Polysulfone hollow fiber membrane system for CO_2/CH_4 separation: Influence membrane module configuration on the separation performance

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Abstract

Separation of CO_2/CH_4 using polysulfone hollow fiber membrane system using cascade and series arrangements was studied. The membranes used were fabricated using 33%wt of polysulfone polymer. Gas permeation properties (pressure-normalized flux and selectivity) were evaluated using pure carbon dioxide and methane as test gases. Results showed that single-stage gas permeation system in cascade arrangement with two-stage of gas permeation system produced the highest CO_2/CH_4 selectivity especially tested at low feed pressure range. Effect of stage cut on feed pressure showed an increasing trend with increasing of CO_2 and CH_4 feed pressure in both configurations. This is due to the increase of the permeation driving force, which causes the passage of larger amounts of more permeable gas through the membrane. On the other hand, effect of stage cut on pressure-normalized flux exhibited a constant trend plots for both gases and configurations. This study showed that, cascade configuration exhibited a smaller stage cut values than series configuration. Hence, cascade configuration produced higher purity of CO_2 in the permeate stream. The results of this work served as a mean in determining the most suitable module configuration to be used for gas separation processes.

Keywords: Hollow fiber, gas separation system, membrane configuration, membrane performance, polysulfone

1. Introduction

Membrane systems have become a viable alternative to conventional gas separation technologies such as pressure swing adsorption, cryogenic distillation and amine absorption especially when high CO_2 concentrations are encountered [1]. The demand for lower production cost and higher product purity motivate research on performance of various cell configurations with a combine serial and cascade arrangements. The economics of membrane separation processes depend critically on the process design. The design of a membrane system consists of two sub problems: (i) selection of an

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appropriate permeator configuration and (ii) determination of the operating conditions of the individual permeators. Membrane systems currently are designed via a sequential procedure in which the permeator configuration is chosen a priori and the operating conditions are determined using some type of optimization procedure [2].

An essential part in the design of gas separation by membranes is the determination of the separation configuration. A single stage arrangement with no recycle is the most common and simplest design form. However the demand for higher product purity and recovery ratio of the desired species necessitates the use of recycle streams as well as multi-stage configurations. Commonly, the multi stage systems are designed using two, three or four stages [3].

Membrane has been the technology of interest in natural gas sweetening, removal of CO_2 in landfill gas recovery processes and CO_2 removal from fractured wells, and removal of CO_2 in enhanced oil recovery applications (EOR). With the progress in materials and membrane fabrication techniques, membrane system for applications in these areas became more competitive compared to conventional separation processes such as amine scrubbing etc. Many researchers had studied the effects of plasticization in commercial glassy polymers when exposed to high pressure of CO_2. However, glassy polymers such as polysulfones, polycarbonates, polyimides, poly(methylmethacrylate, polyurethane, polyaramide and cellulose acetate exposed to a high pressure of CO_2 was found to plasticize at a high pressure of CO_2. Due to the plasticizing effect, the sorption and permeation behavior of the polymer was altered. The polymer matrix swells by the highly sorbed CO_2, which results in an increase in CO_2 permeability. Simultaneously, the CH_4 permeability increases and as it increases more than the CO_2 permeability, the selectivity decreases. This plasticizing action of CO_2 decreases the ability of the membrane to separate molecules on the basis of size, thereby causing the reduction in selectivity [4-20].

However, only few researchers studied the effects of membrane configurations and its effect on gas separation performance. Bhide and Stern [21] studied the process configurations of single and two-stage for oxygen-enrichment of air. Six configurations were proposed either series and cascades arrangements with permeate or retentate streams recycle is used in their experiment. The membranes used were silicone rubber, poly (phenylene oxide) and cellulose acetate. Later, Bhide and Stern [22-23] studied the effect of configuration for the removal of acid gases from natural gas. The seventh configurations, which consist of three-stage cascade configuration, were introduced. The membrane polymer used was cellulose acetate. Ettouney et al. [24] investigated experimentally the separation characteristics of air using polysulfone hollow fiber membrane using one, two and three cells in series. Each cell has a total separation area of 2.22 m^2.

As for Qi and Henson [2], they developed spiral wound membrane network that considered two, three and four-stage of membrane configurations for the separation of CO_2/CH_4. The total membrane area considered in their study ranges from 380 to 600 m^2. The developed system used a random value of membrane area in order to recover the desired amount of CO_2. The cascade configuration used in their study was reported to produce 64.56% of CO_2 in the permeate stream. Lim [25] studied the same cascade configuration as well as series configuration through simulation works. 83.96% of CO_2 in the permeate stream was achieved using three-stage cascade configuration. However, series configurations produced 82.48% of CO_2 in the permeate stream. The developed system was able to simulate variety of membrane configuration in order to study the separation behavior of CO_2/CH_4 and O_2/N_2 mixture in polysulfone and cellulose acetate hollow fiber membranes. These configurations also provided the lowest operating cost among all other configurations studied.

This paper aims to investigate and evaluate the effect of series and cascade module configuration (Figure 1) of three-stage separation system on the performance of CO_2/CH_4 gas separation. The design of this system is a combination of different configurations proposed by Bhide and Stern, Qi and Henson, Ettouney and Majeed together with Lim.

