

EFFECT OF MEMBRANE SYSTEM CONFIGURATION ON THE PERFORMANCE OF POLYSULFONE HOLLOW FIBER MEMBRANE SYSTEM FOR CO₂/CH₄ SEPARATION

N. Yaacob, A. F. Ismail*

Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering,
University Teknologi Malaysia, 81310, Skudai, Johor.

*Corresponding author. Phone: +60-7-5535592, Fax: +60-7-5571463

Email address: afauzi@utm.my

ABSTRACT

In this study we focused on the effect of one- and two-stage membrane system configurations in series arrangement for the CO₂/CH₄ separation. Asymmetric polysulfone hollow fiber membranes were fabricated from 33%wt of polysulfone polymer using a simple dry/wet phase inversion process. Interestingly, the pressure-normalized flux of CO₂ was decreased with increasing of the membrane stages. In addition, the selectivities of the asymmetric hollow fiber membrane showed a more constant trend with increasing of feed pressure. Between the two configurations, two-stage membrane configuration showed the most constant trend of selectivity values. This results confirmed that the two-stage membrane configuration posses a significant influence on gas transport properties which lead to better selectivity values. The effect of stage cut on membrane system configurations was also investigated. This study suggests that the best CO₂/CH₄ separation was achieved by using two-stage membrane system configuration.

Keywords: Hollow Fiber, Gas Separation System, Membrane Configuration, Membrane Performance, Polysulfone

1 INTRODUCTION

The application of membranes for gas separation has grown rapidly since the installation of the first industrial plants in the early 1980s by Monsanto Company. Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. Removal of carbon dioxide is the only natural gas separation currently practiced on a large scale (more than 200 plants have been installed). Most were installed by Grace (now Kavanaugh-GMS), Separex (UOP) and Cynara. All of these plants used cellulose acetate membranes in hollow fiber or spiral wound module form. More recently, hollow fiber polyaramide (Medal) and polyimide (Ubc) membranes have been introduced due to their higher selectivity (Baker, 2000).

Carbon dioxide removal from natural gas has been practiced using cellulose acetate membranes for more than 10 years and the introduction of more selective polyimide membranes has begun and in time is likely to make membrane processes much more competitive with amine absorption. In the area of CO₂/CH₄ separation membranes, natural gas sweetening, the removal of carbon dioxide in landfill gas recovery processes and carbon dioxide removal from fractured wells as well as the removal of carbon dioxide in enhanced oil recovery applications (EOR) are of interest (Staudt-Bickel and Koros, 1999). The carbon dioxide produced can be injected into adjacent oil fields to enhance oil recovery (Lonsdale, 1982). In order to achieve excellent performance in membrane processes, the process reliability need to be enhanced to make the carbon dioxide removal technology the ultimate choice in a variety of processing conditions. It is crucial to transport the field gas through the conventional pipeline without catastrophic corrosion

problems. Hence, an efficient method to reduce the composition of carbon dioxide gas is critically in need and membrane gas separation processes was found to be the best solution.

Even though the separation of CO_2/CH_4 using polymeric membranes is growing rapidly, the plasticization of the membrane material is always a problem. This is due to the permeability of the slower gas is facilitated by the highly soluble, faster gas. This phenomenon is attributed to plasticization effects, caused by the high carbon dioxide solubility or interactions between carbon dioxide and the polymer material. As the membrane is plasticized the permeability increases significantly but the selectivity for gaseous mixtures decreases (Barsema et al., 2003). A good asymmetric membrane for natural gas separation can be achieved if it possesses the following material and performance characteristics: (1) inherently high permselectivity for carbon dioxide and methane gas pair and (2) immunity to plasticization induced by carbon dioxide. The CO_2 -induced plasticization usually causes a severe deterioration of membrane separation performance in the natural gas applications loss (Cao et al., 2003).

