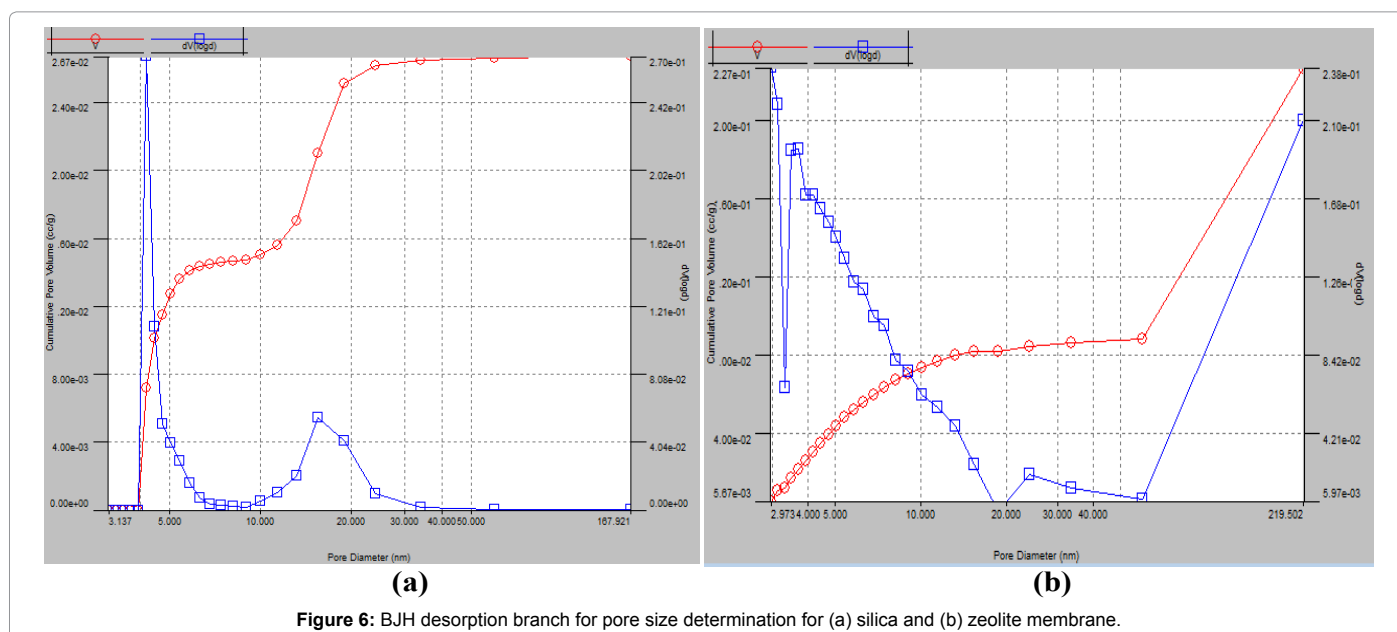


Figure 6: BJH desorption branch for pore size determination for (a) silica and (b) zeolite membrane.

