SUPRESSION OF PLASTICIZATION ON ASSYMETRIC HOLLOW FIBER POLYSULFONE MEMBRANE USING CONSTANT HEATING AND PROGRESSIVE HEATING TECHNIQUES

MUHAMAD AZWAR BIN AZHARI

A thesis submitted in fulfillment of the requirements for the award of the degree of Master of Engineering (Gas)

Faculty of Petroleum and Renewable Energy Engineering
Universiti Teknologi Malaysia

May 2012
Dedicated to those who persevere..
ACKNOWLEDGEMENTS

Alhamdulillah, praise Allah for His grace and guidance throughout this whole studies which I am blessed to finally have completed.

From the bottom of my humble heart, I thank my supervisor, Prof. Dr. Ahmad Fauzi bin Ismail for giving me a chance to be one of his postgraduate student. I thank him for his continuous support, attention, guidance and all the knowledge, understanding and comments that made this study a success.

Greatest gratitude goes to the helpful Research Officers of AMTEC, Mr. Sohaimi Abdullah, Mr. Ng Be Cheer and Mdm. Suhaila Sanip for their kind physical and moral assistance that kept me breathing in times of difficulty. To my fellow research friends in AMTEC, no words can describe my appreciation to what have been shared throughout the years here. The knowledge shared and the moral support given, I can never say enough thank you. May Allah be the one return all the good deeds that you have showered me with.

Last but not least, I thank my whole family for their love and support and my sincere appreciation goes to every organization and personnel that have directly or indirectly contributed into the success of this study. May His blessings be with all. Thank you.
ABSTRACT

This study investigates the effect of heating on suppression of plasticization effect upon asymmetric hollow fiber polysulfone membranes for carbon dioxide/methane separation. The membranes were fabricated using polysulfone (Udel P1700) and heat treated before tested on pure methane and carbon dioxide gases to study their gas separation characteristics. Constant temperature heating and progressive temperature heating were applied to the membranes. The produced membranes were then characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and fiber density calculation. Membranes treated with constant temperature heating exhibits lower pressure-normalize flux for both carbon dioxide and methane while their selectivity increased compared to untreated membranes. This was probably due to densification of membrane skin layer during heating process. Denser skin layer increases the resistance in the membrane which resulted in decreased of pressure-normalize flux. A higher density of membrane skin layer was achieved by progressive temperature heat treatment. This further increased the resistance in the membrane resulted in a lower value of pressure normalized-flux which surpasses the intrinsic value. The application of different feed pressure caused an almost linear value of CO₂ and CH₄ pressure-normalize flux were observed. This indicated that plasticization is successfully suppressed by heat treatment. At progressive heating to 90°C, a modest pressure-normalized flux value of 0.16 GPU and 4.34 GPU were achieved for CH₄ and CO₂, respectively. It is also observed that the CO₂/CH₄ selectivity increases with increment of temperature for both type of heating. However, progressive heating to 90°C shows a promising selectivity result of 27.06. From the results provided in this study, it can be concluded that plasticization of polysulfone hollow fiber membrane is successfully suppressed by heat treatment process.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td></td>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td></td>
<td>DEDICATIONS</td>
<td>iii</td>
</tr>
<tr>
<td></td>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td></td>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td></td>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
<tr>
<td></td>
<td>LIST OF SYMBOLS</td>
<td>xv</td>
</tr>
<tr>
<td></td>
<td>LIST OF APPENDICES</td>
<td>xvii</td>
</tr>
</tbody>
</table>

## 1 INTRODUCTION

1.1 Natural Gas Processing 1
1.2 Membrane for Carbon Dioxide Removal 4
1.3 Problem Statement 6
1.4 Objectives of Research 9
1.5 Scope of Research 9

## 2 LITERATURE REVIEW

2.1 Membrane for Gas Separation 10
2.2 Gas Transport and Separation in Membrane 13
2.2.1 Gas Transport in Porous Membranes 14
2.2.2 Gas Transport in Dense Membranes 15
2.3 Asymmetric Membrane
   2.3.1 Membrane Formation Through Phase Inversion
   2.3.2 Dry/Wet Phase Inversion
   2.3.3 Dry Phase Inversion
   2.3.4 Wet Phase Inversion
2.4 Membrane Module
2.5 CO₂ Induced Plasticization in Glassy Polymers
2.6 Suppression of CO₂ Induced Plasticization
   2.6.1 Cross-Linking
   2.6.2 Polymer Blending
   2.6.3 Heat Treatment

