Polysulfone hollow fiber membrane system for CO$_2$/CH$_4$ separation: Influence of membrane module configuration on the separation performance

N. Yaacob, A. F. Ismail*

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

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...
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, polyyurethane, 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.

![Diagram](image)

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, 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±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 [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\textsubscript{2} and CH\textsubscript{4} gas through hollow fiber polysulfone membranes

Three-stage gas permeation characteristics were measured with a permeation setup as shown in Figure 2. The hollow fiber membrane modules prepared contain ten fibers with an effective membrane area of about 56.56 cm\textsuperscript{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\textsubscript{4} (99.5%) or CO\textsubscript{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:

\[
\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta P \cdot A}
\]

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

\[
\alpha_{A,B} = \frac{P/l_A}{P/l_B}
\]
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].
Table 1 shows the pressure-normalized flux and CO₂/CH₄ selectivity of polysulfone hollow fibers in both series and cascade configurations. Hollow fibers module in cascade configuration exhibited the highest selectivity (~45) compared to hollow fiber module in series configuration that only showed selectivity of about 19. The CO₂/CH₄ selectivity of polysulfone dense membranes is reported to be about 30.

<table>
<thead>
<tr>
<th>Feed Pressure (bar)</th>
<th>CO₂/CH₄ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cascade Configuration</td>
</tr>
<tr>
<td>1</td>
<td>45.39</td>
</tr>
<tr>
<td>2</td>
<td>31.19</td>
</tr>
<tr>
<td>3</td>
<td>23.42</td>
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</tbody>
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Figure 4 and 5 showed the effect of feed pressure on pressure-normalized flux of CH₄ and CO₂ gases in series and cascades configurations respectively. CH₄ gas showed a constant trend of pressure-normalized flux as a function of feed pressure. However, CO₂ 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 CO₂ as a function of feed pressure indicated that CO₂ plasticization in polysulfone membranes occurs for feed pressures greater than 1 bar for both configurations. A high CO₂ 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](image)
Figure 5: Pressure-normalized flux of CH₄ and CO₂ for cascades configuration

Figure 6 showed that cascade configuration exhibited higher CO₂/CH₄ 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 CO₂ environments exhibit different permeability behavior due to plasticization induced by CO₂ sorption. As a result, membrane pressure-normalized flux increases and selectivity decreases.

Figure 6: Selectivities of CO₂/CH₄ 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 CO₂ and CH₄ 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