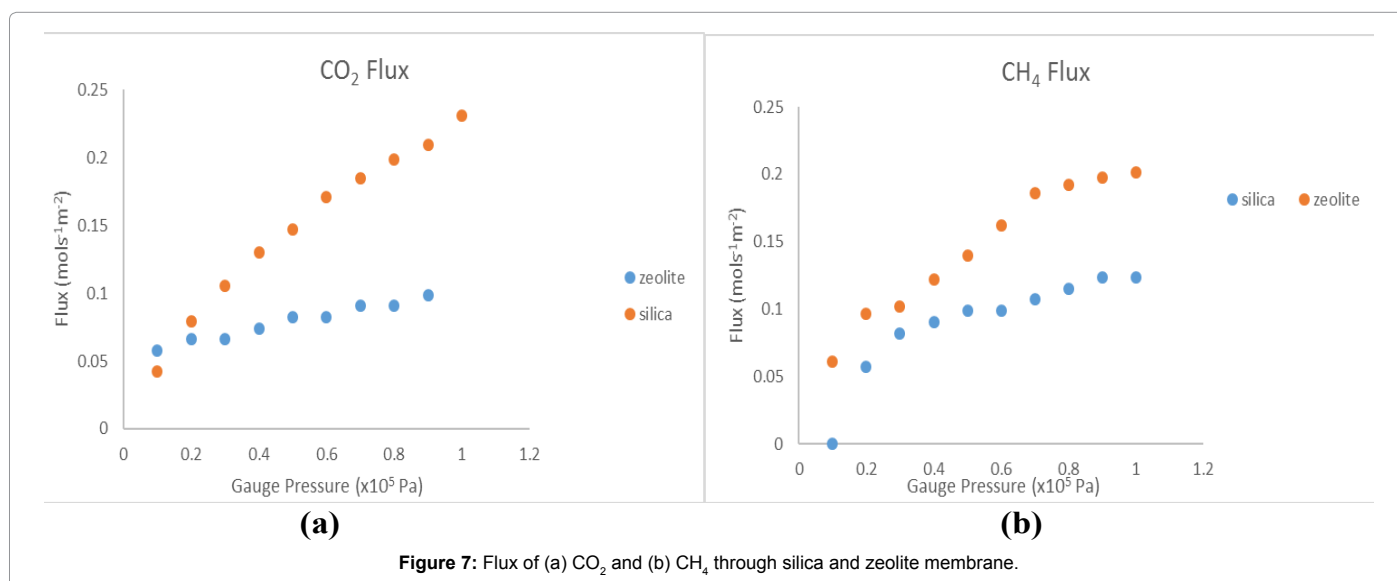


Figure 7: Flux of (a)  $\text{CO}_2$  and (b)  $\text{CH}_4$  through silica and zeolite membrane.

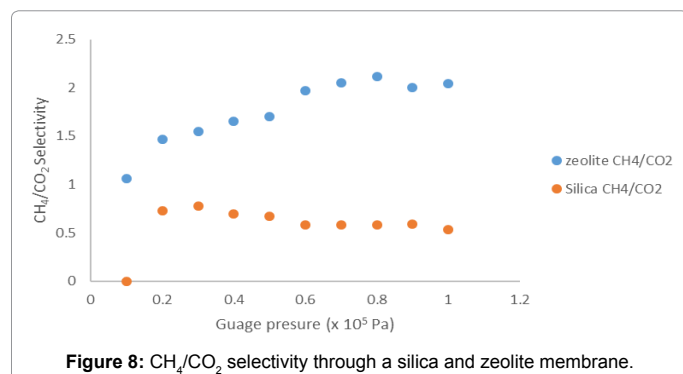


Figure 8: CH<sub>4</sub>/CO<sub>2</sub> selectivity through a silica and zeolite membrane.

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

Table 2: Composition of the modification solution for zeolite membrane.

Parameter	Value
Area (A <sub>2</sub> mol <sup>-1</sup> )	16.2
Non-Ideality (1/mm Hg)	6.58 × 10 <sup>-5</sup>
Sample cell type (mm)	12
Analysis time (mins)	237
Mol weight (g mol <sup>-1</sup> )	28.0134
Ambient temperature (K)	300
Bath temperature (K)	77

Table 3: Optimum operating conditions of the Quantachrome Gas Analyser.

	Silica membrane	Zeolite membrane
Pore size (× 10 <sup>-9</sup> m)	4.183	11.394
Specific surface area (m <sup>2</sup> /g)	10.692	0.619

Table 4: Pore size and surface area of silica and zeolite membranes.

It is obvious from Figure 8 that there is a linear increase in the separation factor of CH<sub>4</sub>/CO<sub>2</sub> with the zeolite membrane with the increase in the pressure drop, it can be assumed that the increase in permeating flux is also an influencing parameter for the selectivity. The silica membrane showed a decrease of selectivity with increase in the pressure drop. At 0.8 bar, zeolite membrane had the highest separation factor of 2.1 while silica membrane had a separation factor of 0.6. Hence it can be assumed that the pressure drop or permeating flux has little or no influence on the selectivity of CH<sub>4</sub>/CO<sub>2</sub>.

## Conclusion

With this work a general impact of pressure drop and pore size on the separation performance of mesoporous membranes for the separation of carbon dioxide and methane was demonstrated. Two different types of membranes were studied and characterized (silica and zeolite). It was found that despite the lower pore of the silica membrane and the higher flux of carbon dioxide through the membrane, the zeolite membrane had a much higher selectivity, which increased linearly with pressure drop across the membrane. This has shown that zeolite membrane could be used for the removal of carbon dioxide from natural gas. Further studies are planned to demonstrate to how the membrane could be used to separate the heavier components of natural gas mixtures that arise during dew point adjustments, thermal

problems during transportation as well as when expanding highly compressed natural gas components.

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