Only few researchers studied the effects of membrane configurations process and its effect on gas separation performance. Bhide and Stern (Bhide and Stern, 1991, 1993a, 1993b), Ettouney and Majeed (Ettouney and Majeed, 1997), Qi and Henson (Qi and Henson, 2000), Lim (Lim, 2002) and Yaacob and Ismail (Yaacob and Ismail, 2004) studied single, two, three, four and multi-stage membrane in both series and cascade configurations especially for the separation of CO_2/CH_4 and O_2/N_2 gas mixture. The glassy polymer membrane materials used were silicone rubber, poly (phenylene oxide), cellulose acetate or polysulfone. Table 1 summarized the type of membrane module and membrane configuration used by previous researchers.

FIGURE 1: Membrane module and membrane configuration studied by previous researchers

Researcher(s)	Membrane Module	Membrane Configuration	Test Gas
Bhide and Stern (1991)	Single and two-stage	Cascade and series	O_2/N_2
Bhide and Stern (1993)	Single, two and three-stage	Cascade and series	CO_2/CH_4
Ettouney and Majeed (1997)	Single, two and three-stage	Series	O_2/N_2
Qi and Henson (2000)	Two, three and four-stage	Cascade and series	CO_2/CH_4
Lim (2002)	Multi-stage	Cascade and series	CO_2/CH_4 and O_2/N_2
Yaacob and Ismail (2004)	Three-stage	Cascade and series	CO_2/CH_4

This paper aims to investigate the effect of series module configuration of a single and two -stage separation system on the performance of CO_2/CH_4 gas separation in order to reduce the extent of plasticization phenomena in glassy polymer membranes. The illustration of the membrane configuration is shown in Figure 1. Therefore, a thorough understanding of plasticization phenomenon is crucial to develop and achieve a high performance membrane in order to make membrane separation application attractive.

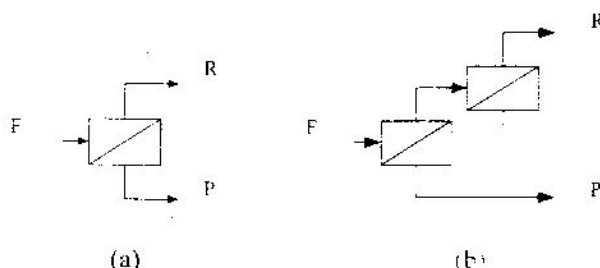


FIGURE 1. Membrane configuration of (a) single stage and (b) two-stage series membrane module

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, tetrahydrofuran 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 speed) 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 (Ismail et al., 1999).

2.2 PURE GAS CARBON DIOXIDE AND METHANE-PERMEATION BEHAVIOR OF UNTREATED MEMBRANES IN SINGLE, TWO AND THREE-STAGE

Pure gas carbon dioxide, CO₂ and methane, CH₄ gas permeation experiments were performed to determine the possibility of using asymmetric polysulfone hollow fiber membrane for CO₂ and CH₄ separation. The hollow fiber prepared had a skin layer thickness of about 2.09 x 10⁻⁵ cm. This value was calculated based on theory proposed by (Ismail and Lai, 2004). In order to minimize gas consumption, all tests were performed on a laboratory scale hollow fiber module made of ten fibers with 30 cm long. During testing, the high pressure feed gas was directed to flow through the shell side of the module at controlled pressure and the permeate was withdrawn from the open fiber bore. The permeate volumetric flow rate was measured by means of a bubble flow meter (Kapantaidakis *et al.*, 1996, Yamasaki *et al.*, 1997, Wang *et al.*, 2002a) reading to 1.0 cm³. The gas bubble flow meter is used because of the small membrane area which results in much lower permeate flow rates with values close to the meter accuracy (Ettouney and Majeed, 1997). A ball valve was installed at the end of the retentate stream to control the retentate flow as a function of feed pressure.

For two-stage series configuration, the retentate stream from the first membrane module was used as the feed stream for the second membrane module. Permeate flow was measured in the same manner as mentioned above.