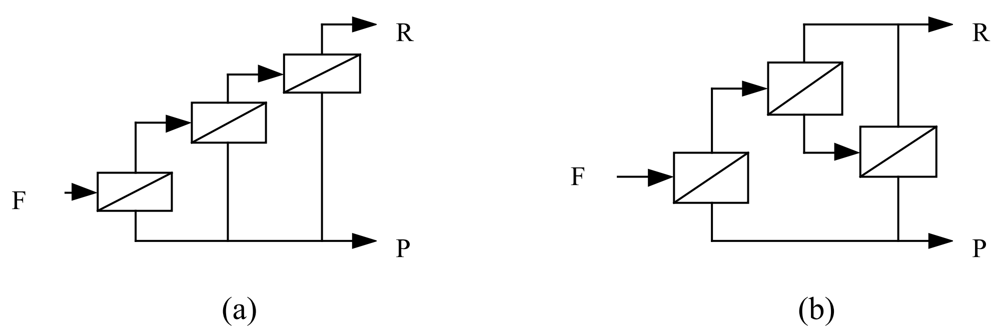

Figure 1: (a) series configuration, (b) cascade configuration

2. Experimental

2.1. Preparation of asymmetric polysulfone hollow fiber membranes

The asymmetric hollow fiber membranes were fabricated using a dry/wet spinning process with forced convection in the dry gap. Dope solution containing of polysulfone (Udel-1700), N, N-dimethylacetamide, tetrahydofuran was used. The dope reservoir was at ambient temperature during spinning. On extrusion from the spinneret (spinneret dimensions: OD 0.6 mm / ID 0.3 mm), the fiber passed through a cylindrical forced convection chamber (length 9 cm, diameter 5 cm), which was flushed with 4 l min-1 of nitrogen gas. The nitrogen was introduced through a ¼ in. tube, which abutted upon the chamber normal to the surface at mid height. A 2 mm clearance existed between the top of the forced convection chamber and the bottom plate of the spinneret and also between the bottom of the chamber and the water level in the first coagulation bath.

Pure water at 14°C±0.5°C was used in the external coagulation bath. The bore coagulant was 20% (w/w) solution of potassium acetate in water at ambient temperature.

This equates to the water activity of 0.9. The hollow fibers were spun at dope extrusion rate (DER) of 2.5. The stretch ratio (wind up speed/extrusion speed0 was fixed at 1 throughout. The ratio of DER to bore fluid injection rate was also kept constant at a value of 3. After spinning, the membranes were steeped in water and then dried using methanol solvent exchange technique [26]. The hollow fiber prepared had an equivalent pore size of 6.07 x 10^{-7} cm, surface porosity of 7.69 x 10^{-7} and skin layer thickness of 2.09 x 10^{-5} cm. These values were calculated based on theory proposed by [27].

2.2. Permeation behavior of pure CO_2 and CH_4 gas through hollow fiber polysulfone membranes

Three-stage gas permeation characteristics were measured with a permeation set-up as shown in Figure 2. The hollow fiber membrane modules prepared contain ten fibers with an effective membrane area of about 56.56 cm^2 with an effective length of about 30 cm. This study considers two types of three-stage permeation both in series and cascades configurations.

Pure CH_4 (99.5%) or CO_2 (99%) was introduced to the shell side of the hollow fiber module and the feed pressure gas was controlled by the pressure regulator from 1 to 15 bars. The feed gas was stabilized for about 20 min before measurement is taken. The pressure-normalized flux was measured in the permeate side at atmospheric pressure and room temperature using a simple and reliable bubble flowmeter. The pressure-normalized gas flux was calculated using the following equations:

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta P.A} \tag{1}$$

Where (*P/l*) is the pressure-normalized flux of gas *i* (GPU = 1 x 10^{-6} cm^3 (STP)/cm^2-s-cmHg); Q_i represents volumetric flowrate of gas *i* at standard temperature and pressure difference (cmHg); ΔP is the pressure difference between the feed side and the permeation side of the membrane (cmHg); *A* represents the membrane surface area (cm^2).

Membrane selectivity, $\alpha_{A, B}$ is defined as the ratio of pressure-normalized flux of gas A to gas B. The equation is as follows.