3 METHODOLOGY

3.1 Research Design
3.2 Material Selection
   3.2.1 Polymer
   3.2.2 Solvents
   3.2.3 Gases
3.3 Fabrication of Asymmetric Hollow Fiber Membrane
   3.3.1 Turbidimetric Titration Method
   3.3.2 Preparation of Multi Component Dope Solution
   3.3.3 Membrane Fabrication Using Dry/Wet Spinning Process
   3.3.4 Hollow Fiber Coating
3.4 Heat Treatment
3.5 Characterization
   3.5.1 Scanning Electron Microscopy (SEM)
   3.5.2 Differential Scanning Calorimetry (DSC)
   3.5.3 Fiber Density Calculation
   3.5.4 Gas Permeation Tests
4 RESULTS AND DISCUSSIONS

4.1 Spinning Solution Formulation

4.2 Effect of Constant Temperature Heating on Polysulfone Asymmetric Hollow Fiber Membrane

4.2.1 Carbon Dioxide and Methane Gas Permeation Behavior in Treated and Untreated Membrane

4.2.2 Effect of Constant Temperature Heating on Physical Morphology of Polysulfone Asymmetric Hollow Fiber Membrane

4.2.3 Effect of Constant Temperature Heating on Fiber Density

4.3 Effect of Progressive Temperature Heating on Polysulfone Asymmetric Hollow Fiber Membrane

4.3.1 Carbon Dioxide and Methane Gas Permeation Behavior in Constant Temperature and Progressive Heated Membrane

4.3.2 Effect of Progressive Temperature Heating on Physical Morphology of Polysulfone Asymmetric Hollow Fiber Membrane

4.3.3 Effect of Progressive Heating on Fiber Density

4.3.4 Effect of Progressive Temperature Heating on Glass Transition Temperature (T_g)

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1 Recommendations
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Principal suppliers of membrane natural gas separation system</td>
<td>5</td>
</tr>
<tr>
<td>1.2</td>
<td>Comparison of amine and membrane CO₂ removal system</td>
<td>7</td>
</tr>
<tr>
<td>2.1</td>
<td>Principal gas separation markets and producers</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Difference of glassy and rubbery polymers for gas separation</td>
<td>12</td>
</tr>
<tr>
<td>2.3</td>
<td>Characteristics of different membrane module</td>
<td>22</td>
</tr>
<tr>
<td>2.4</td>
<td>Comparison of membrane modules</td>
<td>24</td>
</tr>
<tr>
<td>2.5</td>
<td>Summary of heat treatment studies by previous researchers</td>
<td>33</td>
</tr>
<tr>
<td>3.1</td>
<td>Physical and mechanical properties of polysulfone</td>
<td>36</td>
</tr>
<tr>
<td>3.2</td>
<td>Summary of spinning conditions</td>
<td>42</td>
</tr>
<tr>
<td>3.3</td>
<td>Properties of carbon dioxide and methane</td>
<td>45</td>
</tr>
<tr>
<td>4.1</td>
<td>Summary of solution concentration before and after ethanol titration</td>
<td>47</td>
</tr>
<tr>
<td>4.2</td>
<td>Average fiber density for constant temperature heated and untreated membranes</td>
<td>54</td>
</tr>
<tr>
<td>4.3</td>
<td>Average fiber density for progressive temperature heated and untreated membranes</td>
<td>69</td>
</tr>
<tr>
<td>4.4</td>
<td>Glass transition temperature for constant temperature heated, progressive heated and untreated membranes</td>
<td>71</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Typical natural gas amine absorber for carbon dioxide removal</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Gas transport in porous membrane according to convective flow, Knudsen diffusion and molecular sieving</td>
<td>15</td>
</tr>
<tr>
<td>2.2</td>
<td>Solution diffusion mechanism in dense membrane</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic phase diagram consisting polymer, solvent and non-solvent</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Carbon dioxide permeation behavior in glassy polymers</td>
<td>26</td>
</tr>
<tr>
<td>3.1</td>
<td>Research flow chart</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>Molecular structure of polysulfone</td>
<td>35</td>
</tr>
<tr>
<td>3.3</td>
<td>Turbidimetric titration apparatus</td>
<td>38</td>
</tr>
<tr>
<td>3.4</td>
<td>Apparatus for polymer dope solution preparation</td>
<td>39</td>
</tr>
<tr>
<td>3.5</td>
<td>Hollow fiber spinning apparatus</td>
<td>40</td>
</tr>
<tr>
<td>4.1</td>
<td>Pressure-normalized flux of carbon dioxide for constant temperature heated and untreated membranes</td>
<td>49</td>
</tr>
<tr>
<td>4.2</td>
<td>Pressure-normalized flux of methane for constant temperature heated and untreated membranes</td>
<td>50</td>
</tr>
<tr>
<td>4.3</td>
<td>CO\textsubscript{2}/CH\textsubscript{4} selectivity for constant temperature heated and untreated membranes</td>
<td>51</td>
</tr>
<tr>
<td>4.4</td>
<td>Scanning Electron Microscopy Images of partial cross section untreated membrane and membranes treated with constant heating. (a) untreated membranes (b) membranes heated with constant 70°C (c) membranes heated with constant 80°C (d) membranes heated with constant 90°C</td>
<td>54</td>
</tr>
</tbody>
</table>
4.5 Average fiber density for constant temperature heated and untreated membranes