3 RESULTS AND DISCUSSION

Pure gas permeation test was conducted in order to determine whether the membrane prepared is suitable to be used in CO₂/CH₄ separation. Permeation was conducted using pure CH₄ and CO₂ gases respectively. The hollow fiber module was coated with silicone before put to test. The gases were exposed to the hollow fiber membranes for at least 20 minutes to equilibrate. Figure 2 showed the pressure-normalized flux of CO₂ and CH₄ of asymmetric polysulfone hollow fiber membrane in single-stage as a function of the feed pressures.

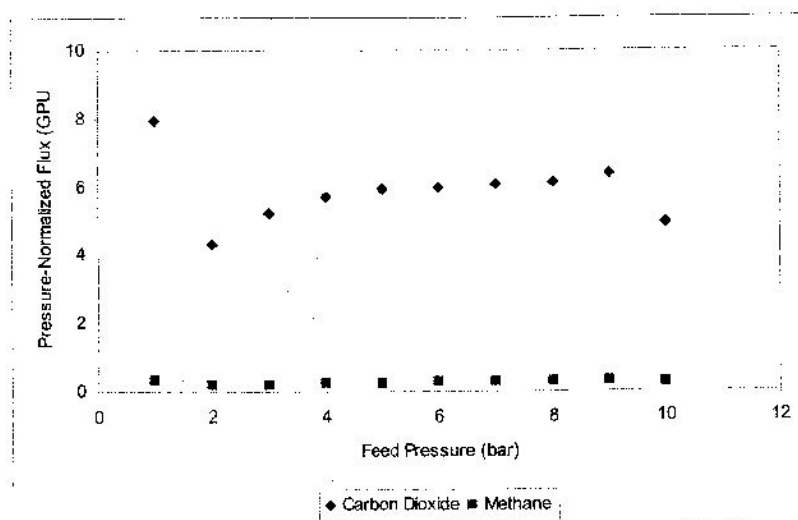


FIGURE 2. Pressure-normalized flux of methane and carbon dioxide of untreated asymmetric polysulfone hollow fiber membrane in single-stage as a function of the feed pressures.

From the figure, the pressure-normalized flux of CO_2 exhibited an immediate increase with increasing feed pressure especially after feed pressure of about 2 bars. According to Chung et al. (Chung et al., 2003), glassy membrane materials exposed to high-pressure CO_2 environments exhibit different pressure-normalized flux behavior due to plasticization induced by CO_2 sorption. As a result, membrane pressure-normalized flux increases and selectivity decreases. This means, at feed pressure of 2 bars the CO_2 gas concentration is already sufficient or high enough to disrupt the chain packing in the polymer material resulting in an increased segmental or chain mobility which leads to the increasing of gas diffusion (Bos et al., 1998, Bos et al., 1999). As the feed pressure is further increased, CO_2 concentration will build up. Increases of CO_2 concentration are the main factor that contributed to the plasticization phenomena or membrane swelling which results in an increase in CO_2 pressure-normalized flux. However, the pressure-normalized flux of CH_4 showed an almost constant trend as the feed pressure increases. This behavior is in agreement with the dual mode sorption transport model as studied and predicted by previous researchers (Bos et al., 1998, Krol et al., 2001 Kawakami et al., 2003). The increasing trend of the pressure-normalized flux of CO_2 results in reduced selectivity with the increasing of the feed pressure as shown in Figure 3.