$$\alpha_{A,B} = \frac{P/l_A}{P/l_B} \tag{2}$$

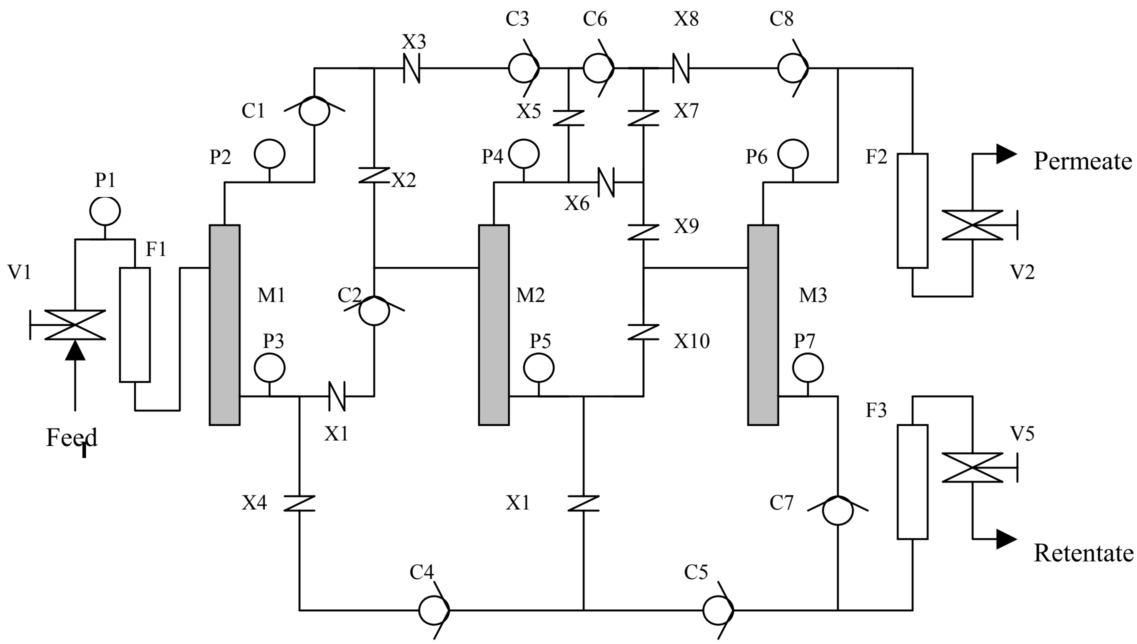

Figure 2: Three-stage permeation system

3. Results and discussion

Figure 3 shows the cross section of polysulfone hollow fiber membrane spun from the 33 wt.% polymer dopes by dry/wet process. The structure of the produced hollow fiber membranes showed an asymmetric structure; a dense top layer supported by a porous, spongy substructure. This figure clearly reveals a thin skin layer with many teardrops or finger microvoids near to the membrane surface. This was due to the high dope extrusion rate used to spin the hollow fiber membrane. The same membrane morphology was reported by Sharpe et al. [28].

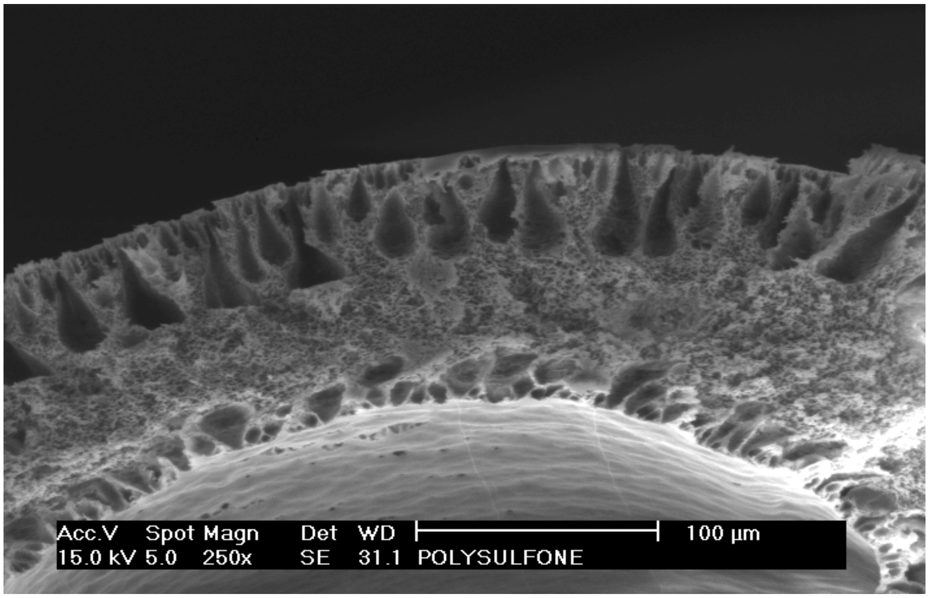

Figure 3: Typical cross-section of asymmetric polysulfone hollow fiber membrane used.

Table 1 shows the pressure-normalized flux and CO_2/CH_4 selectivity of polysulfone hollow fibers in both series and cascade configurations. Hollow fibers module in cascade configuration exhibited the highest selectivity (~45) compare to hollow fiber module in series configuration that only showed selectivity of about 19. The CO_2/CH_4 selectivity of polysulfone dense membranes is reported to be about 30.

Table 1
Comparison of polysulfone hollow fibers in series and cascade configurations

Feed Pressure (bar)	CO_2/CH_4 Selectivity	
	Cascade Configuration	Series Configuration
1	45.39	19.40
2	31.19	17.68
3	23.42	15.00

Figure 4 and 5 showed the effect of feed pressure on pressure-normalized flux of CH_4 and CO_2 gases in series and cascades configurations respectively. CH_4 gas showed a constant trend of pressure-normalized flux as a function of feed pressure. However, CO_2 showed fluctuated trend of pressure-normalized flux with increasing feed pressure that was contrasting to the normal behavior of glassy polymer. Normally, the pressure-normalized flux of a glassy polymer decreases with increasing feed pressure, which has been extensively explained by the dual sorption model. However, in some cases the opposite trend occurs [29]. The increasing trend of CO_2 as a function of feed pressure indicated that CO_2 plasticization in polysulfone membranes occurs for feed pressures greater than 1 bar for both configurations. A high CO_2 concentration in the polymer film disrupts chain packing, resulting in an increased segmental mobility [4].

The pressure-normalized flux of CH_4 in both configurations not only showed the same trend but the values of the pressure-normalized flux is also almost the same. However, the pressure-normalized flux for CO_2 showed a major difference in its values. Cascades configuration exhibited higher value of selectivities compared to series configuration. This is because in cascade configuration, only the first membrane module undergoes separation at high pressure while the other two modules experienced separation at low pressure since the permeate stream was used as the feed stream. Even though, the permeate from the first membrane module will be accumulated with the permeate from the third stage, the resultant permeate flow is still low. Although the build up of CO_2 concentration in the first membrane module occurs as the feed pressure is further elevated, the second and the third membrane module were not severely plasticized by the CO_2 due to an exposure of low concentration of CO_2. As a result, small value of pressure-normalized flux was detected. Hence, a high selectivity is produced. However, in series configuration, all three-membrane modules experienced high feed pressures. As the feed pressure is increased, the CO_2 concentration will build up. When this is occurring, the highly sorbed CO_2 plasticized the membrane, which results in an increase in CO_2 pressure-normalized flux [4, 19].