4.6 Pressure-normalized flux of carbon dioxide in progressive temperature heated membranes

4.7 Pressure-normalized flux of methane in progressive temperature heated membranes

4.8 $\text{CO}_2/\text{CH}_4$ selectivity for progressive temperature heated and untreated membranes.

4.9 Pressure-normalized flux of carbon dioxide for untreated and heat treated membranes at constant 70ºC and progressive 70ºC

4.10 Pressure-normalized flux of methane for untreated and heat treated membranes at constant 70ºC and progressive 70ºC

4.11 $\text{CO}_2/\text{CH}_4$ Selectivity for untreated and heat treated membranes at constant 70ºC and progressive 70ºC

4.12 Pressure-normalized flux of carbon dioxide for untreated and heat treated membranes at constant 80ºC and progressive 80ºC

4.13 Pressure-normalized flux of methane for untreated and heat treated membranes at constant 80ºC and progressive 80ºC

4.14 $\text{CO}_2/\text{CH}_4$ Selectivity for untreated and heat treated membranes at constant 80ºC and progressive 80ºC
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.15</td>
<td>Pressure-normalized flux of carbon dioxide for untreated and heat treated membranes at constant 90°C and progressive 90°C</td>
<td>65</td>
</tr>
<tr>
<td>4.16</td>
<td>Pressure-normalized flux of methane for untreated and heat treated membranes at constant 90°C and progressive 90°C</td>
<td>65</td>
</tr>
<tr>
<td>4.17</td>
<td>CO₂/CH₄ Selectivity for untreated and heat treated membranes at constant 90°C and progressive 90°C</td>
<td>66</td>
</tr>
<tr>
<td>4.18</td>
<td>Scanning Electron Microscopy Images of partial cross section membranes treated with constant heating. (a) membranes heated with progressive 70°C (b) membranes heated with constant 70°C (c) membranes heated with progressive 80°C (a) membranes heated with constant 80°C (b) membranes heated with progressive 90°C (c) membranes heated with constant 90°C</td>
<td>67</td>
</tr>
<tr>
<td>4.19</td>
<td>Average fiber density for progressive temperature heated and untreated membranes</td>
<td>69</td>
</tr>
<tr>
<td>4.20</td>
<td>Average fiber density for constant temperature heated and untreated membranes</td>
<td>70</td>
</tr>
<tr>
<td>4.21</td>
<td>Glass transition temperature for constant temperature heated, progressive heated and untreated membranes</td>
<td>73</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

A  Membrane surface area (cm$^2$)

