A STUDY OF BIOGAS UPGRADING TO BIO-METHANE WITH CARBON DIOXIDE CAPTURE USING CERAMIC MEMBRANES

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ABSTRACT

Greenhouse gas emissions (GHGs) and their effects have been a matter of global concern over the past decade. With growing energy demands to support developing economies, there has been a challenge of harnessing and utilizing sustainable forms of energy to meet these demands and despite the effect of global warming and the problems associated with it, the use of fossil fuels is still increasing. This problem has negatively impacted the climate because the greenhouse gasses evolved from burning fossils increase the concentration of carbon dioxide in the atmosphere and lead to global warming. This study investigates a method of channelling biogas for use as a sustainable energy source by using membrane technology. Initially, by observing the behaviour of biogas components as they travel selectively through the membrane support, findings showed that both fluid and structural properties have significant impact on the separation process. The next approach is to modify the membrane to obtain these optimal conditions. Furthermore, by introducing an agent that serves as an adsorptive medium for maximizing contact between the pore walls and the gas molecules, to create an adsorptive layer that preferentially draws the target gas to its surface to deliver both high permeability and selectivity of the membrane.

KEYWORDS: Biogas, upgrading, sustainable, membrane, carbon dioxide capture, biomethane.

1 INTRODUCTION

A membrane may be defined as a permeable or semi-permeable layer which controls the flow of compounds and hence delivers one product with less of another component thus resulting in the product concentration in those components (Beil and Beyrich, 2013). This process is used in industry for recovery of reactants and valuable gases, isolation of products and pollution control (Sridhar et al., 2014). The flow of gases is based on their differences in permeability which is a function of membrane properties and the nature of gases (Wiheeb et al., 2015). Generally, the performance of a membrane is defined by its permeability and selectivity and a good indication is with high values of both achieved for efficiency in commercial applications but in practicality, there is a trade-off between these parameters. However, in any given process, there is an economic optimum in the combination of selectivity and permeance.

Permeance/permeation is a measure of the amount of permeate that flows through the membrane and is evaluated by the flowrate at which a fluid passes through the area of the membrane. Selectivity refers to the ability of the membrane to separate gases and gives a measure of the purity of the permeate gas and losses. It is evaluated by the concentration of component passing through the membrane versus the concentration in the feed (Havas and Lin, 2017). For single gases, it is calculated by the ratio of their permeation rates.

2 CHARACTERISATION OF SEPARATION PROPERTIES

In order to make efficient use of resources and achieve effective membrane separation, high permeability and selectivity are required. There are several factors that have been identified by previous authors to affect gas flow in porous media (Abunumah etal, 2021; Chen et al., 2020; Liu and He, 2017; Ogunlude et al., 2020; Ogunlude et al, 2019; Peng and Li, 2018; Pillalamarry et al., 2011). This study has classified them into fluid properties and structural parameters.

3 FLUID PROPERTIES

These include the properties of the fluid that affect the movement or rate of flow of fluids through the membrane.

3.1 Molecular Weight

Molecular weight can be defined as a measure of the total atomic weight values of atoms present in each molecule. In relation to this work, we examine methane and carbon dioxide gases which have molecular weights of 16 g/gmol and 44 g/gmol respectively and try to describe how this fluid property affects the flow of gases through the membranes. In other words, how the weight of atoms present in each molecule of CH_4 and CO_2 changes the rate at which they flow through. Authors have stated that flux is inversely proportional to the square root of the gas molecular weight (Meis, 2017), it is therefore expected that in a separation process, CH_4 (16g/gmol) would be more selectively convened than CO_2 (44g/gmol).

3.2 Kinetic Diameter

Kinetic diameter is an indication of the size of a molecule (3.3 and 3.8 for CO_2 and CH_4 respectively) which estimates the possibility of a molecule colliding with another. Thus, it is associated to the mean free path of molecules in a gas, that is, the average distance that a particle will travel without collision. This is imperative when discussing the behaviour of gases as it plays an important role in the determination of gas flow mechanism. For instance, in viscous flow - the pore diameter is large compared to the mean free path of the gas molecules and there is frequent collision between the molecules, whilst for Knudsen flow - the pore size is larger than that of the gas molecules but smaller than its mean free path, there is elastic collision between the gas molecules and the pore wall but no interaction between the molecules. Hence, the molecule to wall collisions are frequent thereby, allowing lighter molecules preferentially diffuse though the pores (Sridhar et al, 2014).

3.3 Flowrate

Flowrate is a quantification of bulk fluid movement. In terms of this research, we consider volumetric flow rate which is the rate at which a volume of fluid moves per unit time. The rate at which CH_4 and CO_2 gases flow through the membrane is strongly related to invading pressure and permeability. The faster a gas flows, the higher the flux and permeance which thus increases the selectivity of that gas in each membrane.

