Experimental study of carbon dioxide separation with nanoporous ceramic membranes

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Abstract

This paper examines carbon dioxide (CO_2) separation from natural gas, mainly methane, through a 15 nm alumina tubular ceramic membrane before and after silica modification. A laboratory scale of tubular silica membrane with a permeable length of 348 mm, I.D and O.D of 7 and 10 mm respectively was used in this experiment. Scanning electron microscopy (SEM) i.e. inner surface, outer surface and cross sectional area of the membrane were analyzed in this experiment. Single gas permeation of helium, methane, nitrogen, argon and carbon dioxide were determined at permeation temperature range between 25°C and 100°C and feed gauge pressure of 0.05 to 1.0 barg. Helium recorded the highest flow rate (0.3745 l/min) while carbon dioxide recorded the least flow rate (0.1351 l/min) at 0.4 barg and 25°C before silica modification. After silica modification, the flow rate of CO_2 rose to 3.1180 l/min at 1.0 barg whereas CH_4 recorded 2.1200 l/min at the same gauge pressure. Temperature variation described the applicability of Knudsen diffusion. A combination of viscous, surface and Knudsen diffusion mechanisms were obtained throughout the silica modification experiment.
Keywords: nanoporous ceramic membranes, gas permeation, permeation temperature, dip-coating, carbon dioxide removal, surface flow, natural gas separation.

1 Introduction

Among the industrial energy consumers (chemical, steel, aluminium, and paper, etc.); the steel industry denote almost 20% of the worldwide industrial energy consumption which has the highest source of industrial carbon dioxide (CO_2)

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emissions with about 15%. Almost 50 percent of the global crude steel production is supplied by the United States, Japan and China. After the steel industry, the chemical industry is the second largest industrial energy consumer with over 14% energy consumption. The United States alone accounted for 25% industrial energy consumption from the chemical industry in the last five years which is the largest energy-intensive branch globally [1]. Furthermore, the United States' energy intensity rose up to 0.8% annually for almost two and a half decades but in the case of all other producers their energy decreased even though China's energy intensity is also high [1]. Fossil fuels continue to maintain the world's energy demand which implicates the links between energy, the environment and climate change [2]. The production of electricity from fossil fuels needs substantial attention due to its increasing concerns that significantly contributes to the global climate change which occurred through man-made emission of greenhouse gases such as carbon dioxide, methane, [3] carbon monoxide, [4] nitrous oxide and water vapour among others. In fact, the current existing coal power plants worldwide emits 2 billion tons of CO_2 annually [4] although in recent years, some carbon reduction policies were introduced such as the Climate Action Plan in the US, the European energy 2030 target and climate debate, the plan for the Chinese to limit the domestic energy mix coal share as well as the Japan's new energy plan talk in order to halt or rather mitigate the increase of CO_2 emission policies [2].

From the environmental point of view, there are a few processes where research and development on membranes technology plays a key role in order to meet the industrial scale. These processes includes; CO_2 separation from natural gas [5–7], volatile organic components (VOC) air separations [8, 9], landfill gas [10], upgrading biogas [10, 11], etc. Cost-effective, inexpensive materials, high chemical resistance and energy saving [7] among others are the approach for novel membranes in the chemical industry. The efficient preparation of ceramic membranes have received substantial attention because the presence of pinhole defects on the membrane could lead to the reduction of the selectivity as well as the integrity of the subsequent skin layer [12] in the past decades. It is therefore very important to take these into account throughout the membrane preparation in order to avoid any occurrence of the defects to transfer into the separation layer. There are several methods for porous ceramic membrane modification including; dip-coating, chemical vapour deposition, and pulsed layer deposition [13–15]. Dip-coating method has many merits over the other methods such as its simplicity, uniform surface and the ability of controlling the pore structure of the membrane [13]. However, a lot of research is still needed to examine membrane modification through dip-coating method in order to elucidate the morphological effects of dip-coated membranes. Gas transport through inorganic membranes depends on pore size and pore size distribution, membrane materials as well as the chemical interaction between the diffusing gases [16]. The main transport mechanisms are viscous flow, Knudsen diffusion, surface diffusion, and Solution-diffusion separation [17–19].