$b$  Hole affinity constant, atm$^{-1}$

$C$  Solubility, cc (STP)/cc polymer

$C_H$  Hole saturation constant, cc (STP)/cc polymer

$C_i$  Concentration of component i

$D_i$  Diffusion coefficient

GPU  Gas permeation unit

$J_i$  Flux diffusion of penetrant gas

$k_D$  Henry’s Law dissolution coefficient

$kV$  Kilovolt

$l$  Thickness of membrane

$M$  Molecular weight, g/mol

$m^2/m^3$  Surface to volume ratio

$m^3$  meter cube

$mm$  millimeter

$P$  Pressure-normalized flux of gas through a membrane

$p$  Pressure

$P/l$  Pressure-normalized flux

$Q$  Volumetric flowrate of penetrant gas through membrane

(cm$^3$ (STP)s$^{-1}$ or mol$^{-1}$)

$S$  Solubility coefficient

$S_i$  Solubility of component i

$s$  second

$T$  Temperature, K

$T_g$  Glass transition temperature

Å  Angstrom

µm  micrometer

$\Delta P$  Pressure difference

$\Delta C$  Concentration difference
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T$</td>
<td>Temperature difference</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>Electrical potential difference</td>
</tr>
<tr>
<td>$^\circ C$</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>$\alpha_{ij}$</td>
<td>Selectivity</td>
</tr>
</tbody>
</table>
LIST OF APENDICES

Appendix A - Pressure-Normalized Flux and Selectivity of Pure Gas
Appendix B - Density Measurements
CHAPTER I

INTRODUCTION

1.1 Natural Gas Processing

Natural gas is a natural mixture of hydrocarbons found issuing from the ground, or obtained from specially driven wells. Its composition varies across the board depending on where it is found. Its main component is methane, which usually makes up about 80-95% of the gas (Lee, 1997). The rest of the gas is made up of varying amounts of other gases like ethane, propane, butane, and a host of hydrocarbons. Other substance that may occur as impurities in natural gas stream includes carbon dioxide, nitrogen, water vapor, mercury and hydrogen sulfide (Baker and Lokhandwala, 2008).

Pure methane is widely used around the world for many applications. A total of approximately 22 trillion standard cubic feet of natural gas was used in the United States while the total global used approached an amount of 95 trillion scf/year (Baker and Lokhandwala, 2008). This amount of consumption contributes to a worldwide market of approximately USD 5 billion per year.

As mentioned earlier, natural gas from wells contains impurities. In order to meet pipeline specifications, these impurities shall be removed. Carbon dioxide, which is an acid gas, shall be removed from natural gas stream as it will prevent corrosion and destruction of pipeline (Baker, 2001). The existence of carbon dioxide in natural gas will also reduce its heating value. As such, removal of acid gas from the stream is essential to get a better quality of natural gas.
The most widely applied technologies to remove relatively low quantities of CO$_2$ from natural gas are based on absorption by chemical (amine), physical (selexol and rectisol) or hybrid (sulfinol-M) solvents (Jarwaarde, 2007). Currently, CO$_2$ is removed by absorption from fields containing not more than 10 mol% CO$_2$, although absorption seems economically the best option up till a concentration of 20 mol%. However, there are also other commercial technologies that include adsorption by alumina, zeolite and activated carbon beds, cryogenic distillation and membranes.

In operation, separation technology will upgrade the raw natural gas to international sales gas specifications or to the specifications for use in LNG processes. The conventional technologies, as mentioned above, could be used for effective CO$_2$ capture. Each process has its own advantages and disadvantages, but membranes increasingly are being selected for newer technology of CO$_2$ removal, especially for applications that have large flows, have high CO$_2$ contents, or are in remote locations (Jarwaarde, 2007).

Reaction of carbon dioxide in natural gas stream with water will create a substance which is highly corrosive and will easily damage the pipelines and equipments (Baker, 2002). The standard technique employed for carbon dioxide removal from natural gas is the amine absorption (Baker and Lokhandwala, 2008). A typical absorption process is illustrated in Figure 1.1. Two towers are used. In the first tower, the feed gas, usually at high pressure, and an absorbent liquid flow countercurrent to each other. The absorbent liquid that contains the absorbed component (carbon dioxide, water or heavy hydrocarbon) is removed from the bottom of the tower. The liquid is then heated and sent to a low-pressure stripper tower. The combination of heat and lower pressure liberates the sorbed component which leaves the stripper tower as a low pressure overhead gas. The regenerated absorbent liquid is then recycled to the first tower. Heat exchangers are used to minimize the cost of heating the absorber fluid (Baker and Lokhandwala, 2008).
Figure 1.1: Typical natural gas amine absorber for carbon dioxide removal (Baker and Lokhandwala, 2008).