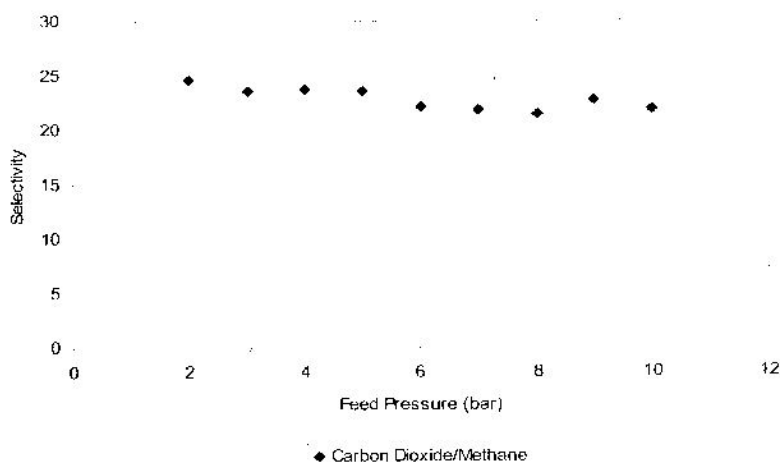


FIGURE 3. CO_2/CH_4 selectivity of untreated asymmetric hollow fiber membrane in single-stage as a function of feed pressures.

The decreasing of the CO_2 pressure-normalized flux with increasing CO_2 pressure in glassy polymer is consistent with the well-known dual mode sorption and transport model

predictions (Staudt-Bickel and Koros, 1999). However, in some cases the pressure-normalized flux does not further decrease with increasing feed pressure but even continue to increase. The pressure at which the increase in permeance occurs (i.e. the minimum in the pressure-normalized flux versus pressure plot) is called the plasticization pressure. At such feed pressures the gas concentration in the polymer material disrupts the chain packing. The polymer matrix swells and the segmental mobility of the polymer chains increases. This results in an increase in the gas diffusivity and therefore the permeability increases (Krol et al., 2001). The selectivity increase is mainly due to the tightened chain packing induced by shear rates while the selectivity decrease is mainly due to relatively porous skin structures induced by low viscosity (Chung *et al.*, 2000a). Selectivity increase can also be attributed to the enhanced polymer molecule orientation attributed at high shear (Shilton et al., 1997). According to Ismail et al, (Ismail et al., 1997) enhanced molecular orientation may enable membrane selectivities to be elevated beyond the recognized, intrinsic value of the polymer.

It is clear that sorption of CO₂ causes severe plasticization effects in single-stage hollow fiber membrane. In order to compare the plasticization effects in single-stage hollow fiber membrane module, gas permeation of a two-stage hollow fiber membrane module in series configuration was conducted. This is to determine whether membrane configuration can be manipulated in order to control plasticization effects. Figure 4 exhibited the pressure-normalized flux trend in two-stage hollow fiber membrane module in series configuration of asymmetric polysulfone hollow fiber membrane. This configuration is suitable for the production of the less permeable species or retentate component. According to Callahan (Callahan, 1999), two-stage membrane module was able to produce about 98% pure CH₄ retentate product in the separation of CO₂ from wellhead natural gas using polycarbonate membrane and produce about 99% pure nitrogen, N₂ retentate product in the production of N₂ enriched air using cellulose acetate membrane.

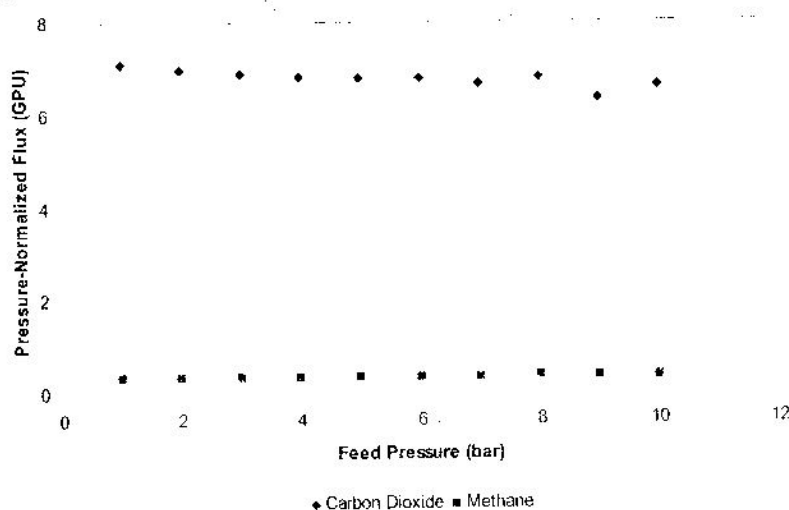


FIGURE 4. Pressure-normalized flux of methane and carbon dioxide of untreated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressures.