A defect free novel tubular inorganic membrane consisting of a thin silica active layer was obtained via the repeat dip-coating method [19] in this work. The

effect of temperature and feed pressure on permeate flux has been experimentally studied on single gases for gas separation applications.

2 Experimental

2.1 Experimental and membrane preparation

The experimental arrangement used in this study is shown in fig. 1. It consists of a stainless steel tubular membrane reactor cell. Graphite rings with an I.D and O.D of 10.2 and 24 mm was used at each end of the stainless steel reactor, gas flow system used were single gases helium (He), nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4) and argon (Ar), with a purity of $\geq 99.99\%$) supplied by BOC (UK), a digital flowmeter to measure the permeation rates by increasing pressure drop across the membrane was also used.

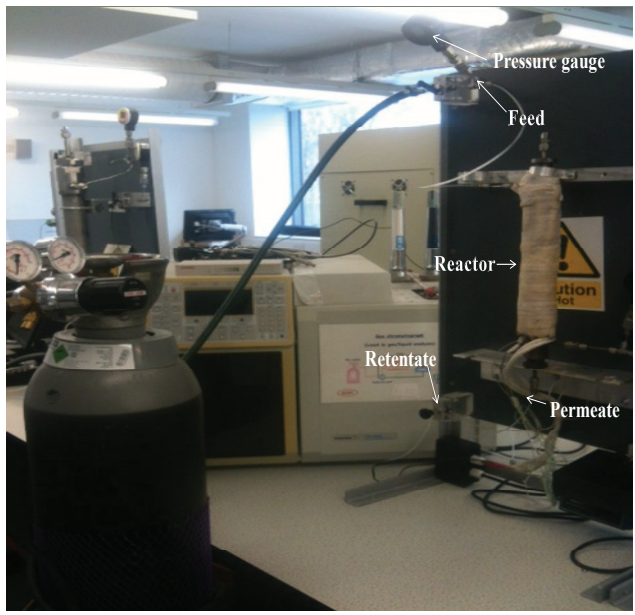

Figure 1: Experimental arrangement for the membrane reactor.

The tubular ceramic membrane consists of 77% α-alumina and 23% TiO_2 possess a nominal pore size of 15 nm. The membrane has a permeable length of 348 mm with I.D and O.D of 7 and 10 mm respectively. Figs 2 and 3 show a SEM image of inside and outside surface of the porous ceramic membranes where the membrane's structure can be distinguished. The cross section of the membrane is shown in fig. 4. Silica layer membrane was prepared using the repeated dip-coating method [20] which allows CO_2 to permeate faster by maintaining a pressure drop across the membrane due to surface diffusion despite its higher molecular weight.

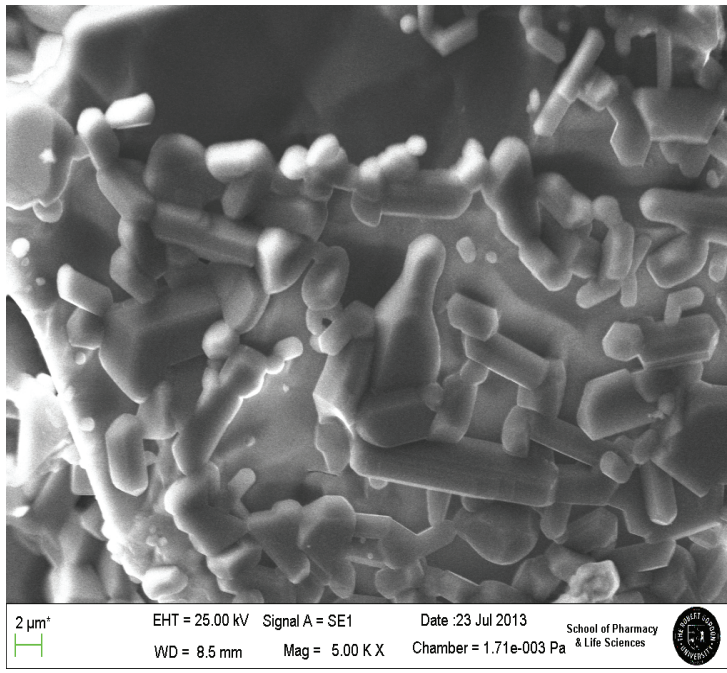

Figure 2: SEM image of the membrane's inside surface.