3.4 Pressure

Pressure is an important engineering quantity that affects many aspects of fluid mechanics. It has been identified that pressure significantly affects CH_4 diffusion at lower pressure than high pressure (Pillalamarry et al, 2011). This is confirmed in Figure 5, however, the authors did not relate this to CO_2 diffusion rate and other system factors which is crucial to a biogas separation unit. Hence, these experiments used up to eight isobars to investigate the effect of the coupling of pressure and other parameters on the separation process.

4 STRUCTURAL PARAMETERS

These are the inherent properties of the membrane matrix system that affect the mode at which fluids pass through based on its components, symmetry, and general make up.

4.1 Pore size

Pore size is the distance between two opposite walls of a pore; thus, it is a measure of how large or small each pore within a material is. Due to the nature and mode of membrane preparation, we generally have non-uniform range of pores and hence the mean pore size is used. Pore size is characterised in the laboratory using Nitrogen Physisorption where the sample is degassed by loading the insulated sample containing cell into the degassing station (for 3 hours at 300ºC) of the physisorption equipment to remove any moisture and impurities. The degassed samples are re-weighed and moved to the analysis station where sample containing cell is immersed into the liquid nitrogen dewar and analysed at 77K to provide pore size measurements. The effect of pore size to flow rate has been studied extensively (Chen et al., 2020; Liu and He, 2017; Peng and Li, 2018; Pillalamarry et al., 2011). However only limited study has touched on it from the perspective of gas separation. From the studies (8,9), it can be deduced that that displacement of CH_4 by CO_2 in coal bed reservoirs is affected by pore size. Another investigation (Chen et al., 2020; Pillalamarry et al., 2011) revealed that pore size significantly affects the diffusion and separation of N_2/CO_2. Drawing an analogy from these authors, it is expected that pore size would affect biogas separation. Thus, in this study, different pore sizes were experimentally tested to identify separation opportunities.

4.2 Porosity

Porosity can be described as a measure of the void or free spaces in a material. It is defined as the fraction of void volume to the total volume. Its contribution for fluid flow is well known. However, this study further pry into how it affects the preferential flow of mixed gas components in biogas separation. In this study samples of the different porosity were used to investigate how porosity would affect CH_4/CO_2 separation in membrane system.

4.3 Surface Area

The effect of surface area is also examined to ascertain if and to what extent this improves the performance parameters (permeability and selectivity) of the membrane system. Generally, higher surface area to a higher rate of reaction due to more acting sites for reaction progression. With this in view, this work proceeds to utilise two membranes with the same mean pore size (15nm), similar characteristics but different surface area and thickness (3mm and 5mm) to confirm this in relation to fluid flow in porous media.

4.4 Operating Temperature

Consequently, the experiment included varying temperature of the core sample to investigate the effect of the coupling of temperature and other parameters on the separation process.

5 RESULTS AND DISCUSSION

Based on the results from laboratory experiments, it is evident that fluid flow through the membrane is governed by both fluid and structural properties or factors.

5.1 Pore Size

The membranes were made to specification by CTI France and have mean pore sizes of 15, 200 and 6000nm. These pore size have been selected be be because it covers the spectrum of meso and macro pores. It was confirmed that lower pore sizes improved the separation performance of the membrane. The 15nm membrane offered greater permeance when compared with membranes of higher pore size as shown in Figure 1 below. Nonetheless, with regards to preferential gas flow, methane had a higher flux than carbon dioxide, this was not to be expected as the kinetic diameter of CO_2 is less than that on CH_4. This means that molecular sieving (or size exclusion) is not the prevalent flow mechanism at play within the pressure and temperature ranges used. In this case, Knudsen diffusion is prevalent following the relation between fluid flow and molecular weight as deduced from Graham's law of diffusion.

5.2 Porosity

The porosity of the 15, 200 and 6000nm membrane were found to be 4, 13 and 20% respectively using particulate density equation for measuring porosity. As shown in the figure below, permeance is optimised when the membrane porosity is 13% despite having a pore size of 200nm. This means that porosity and pore size can be mutually exclusive when dealing with membrane gas separation under these operating conditions. At a porosity of 20% the permeance reduced, this may be attributed to the very high pore size of the membrane that limits it performance.