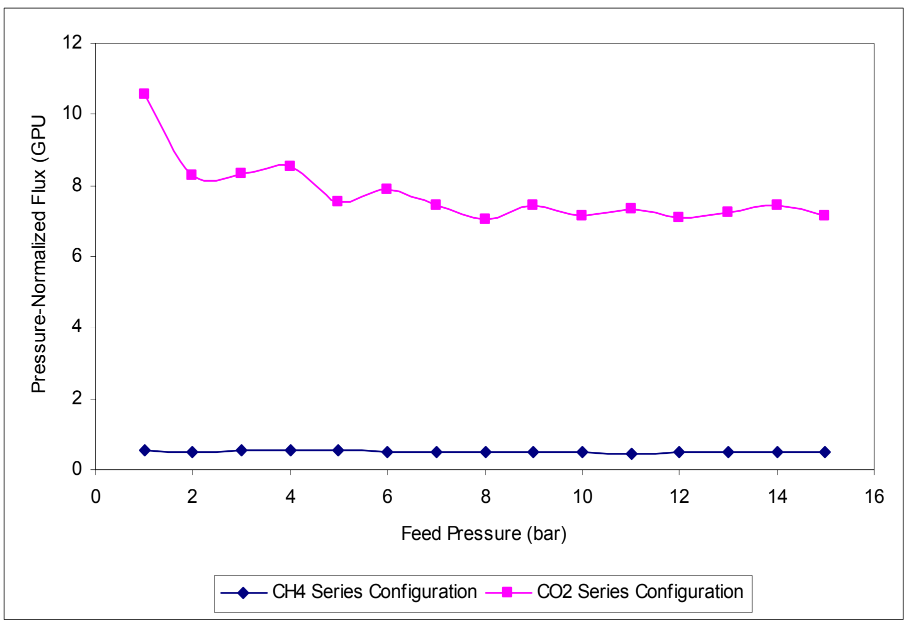

Figure 4: Pressure-normalized flux of CH_4 and CO_2 for series configuration

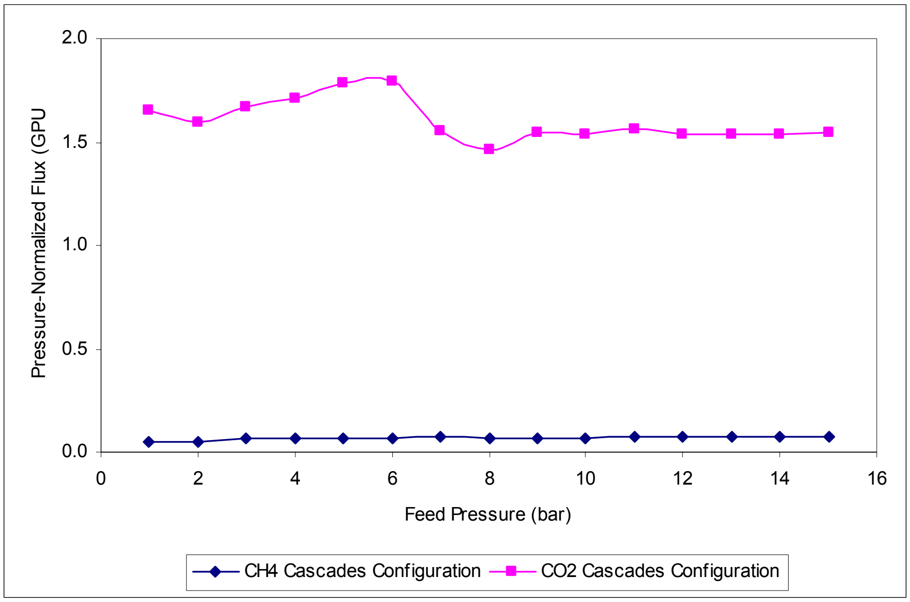

Figure 5: Pressure-normalized flux of CH_4 and CO_2 for cascades configuration

Figure 6 showed that cascade configuration exhibited higher CO_2/CH_4 selectivity values than the series configuration. In fact, the results for the first two feed pressures exhibited selectivities exceeded the recognized polysulfone intrinsic selectivity of 28. According to Chung et al. [8], glassy membrane materials exposed to high pressure CO_2 environments exhibit different permeability behavior due to plasticization induced by CO_2 sorption. As a result, membrane pressure-normalized flux increases and selectivity decreases.