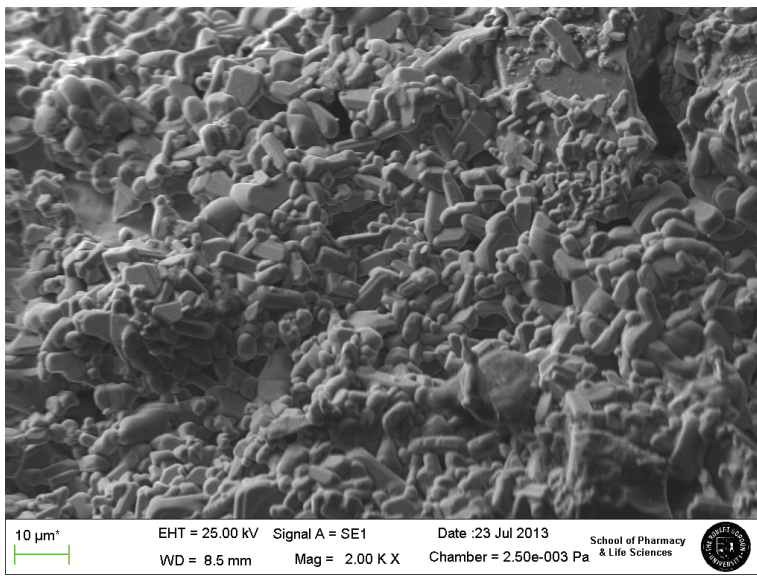

Figure 3: SEM image of the membrane's outside surface.

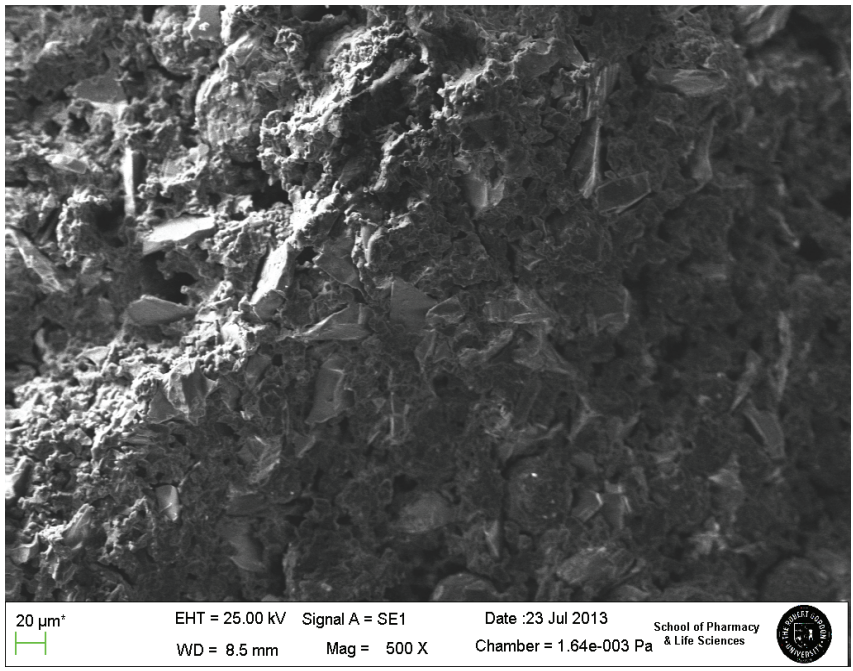

Figure 4: SEM image of the membrane's cross-sectional area.

3 Results and discussion

Different gas permeation and feed pressure relationship were obtained from the unmodified and the modified alumina membrane at temperatures up to 100°C. Fig. 5 shows a typical example of single gases permeation behaviour for the unmodified membrane for fully opened retentate at 25°C. The feed pressure tested were between 0.05 to 0.40 bar and was found that the permeate flux increases linearly with increasing feed pressure which indicates the presence of viscous flow. It can be seen that He recorded the highest permeate flux while CO_2 recorded the least permeate flux. In that case, an unmodified membrane does not support CO_2 removal from natural gas process with a 15 nm membrane due to its higher molecular weight. Fig. 6 depicts the relationship between CH_4 and CO_2 separation against feed gauge pressure at 25°C for fully opened retentate. It is obvious that CO_2 has been positively separated from CH_4 after silica modification via the repeat dip-coating method. This indicates that silica membranes offers good separation performance for the removal of carbon dioxide from natural gas, mainly methane.