The pressure-normalized flux of methane showed a constant trend as a function of feed pressure. This means that pressure-normalize flux of methane followed the dual mode transport theory. However, the main attraction here is the pressure-normalized flux of CO₂. Since the pressure-normalized flux of CO₂ increases in single-stage membrane module, the same trend might also be exhibited in two-stage membrane module. However, the pressure-normalized flux of CO₂ seems to decrease slightly as a function of feed pressure. This is probably due to less pronounced of CO₂-induced plasticization effects that took place. This might be because the more permeable CO₂ permeated through the first membrane module so rapidly leaving behind the residue gas to be further separated in the second membrane module. The second membrane module experience a much more efficient separation since the retentate stream contain less fast permeated gas. As a result,

the second membrane module was less plasticized. The separation took place in two-stage membrane module is more efficient than in single-stage membrane module. As a result, the selectivity of two-stage membrane module revealed a much more constant trend compared to the selectivity of the single-stage membrane module as shown in Figure 5.

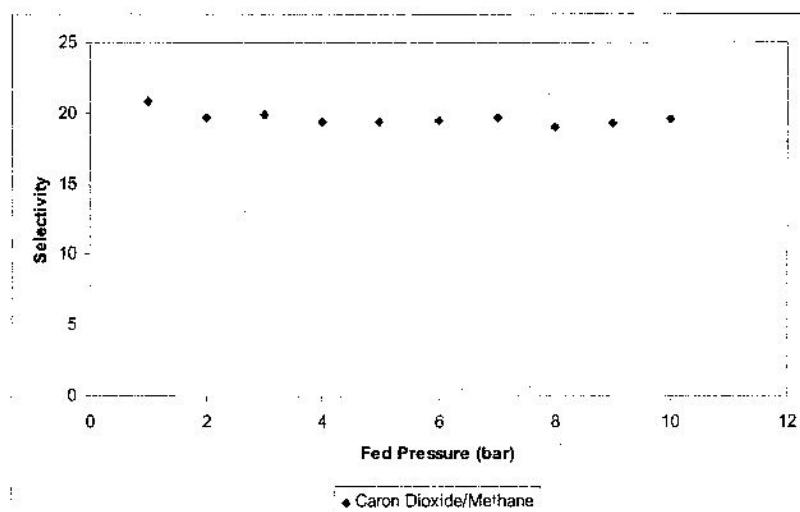
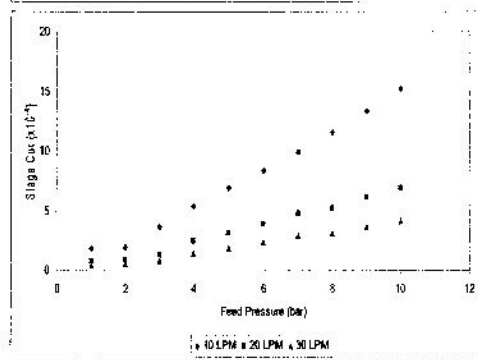
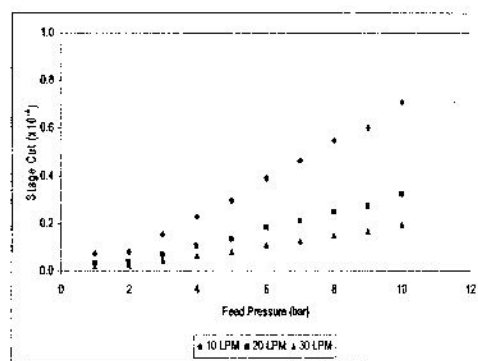


FIGURE 5. CO₂/CH₄ selectivity of the untreated asymmetric hollow fiber membrane in two-stage series configuration as a function of feed pressures.

The stage cut can be changed by varying the feed flow rate at constant feed pressure and temperature. Stage cut is the ratio of permeate flow rate to feed flow rate (Coker et al., 1999). Figure 8(a-f) presents the impact of feed flow rate on stage cut of single, two and three-stage membrane module.