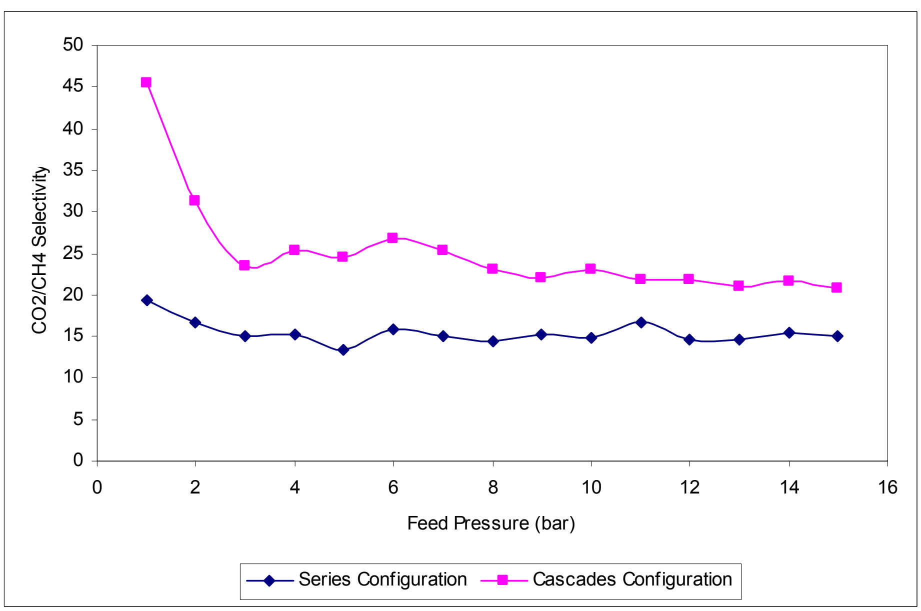

Figure 6: Selectivities of CO_2/ CH_4 for series and cascades configurations

Varying the feed flow rate at a constant feed pressure can alter the stage cut. In a membrane system, the first gas that permeated is the most highly enriched in the rapidly diffusing component. A very small stage cut across the membrane yields the purest permeate product. As larger stage cuts are taken, the feed gas becomes enriched in the gases which permeate more slowly and both their driving force and their concentration in the permeate are increased. The permeates becomes less pure as a larger fraction of the feed gas is permeated [30].

The effect of stage cut on CO_2 and CH_4 feed pressure is shown in Figure 7 and 8. The stage cut increased with increasing CO_2 and CH_4 feed pressure for both configurations. This is because at higher feed pressure, the permeation driving force increases and causes the passage of larger amounts of the more permeable gas to diffuse through the membrane. Basically, the purity of the permeate stream, expressed in terms of CO_2 removal, decreases at higher stage cuts. So, as the stage cut is increased, the CO_2 permeate purity decreases [24]. However, the stage cut values decreases as the feed flowrate is further increased. This is due to the released of high-pressure gas in the retentate stream that reduces the permeation driving force. Between the two configurations studied, cascades configuration exhibit lower values of stage cut due to low pressure-normalized flux. In other words, CO_2 concentration in the permeate stream in cascade configuration is higher than in the series configuration.

Figure 9 and 10 showed the effect of stage cut on pressure-normalized flux of CO_2 and CH_4 gases. Generally, series configurations exhibited higher value of pressure-normalized flux with an almost a constant trend of pressure-normalized flux plots for both gases compare to cascade configuration. This is because of the reduction in the permeation driving force in cascade configuration.

4. Conclusions

Asymmetric hollow fiber gas separation membranes were prepared from polysulfone. The fibers were characterized by gas permeation experiment. We have studied the effect of series and cascade configuration of three-stage separation system.

In CO_2 permeation experiments, the pressure-normalized flux of CO_2 was found to increase with increasing feed pressure. This indicated that CO_2 had plasticized the membrane material. For series configuration, the pressure-normalized flux of CO_2 is in the range of 7 to 10 GPU with CO_2/CH_4 selectivity of about 13 to 19. Meanwhile, for cascades configuration, the pressure-normalized flux of CO_2 is in the range of 1.3 to 1.7 GPU with CO_2/CH_4 selectivity in the ranges of 20 to 45. As a result, three-stage membrane permeation system with cascades configuration exhibited selectivity exceeding the intrinsic selectivity of polysulfone polymer.

The performance of the hollow fiber membrane produced is measured through stage cut measurements. The effect of stage cut on feed pressure showed an increasing trend with increasing of CO_2 and CH_4 feed pressure for both configurations. This is due