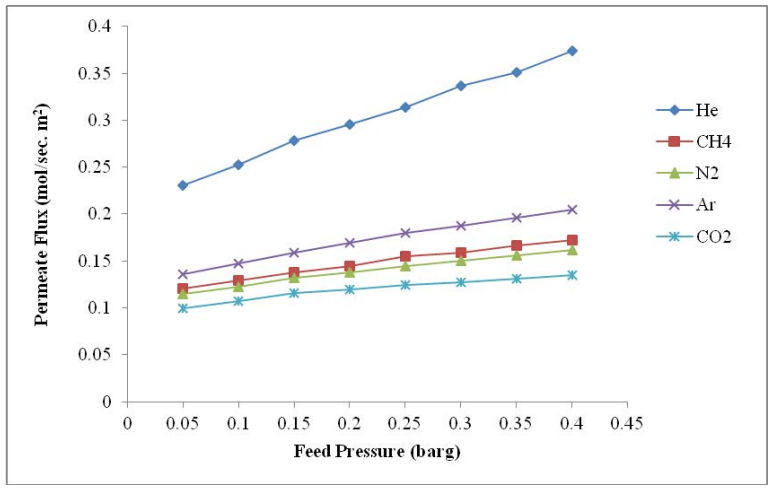

Figure 5: Gas permeates flux for unmodified membrane against feed pressure at 25°C (fully opened retentate).

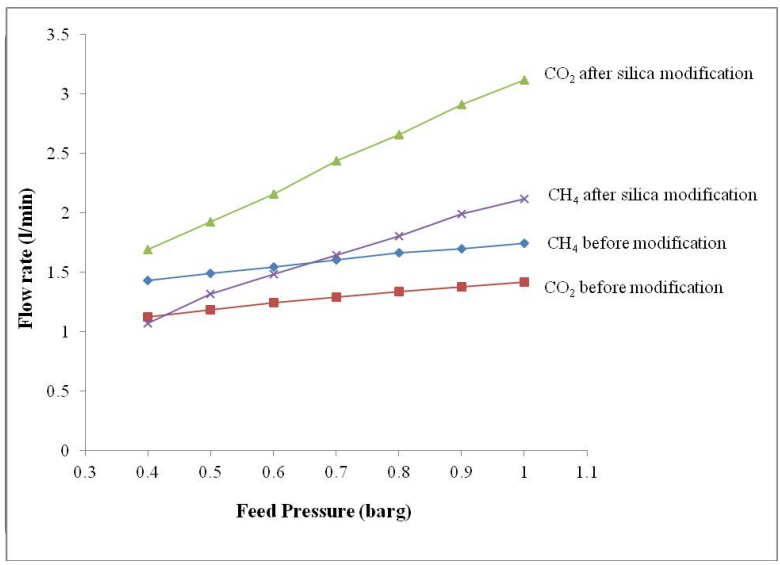

Figure 6: Flow rate of CO_2 separation against feed pressure at 25°C.

Fig. 7 depicts the relationship between CO_2 flow rates against feed pressure before and after modification at 25°C for fully opened retentate. It is obvious that CO_2 permeation rose after membrane's modification which clearly indicates that CO_2 removal is achieved through the repeat dip-coated membrane which corroborates with the result obtained by [19] which indicates the presence of surface flow mechanism.

It can be seen in fig. 8 that He permeate flux decreases with increasing temperature for fully closed retentate at different trans-membrane pressures. These slopes also indicate the existence of Knudsen flow.