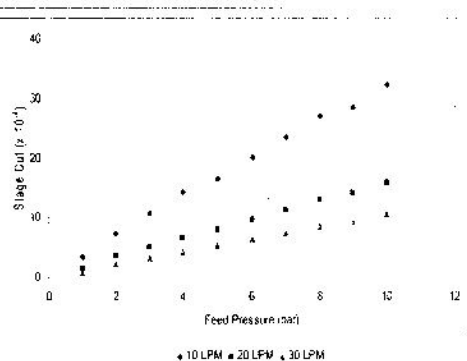
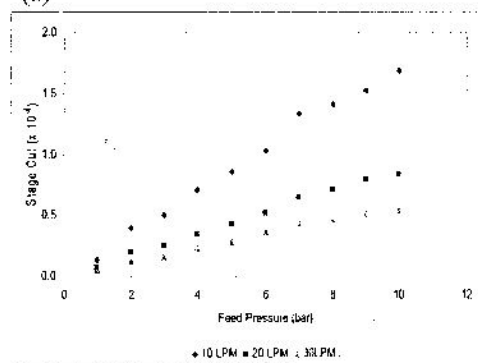
The stage cut exhibited an increased trend with increasing CO₂ and CH₄ feed pressure in all both membrane module configurations. More interestingly, the stage cut values increases with increasing of membrane stages or membrane area. The stage cut in single stage varies from 0.02×10^{-4} to 0.7×10^{-4} for CH₄ and from 0.5×10^{-4} to 15.2×10^{-4} for CO₂; and stage cut of two-stage ranges from 0.05×10^{-4} to 1.7×10^{-4} for CH₄ and from 0.9×10^{-4} to 32.3×10^{-4} for CO₂. Two-stage membrane module exhibited higher stage cut compared to single-stage due to larger permeation area. 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 CO₂ removal, decreases at higher stage cuts. So, as the stage cut is increased, the CO₂ permeate purity decreases (Ettouney and Majeed, 1997).

However, the stage cut values decreases as the feed flow rate is further increased. This is due to the released of high-pressure gas in the retentate stream that reduces the permeation driving force.



(a)

(c)



(b)

(d)

FIGURE 8. Effect of methane stage cut on feed pressure in (a) single-stage and (b) two-stage series configuration and effect of carbon dioxide stage cut on feed pressure in (c) single-stage and (d) two-stage series configuration

4 CONCLUSIONS

The present results are consistent with the studies of previous researchers in showing that the more permeable CO_2 in glass polymers will cause the polymer to plasticize to an extent depending on the concentration of the dissolved gas. As the feed pressure is further increased, CO_2 concentration will build up and is sufficient enough to disrupt the chain

packing in the polymer material resulting in an increased segmental mobility which leads to the increasing of gas diffusion.

Pressure-normalized flux of CO₂ in single-stage membrane module exhibited poor result indicating that plasticization phenomena had takes place at low feed pressure. However, the pressure-normalized flux of CO₂ decreased slightly in two-stage membrane module. The decreased in the pressure-normalized flux is well described in terms of a dual ode transport model. This is probably due to more permeable CO₂ had permeated in the first membrane module leaving behind small concentration of the more permeable CO₂ to be refined in the next stages. As a result a better selectivity value is exhibited. Two-stage membrane module posses the best selectivity value with a constant trend.

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 CO₂ and CH₄ feed pressure in all three configurations. This is due to the increased of the permeation driving force, which causes the passage of larger amounts of more permeable gas through the membrane. Three-stage membrane module showed the highest stage cut while single-stage membrane module had the lowest stage cut values.

Two-stage membrane module in series configuration exhibited a decreased trend of CO₂ pressure-normalized flux and results in the most constant selectivity values which is slightly below the intrinsic selectivity of polysulfone compared to single and three-stage membrane module. Therefore, two-stage membrane module is the most suitable configuration to be used for CO₂/CH₄ separation.