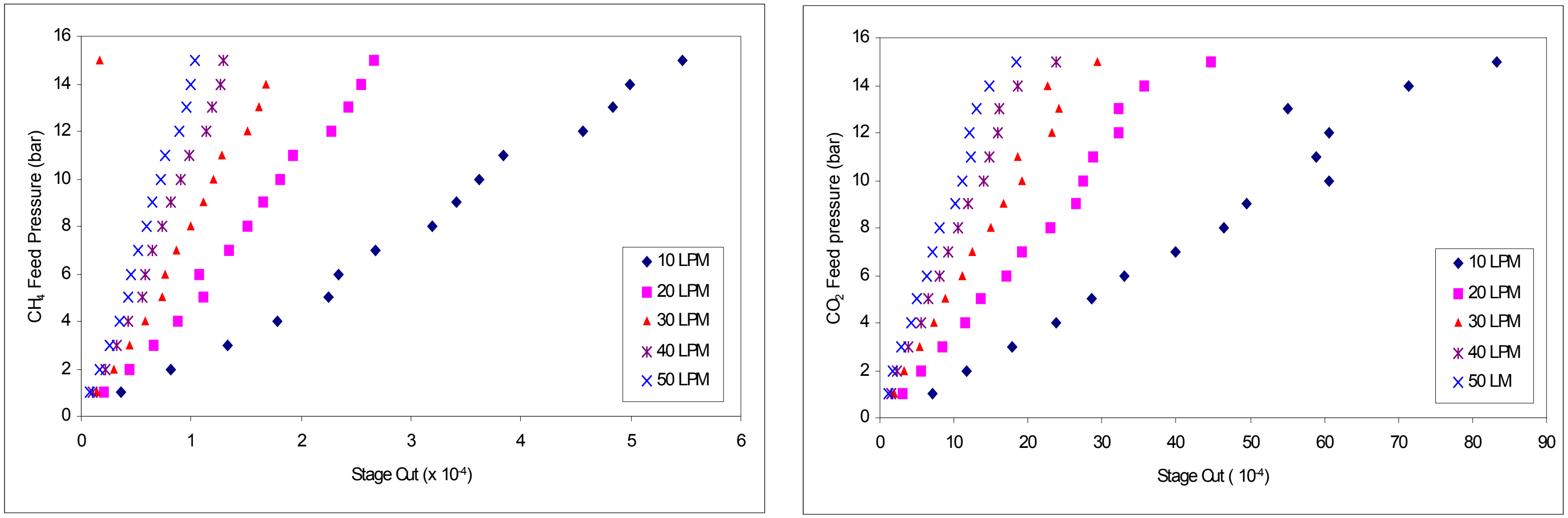

Figure 7: Effect of stage cut on feed pressure in series configuration

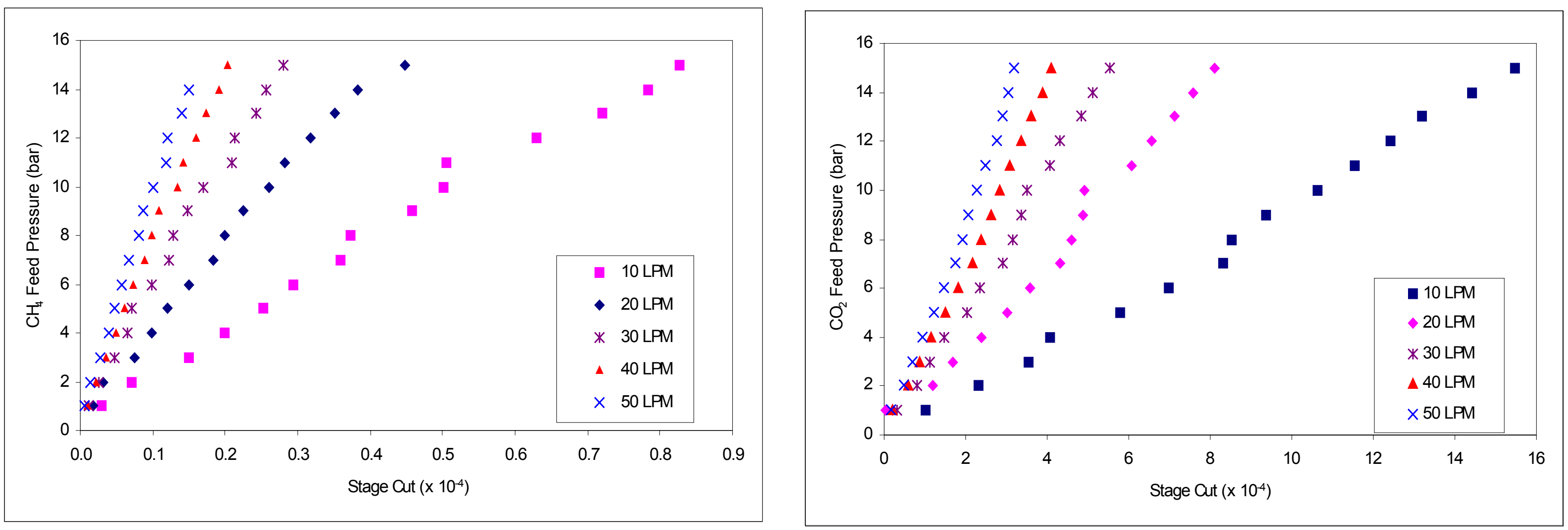

Figure 8: Effect of stage cut on feed pressure in cascade configuration

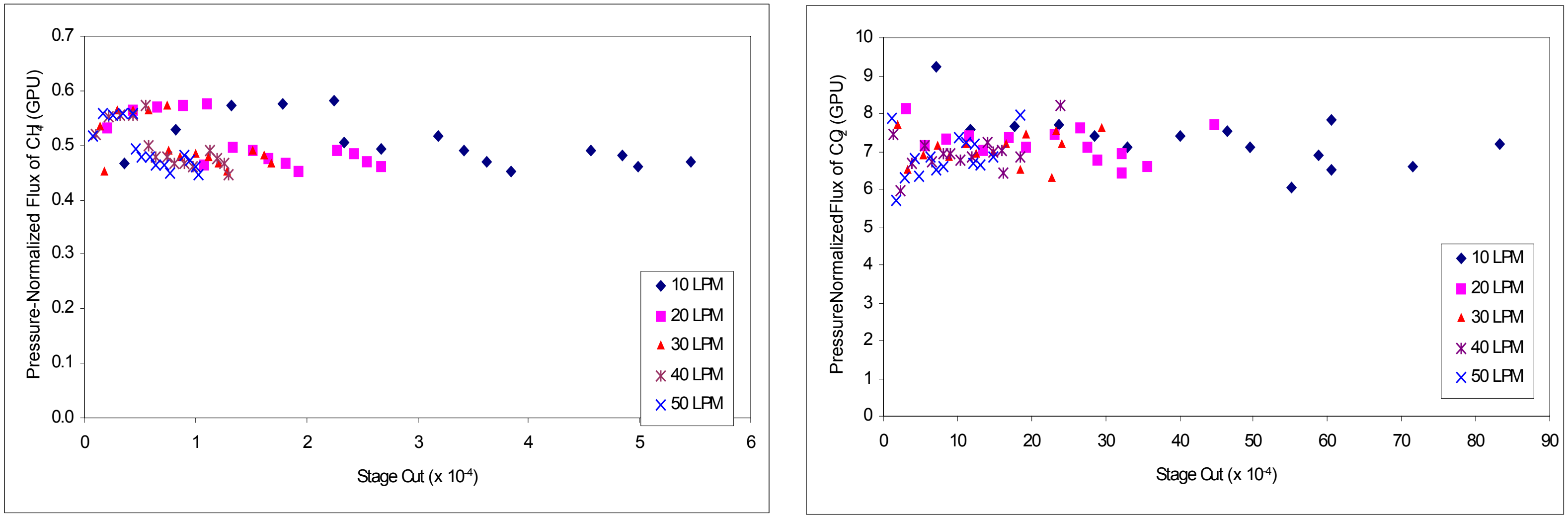

Figure 9: Effect of stage cut on pressure-normalized flux in series configuration