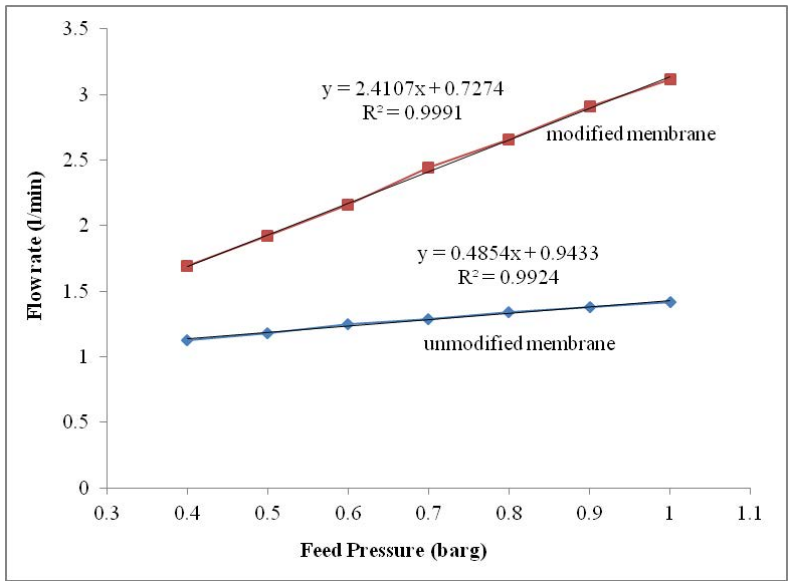

Figure 7: CO_2 flow rate depending on feed pressure before and after modification at 25°C.

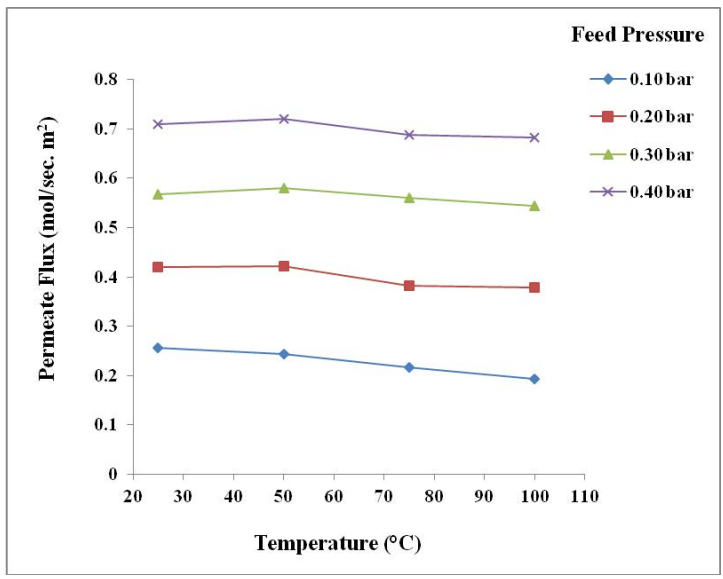

Figure 8: Helium permeation depending on temperature at different pressures.

4 Conclusions

The application of inorganic membranes in the chemical industry continues to receive substantial attention due to their improved performance e.g. acid gas removal such as carbon dioxide from natural gas, as well as thermal and mechanical stabilities. In this experiment, a laboratory scale of tubular silica membrane with a permeable length of 348 mm was used. The influence of permeation temperature (25–100°C) and feed gauge pressure (0.05–1.0 barg) of helium, methane, nitrogen, argon and carbon dioxide were examined from unmodified and silica modified alumina tubular ceramic membrane. The silica membrane offers carbon dioxide separation from methane with the retentate fully opened for up to 1.0 barg at 25°C via the repeat dip-coating method. A linear line was also obtained for the modified membrane with good regression fits (0.9991) at 25°C (fig. 7). Surface diffusion is considered to be negligible for He permeate flux against the tested temperature (25–100°C) at different feed pressures (0.10–0.40 barg). Between 25 and 100°C at 0.10 barg the permeate flux drops from 0.2559 to 0.1936 whereas between 25 and 100°C at 0.40 barg, the permeate flux is almost horizontal with a slight decrease of 0.7102 to 0.6821 (fig. 8). Therefore, the influence of Knudsen diffusion is suspected. In general, the basis of surface, viscous and Knudsen flow mechanisms were obtained.

References

[1] ABB, Overview of Energy Efficiency in Industry and Utilities, in Trends of Global Energy Efficiency, 2011, http://www05.abb.com/global/scot/scot316.nsf/veritydisplay48d2bfc08d960244c1257864004caf9e/$file/the%20global%20report.pdf.

[2] International Energy Outlook 2013, http://www.iea.org/Textbase/npsum/WEO2013SUM.pdf.