REFERENCES

- Baker, R. W. (2000). *Membrane Technology and Applications*. McGraw-Hill, New York.
- Staudt-Bickel, C., Koros, W. J. (1999). "Improvement of CO₂/CH₄ Separation Characteristics of Polyimides by Chemical Crosslinking." *J. Membr. Sci.* 155: 145-154.
- Lonsdale, H. K. (1982). "The Growth of Membrane Technology". *J. Membr. Sci.* 10: 81-181.
- 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. Membr. Sci.* 216: 195-205.
- Cao, C., Chung, T. -S., Liu, Y., Wang, R., Pramoda, K. P. (2003). "Chemical Cross-Linking Modification of 6FDA-2, 6-DAT Hollow Fiber Membranes for Natural Gas Separation." *J. Membr. Sci.* 216: 257-268.
- 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.
- 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.
- 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.
- 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.
- 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.

- Lim, P. C. (2002). "Development of Gas Separation Hollow Fiber Network." Ms.c Thesis.
- Yaacob, N., Ismail, A. F. "Polysulfone Hollow Fiber membrane System for CO₂/CH₄ Separation: Influence of Membrane Module Configuration on the Separation Performance." Presented at the Membrane Science and Technology Symposium 2004, 21-25 April 2004, Johor Bharu.
- 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.
- Ismail, A. F., Lai, P. Y. (2004). "Development of Defect-Free Asymmetric Polysulfone Membranes for Gas Separation using Response Surface Methodology." *Sep. Purif. Tech.*, In Press.
- 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.
- Yamasaki, A., Tyagi, R. K., Fonda, A. E., Matsuura, T., Jonasson, K. (1997). Effect of Gelation Conditions on Gas Separation Performance for Asymmetric Polysulfone Membranes. *J. Membr. Sci.* 123: 89-94.
- Wang, R., Liu, S. L., Liu, T. T., Chung, T. -S. (2002a). Characterization of Hollow Fiber Membranes in a Permeator using Binary Gas Mixtures. *Chem.Eng. Sci.* 57: 967-976.
- 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 CO₂/CH₄ Separation Part 2. Suppression of Plasticization." *J. Membr. Sci.* 214: 57-69.
- Bos, A., Punt, I. G. M., Wessling, M., Strathmann, H. (1998). "Plasticization-Resistant Glassy Polyimide Membranes for CO₂/CO₄ Separations" *Sep. Purif.Tech.* 14: 27-39.
- Bos, A., Punt, I. G. M., Wessling, M., Strathmann, H. (1999). "CO₂-Induced Plasticization Phenomena in Glassy Polymers." *J. Membr. Sci.* 155: 67-78.
- 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. Membr. Sci.* 184: 275-286.
- 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. Membr. Sci.* 212: 195-203.
- Chung, T. -S., Lin, W. H., Vora, R. H. (2000a). "The Effect of Shear Rates on Gas Separation Performance of 6FDA-Durene Polyimide Hollow Fibers." *J. Membr. Sci.* 167: 55-66.
- Shilton, S. J., Ismail, A. F., Gough, P. J., Dunkin, I. R., Gallivan, S. L. (1997). "Molecular Orientation and the Performance of Synthetic Polymeric Membranes for Gas Separation." *Polymer*. 38:2215-2220.
- Ismail, A. F., Shilton, S. J., Dunkin, I. R., Gallivan, S. L. (1997). "Direct Measurement of Rheologically Induced Molecular Orientation in Gas Separation Hollow Fibre Membranes and Effects on Selectivity." *J. Membr. Sci.* 126:133-137.
- Callahan, R. A. (1999). "Multiple Stage Semi-Permeable Membrane Process and Apparatus for Gas Separation." US Patent 5,873,928.
- Coker, D. T., Allen, T., Freeman, B. D., Fleming, G. K. (1999). "Nonisothermal Model for Gas Separation Hollow-Fiber Membranes." *AIChE Journal*. 45: 1451-1468.