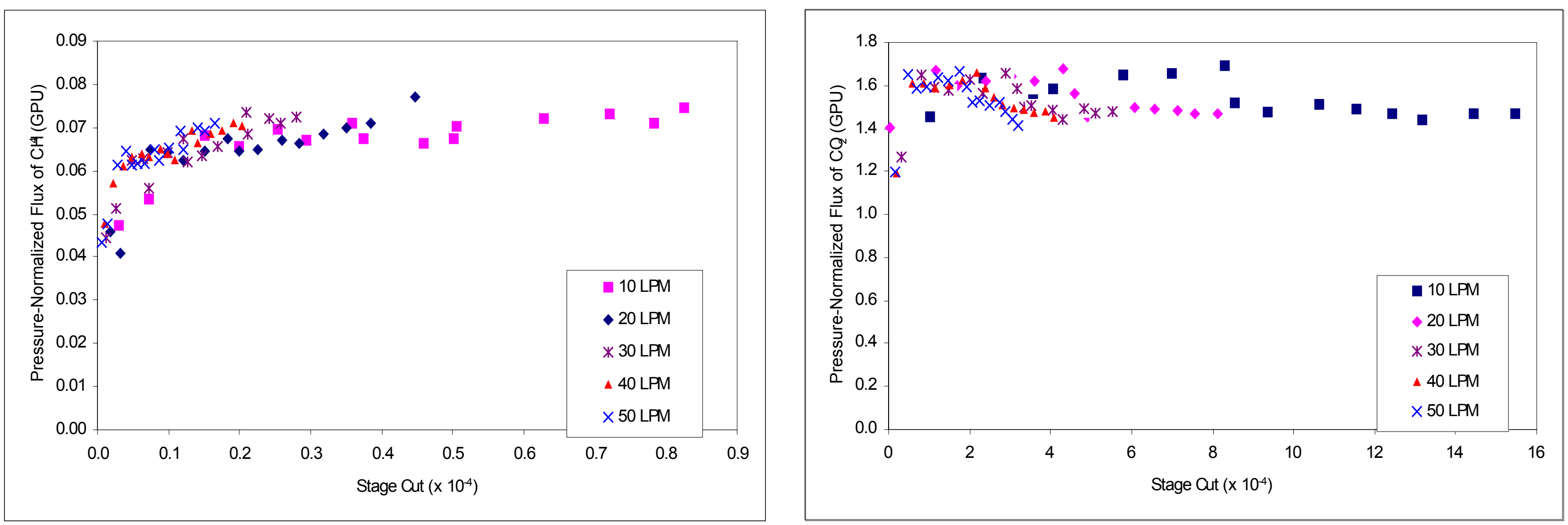

Figure 10: Effect of stage cut on pressure-normalized flux in cascade configuration

to the increased of the permeation driving force, which causes the passage of larger amounts of more permeable gas through the membrane. On the other hand, the graph explaining the effect of stage cut on pressure-normalized flux exhibit the same constant trend plots in both gases and configurations. However, the series configurations showed a much higher values of pressure-normalized flux compared to cascade configuration.

Cascade configuration exhibited a smaller stage cut values. A smaller stage cut promise purer CO_2 compare to higher stage cut. Therefore, cascades configurations promised a high purity of permeate CO_2. The results of this work are useful in determining the best configuration to be used with CO_2/CH_4 mixture.

References

[1] Scott, K. (1998). “Handbook of Industrial Membranes.” Elsevier Advanced Tech, 2nd Edition.

[2] Qi, R., Henson, M.A. (2000). “Membrane System Design for Multicomponent Gas Mixtures via Mixed-Integer Nonlinear Programming.” Computers and Chemical Engineering, 24; 2719-2737.

[3] Lababidi, H, Al-Enezi, G. A, Ettouney, H. M., (1996). “Optimization of Module Configuration in Membrane Gas Separation.” J. Memb. Sci., 112; 185-197.

[4] Bos, A., Punt, I. G. M., Wessling, M., Strathmann, H. (1998). “Plasticization-Resistant Glassy Polyimide Membranes for CO_2/CO_4 Separations.” Sep. Purif. Tech., 14; 27-39.

[5] Staudt-Bickel, C., Koros, W. J. (1999). “Improvement of CO_2/CH_4 Separation Characteristics of Polyimides by Chemical Crosslinking.” J. Memb. Sci., 155; 145-154.

[6] Chen, S. –H., Huang, S. –L., Yu, K. –C., Lai, J. –Y., Liang, M, –T. (2000). “Effect of CO_2 Treated Polycarbonate Membranes on Gas Transport and Sorption Properties.” J. Memb. Sci., 172; 105-112.

[7] Ismail, A. F., Lorna, W. (2002). “Penetrant-Induced Plasticization Phenomenon In Glassy Polymers For Gas Separation Membrane.’ Sep. Purif. Tech., 27; 173-194.