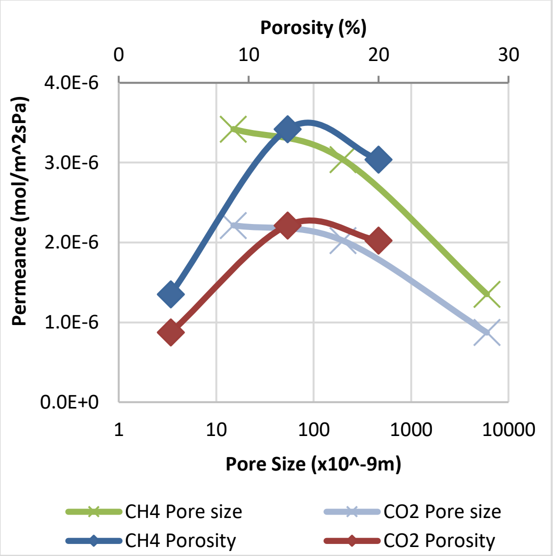

Figure 1: Permeance vs pore size and porosity at 3 bar and 20^{o}C

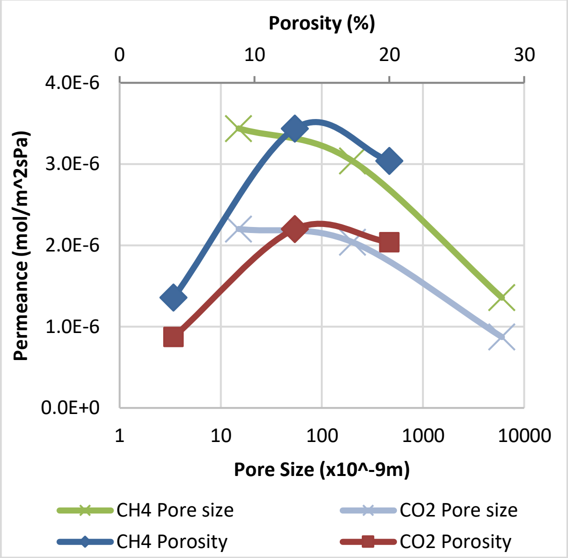

Figure 2: Permeance vs pore size and porosity at 3 bar and 100^{o}C

5.3 Surface Area

With respect to the thicker membrane (5mm/Big15nm), pressure was increased considerably to force the flow of gases through the pores. The results also reveal that the membrane with a larger surface area achieved higher performance compared with the other of smaller surface area. As expressed in literature, this is an effect of more acting site that maximized contact between the gases and the surface of the inorganic membrane creating more active channels for gas permeation (Figures 3 and 4 below).

5.4 Pressure

Figures 3 and 4 show that at low pressures, the gas molecules flow through each membrane (regardless of pore size and surface area) at their standard rates based on the inherit gas properties but a significant increase in pressure forces the gas molecules to travel through the membranes at the maximum velocities causing them to overcome any barriers with supporting activation energies meaning there is a transition from Knudsen to viscous flow regime or fluids go through parallel flow regimes.

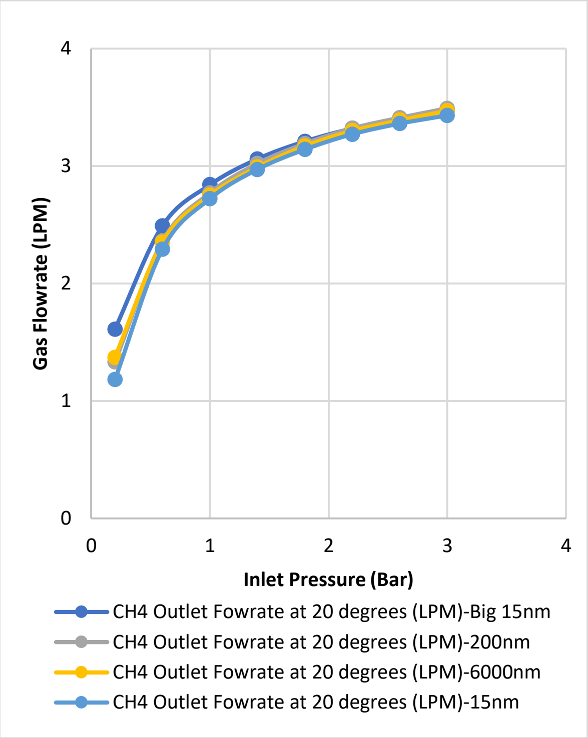

Figure 3: Isothermic Effect of Pressure on Methane Flowrate with each membrane at 20^{o}C