[3] Rui, Z. Ji, H. & Lin, Y.S., Modeling and analysis of ceramic-carbonate dual-phase membrane reactor for carbon dioxide reforming with methane. *International Journal of Hydrogen Energy*, **36**, pp. 8292-8300, 2011.

[4] Brunetti, A. Scura, F. Barbieri, G. & Drioli, E., Membrane technologies for CO_2 separation. *Journal of Membrane Science*, **359**, pp. 115-125, 2010.

[5] Singh, R.P. Way, J.D. & McCarley, K.C., Development of a model surface flow membrane by modification of porous vycor glass with a flouorosilane. *Ind. Eng. Chem. Res.*, **43**, pp. 3033-3040, 2004.

[6] Czyperek, M. Zapp, P. Bouwmeester, H.J.M. Modigell, M. Ebert, K. Voigt, I. Meulenberg, W.A. Singheiser, L. & Stoover, D., Gas separation membranes for zero-emission fossil power plants: MEM-BRAIN. *Journal of Membrane Science*, **359**, pp. 149-159, 2010.

[7] Nwogu, N.C. Gobina, E. & Kajama, M.N., Improved carbon dioxide capture using nanostructured ceramic membranes. *Low Carbon Economy*, **4**, pp. 125-128, 2013.

[8] Degreve, J. Everaert, K. & Baeyens, J., The use of gas membranes for VOC-air separations. *Filtration & Separation*, pp. 49-54, 2011.
[9] Huang, P. Xu, N. Shi, J. & Lin, Y.S., Recovery of volatile organic solvent compounds from air by ceramic membranes. *Ind. Eng. Chem. Res.*, **36**, pp. 3815-3820, 1997.
[10] Rasi, S. Lantela, J. & Rintala, J., Trace compounds affecting biogas energy utilisation – A review. *Energy Conversion and Management*, **52**, pp. 3369-3375, 2011.
[11] Favre, E. Bounaceur, R. & Roizard, D., Biogas, membranes and carbon dioxide capture. *Journal of Membrane Science*, **328**, pp. 11-14, 2009.
[12] Zhu, J. Fan, Y. & Xu, N., Modified dip-coating method for preparation of pinhole-free ceramic membranes. *Journal of Membrane Science*, **367**, pp. 14-20, 2011.
[13] Pejman, A.N. Akbar, B.A. Elham, J. Majid, P. & Masoumeh, A.A., An optimum routine for surface modification of ceramic supports to facilitate deposition of defect-free overlaying micro and meso (nano) porous membrane. *Iran. J. Chem. Eng*., **30(3)**, pp. 63-73, 2011.
[14] Benito, J.M. Conesa, A. Rubio, F. & Rodrıguez, M.A., Preparation and characterization of tubular ceramic membranes for treatment of oil emulsions. *Journal of the European Ceramic Society,* **25**, pp. 1895-1903, 2005.
[15] Koutsonikolas, D. Kaldis, S. Sakellaropoulos, G.P. Van Loon, M.H. Dirrix, R.W.J. & Terpstra, R.A. Defects in microporous silica membranes: Analysis and repair. *Separation and Purification Technology,* **73**, pp. 20-24, 2010.
[16] Lee, H-J. Suda, H. & Haraya, K., Gas permeation properties in a composite mesoporous alumina ceramic membrane. *Korean J. Chem. Eng.*, **22**, pp. 721-728, 2005.
[17] Scholes, C.A. Kentish, S.E. & Stevens, G.W., Carbon dioxide separation through polymeric membrane systems for flue gas applications. *Recent Patents on Chemical Engineering*, **1**, pp. 52-66, 2008.
[18] Kim, Y. Kusakabe, K. Morooka, S. & Yang, S., Preparation of microporous silica membranes for gas separation. *Korean Journal of Chemical Engineering*, **18**, pp. 106-112, 2001.
[19] Ohwoka, A. Ogbuke, I. & Gobina, E., Performance of pure and mixed gas transport in reconfigured hybrid inorganic membranes part 2. *Membrane Technology*, pp. 7-9, 2012.
[20] Gobina, E., Apparatus and Methods for Separating Gases. United States Granted Patent No. US 7048778, May 23, 2006.