[8] Chung, T. –S., Ren, J., Wang, R, Li, D., Liu, Y, Pramoda, K. P., Cao, C., Loh, W. W. (2003). “Development of Asymmetric 6FDA-2, 6 DAT Hollow Fiber Membranes For CO_2/CH_4 Separation Part 2. Suppression of Plasticization. “J. Memb. Sci., 214; 57-69.

[9] Wonders, A. G., Paul, D. R., (1979). “Effect of CO_2 Exposure History on Sorption and Transport in Polycarbonate.’ J. Memb. Sci., 5; 63-75.

[10] Donohue, M. D., Minhas, B. S., Lee, S. Y. (1989). "Permeation Behavior of Carbon Dioxide-Methane Mixtures in Cellulose Acetate Membranes." J. Memb. Sci., 42; 197-214.

[11] Story, B. J., Koros, W. J., (1992). "Sorption and Transport of CO_2 and CH_4 in Chemically Modified Poly(phenylene oxide)." J. Memb. Sci., 67; 191-210.

[12] Houde, A. Y., Kulkarni, S. S., Kulkarni, M. G. (1992). "Permeation and Plasticization Behavior of Glassy Polymers: A WAXD Interpretation." J. Memb. Sci., 71; 117.

[13] Briscoe, B. J., Kelly, C. T. (1995). "The Plasticization of Polyurethane by Carbon Dioxide at High Pneumatic Stresses." Polymer, 36; 3099-3102.

[14] Kapantaidakis, G. C., Kaldis, S. P., Dabou, X. S., Sakellaropoulos, G.P. (1996). "Gas Permeation through PSF-PI Miscible Blend Membranes." J. Memb. Sci., 110; 239-247.

[15] Bos, A., Punt, I. G. M., Wessling, M., Strathmann, H. (1998). "Plasticization-Resistant Glassy Polyimide Membranes for CO_2/CO_4 Separations." Sep. Purif. Tech. , 14; 27-39.

[16] Wessling, M., Lidon Lopez, M., Strahmann, H. (2001). Accellerated Plasticization of Thin-Film Composite Membranes Used in Gas Separation." Sep. Purif. Tech. 24; 223.

[17] Koros, W. J., Woods, D. G. (2001). "Elevated Temperature Application of Polymer Hollow-Fiber Membranes." J. Memb. Sci., 181; 157-166.

[18] Mikawa, M, Nagaoka, S, Kawakami, H. (2002). "Gas Separation Stability of Asymmetric Polyimide Membrane with Thin Skin Layer: Effect of Molecular Weight of Polyimide." J. Memb. Sci., 208; 405-414.

[19] Kawakami, H., Nakajima, K., Shimizu, H., Nagaoka, S. (2003). "Gas Permeation Stability of Asymmetric Polyimide Membrane with Thin Skin Layer: Effect of Polyimide Structure." J. Memb. Sci., 212: 195-203.

[20] Barsema, J. N., Kapantaidakis, G. C., van der Vegt, N. F. A., Koops, G. H., Wessling, M. (2003). "Preparation and Characterization of Highly Selective Dense and Hollow Fiber Asymmetric Membranes Based on BTDA-TDI/MDI co-Polyimide." J. Memb. Sci., 216; 195-205.

[21] Bhide, B. D., Stern, S. A. (1991). "A New Evaluation of Membrane Processes For The Oxygen-Enrichment Of Air. I. Identification of Optimum Operating Conditions and Process Configuration." J. Memb. Sci., 62; 13-35.

[22] Bhide, B. D., Stern, S. A. (1993 (a)). "Membrane Processes for the Removal of Acid Gases From Natural Gas. I. Process Configurations and Optimization of Operating Conditions." J. Memb. Sci., 81; 209-237.

[23] Bhide, B. D., Stern, S. A. (1993 (b)). "Membrane Processes for the Removal of Acid Gases From Natural Gas. I. Effects of Operating Conditions, Economic parameters and Membrane Properties." J. Memb. Sci., 81; 239-252..

[24] Ettouney, H., Majeed, U. (1997). "Permeability Functions For Pure and Mixture Gases in Silicone Rubber and Polysulfone Membranes: Dependence on Pressure and Composition." J. Memb. Sci., 135; 251-261.

[25] Lim, P. C. (2002). "Development of Gas Separation Hollow Fiber Network." Ms.c Thesis.

[26] Ismail, A. F., Dunkin, I. R., Gallivan, S. L., Shilton, S. J. (1999). "Production of Super Selective Polysulfone Hollow Fiber Membranes for Gas Separation." Polymer, 40; 6499-6506.

[27] Yean, L. P., Ismail, A. F. (2004). "Development of Defect-Free Asymmetric Polysulfone Membranes for Gas Separation using Response Surface Methodology." Sep. Purif. Tech., In Press.

[28] Sharpe, I. D., Ismail, A. F., Shilton, S. J. (1999). "A Study of Extrusion Shear and Forced Convection Residence Time in the Spinning of Polysulfone Hollow Fiber Membranes for Gas Separation." Sep. Purif, Tech., 17; 101-109.

[29] Krol, J. J., Boerrigter, M., Koops, G. H. (2001). "Polyimide Hollow Fiber Gas Separation Membranes: Preparation and the Suppression of Plasticization in Propane/Polypropylene Environments." J. Memb. Sci., 184; 275-286.

[30] Ho, W. S. W., Sirkar, K. K. (1992). "Membrane Handbook." Chapman & Hall.