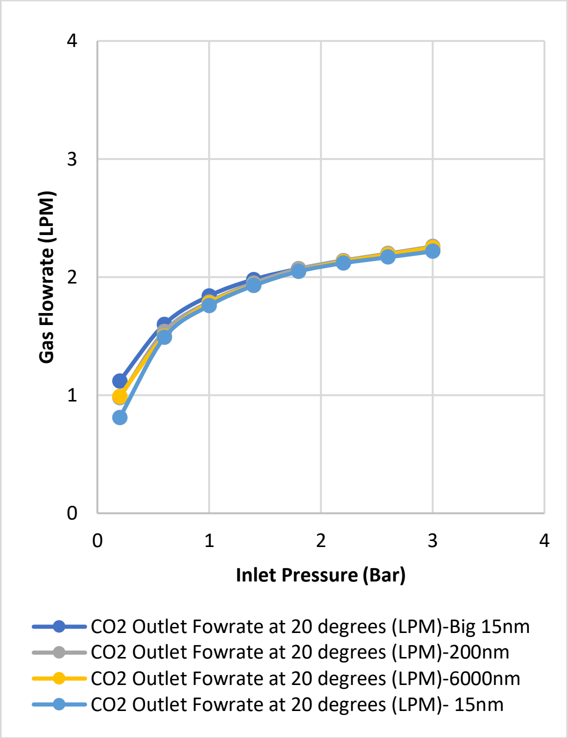

Figure 4: Isothermic Effect of Pressure on Methane Flowrate with each membrane at 100^{o}C

5.5 Temperature

The results show an overall increase in gas flowrate as temperature increases from 20^{o}C to 100^{o}C. This can be explained by the influence of temperature on the kinetic energy of gas molecules which make the molecules move faster with increase in temperature. On the other hand, the flow mechanism is confirmed. From the Knudsen equation, it is known that the permeating flux decreases as temperature increases in this regime, usually in mesoporous membranes, because the temperature increase causes the decrease in surface concentration to overcome the increased effect on diffusivity.

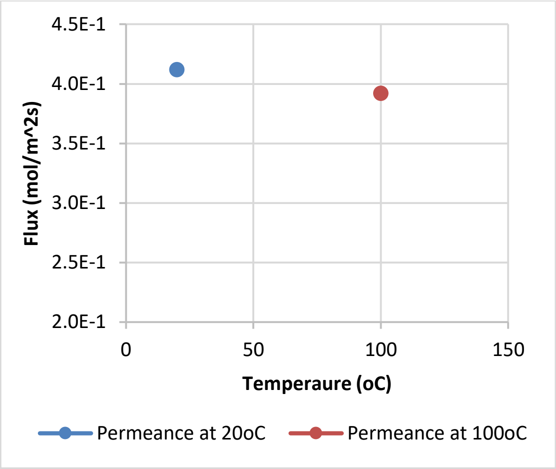

Figure 5: Effect of temperature on flux for CH_4 gas through 15nm membrane at 1 bar

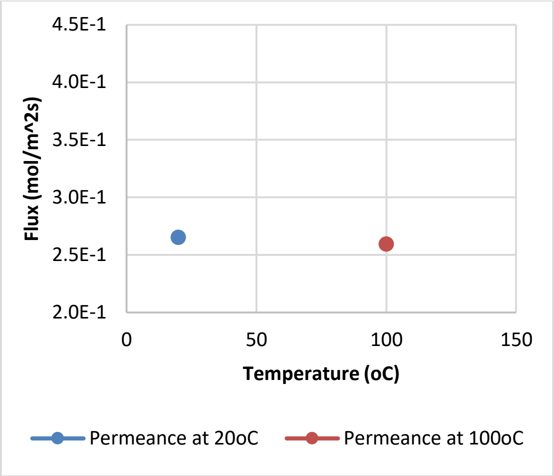

Figure 6: Effect of temperature on flux for CO_2 gas through 15nm membrane at 1 bar

6 CONCLUSIONS

This study confirms that both fluid and structural properties play a vital role in determining the performance of methane and carbon dioxide gas separation with inorganic ceramic membranes. The results show that permeance of gases increase with increasing porosity and permeance of gases decreased with increasing pore size, this means that to achieve optimal permeance, the membrane must have a high porosity and surface area, low pore size as well as maintained pressure and temperature. This will enable the investigation of the effect of loading the membrane support of high porosity with high affinity material that will not only improve the selectivity of the membrane but will also reduce pore size. The effect of subsequent loadings on permeance will be studied and compared with the permeance achieved from modelling this initial support flow equations. By adapting the dip- coating technique which allows easy manipulation of the deposition properties, quantity and thickness and therefore possible to achieve a finely modified membrane with reduced pore size that can enhance the mass transport of carbon dioxide through the membrane as the permeate leaving methane at the retentate side still possessing sufficient pressure for transport and storage (Xomeritakis et al, 2003). Thus, removing the need and cost for methane re-pressurization and thus increasing the overall process efficiency**.** By combining the method of adsorption and molecular sieving it is possible to increase the yield of the target gas without a need to desorb the adsorbent material as it is in the case of cyclical operations. This significantly reduces the amount of energy used for the upgrading process.

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