Although the absorber-stripper units represent a proven, well-accepted technology in the gas processing industry, however the high-pressure absorber tower in particular is an expensive, large, thick-walled, heave vessel. The size of such a tower is proportional to the mass of the material to be absorbed. On the other hand, the removal of carbon dioxide from natural gas may require 10% - 20% of the gas to be removed, which means large amounts of absorbent fluid must be used in large towers. Carbon dioxide absorber-strippers are also relatively high maintenance units. The need to heat and cool the recirculating fluids requires careful, well-monitored operating procedures. Apart from that, another critical maintenance issue for this unit is corrosion. Amines are the most common sorbents for carbon dioxide. The degradation of amines leads to corrosive mixtures that can destroy the system. Constant monitoring of the amine absorbent chemistry is needed.

Several innovative technologies have been developed over the last decade. Novel membrane processes for CO$_2$ removal from contaminated natural gas, are seen as one of the promising, upcoming technologies (Baker, 2001). Several new membrane materials create opportunities for effective gas sweetening processes to
compete with conventional gas separation processes. These developments seem to place membrane processes in the picture as increasingly cost-effective alternatives for conventional processes.

There are always advantages and disadvantages in every systems employed for CO₂ gas removal. According to Baker and Lokhandwala (2008), it is best to employ amine systems for treatment of natural gas at high gas flow rate but contain a low amount of CO₂ in the stream. However, on the other hand, at low gas flow rate and high concentration of CO₂, it is best to employ membrane system for CO₂ gas removal. At high concentration of CO₂ and high flow rate of feed stream, a hybrid system of amine and membrane is advised to be used.

1.2 Membrane for Carbon Dioxide Removal

In 1980, Permea launched its first Prism membrane for hydrogen separation (Baker, 2002). Since then, membrane usage for various gas separations has widely grown. Initial acceptance was slow when it was first introduced to the market due to many process design parameters were largely unknown (Dortmund and Doshi, 1999). A list of principal suppliers of membrane is shown in Table 1.1.

During late 1980s, the development of CO₂/CH₄ separation in natural gas by Cynara (now part of Natco), Separex (now part of UOP) and Grace Membrane System (a division of W.R Grace), led to substantial innovation in asymmetric cellulose acetate membrane that was produced by using Loeb-Sourirajan technique (Sandra, 2008). Besides that, Perfluoro composite aromatic polyimide membrane were also coomercialized by ABB/MTR for CO₂/CH₄ separation. These innovations have improved the gas separation efficiency and membrane durability, making membrane gas separation commercially competitive with existing separation technologies such as chemical absorption, physical adsorption and cryogenic Baker and Lokhandwala, 2008).
Table 1.1: Principal suppliers of membrane natural gas separation systems (Baker and Lokhandwala, 2008)

<table>
<thead>
<tr>
<th>Company</th>
<th>Principal natural gas separation</th>
<th>Membrane module type</th>
<th>Membrane material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medal (Air Liquide)</td>
<td>CO₂</td>
<td>Hollow fiber</td>
<td>Polyimide</td>
</tr>
<tr>
<td>W.R.Grace</td>
<td>CO₂</td>
<td>Spiral-wound</td>
<td>Celulose Acetate</td>
</tr>
<tr>
<td>Separex (UOP)</td>
<td>CO₂</td>
<td>Spiral-wound</td>
<td>Celulose Acetate</td>
</tr>
<tr>
<td>Cynara (NATCO)</td>
<td>CO₂</td>
<td>Hollow fiber</td>
<td>Celulose Acetate</td>
</tr>
<tr>
<td>ABB/MTR</td>
<td>CO₂, N₂, C₃+ Hydrocarbons</td>
<td>Spiral-wound</td>
<td>Perfluoro polymers, silicon rubbers</td>
</tr>
<tr>
<td>Permea (Air Products)</td>
<td>Water</td>
<td>Hollow fiber</td>
<td>Polysulfone</td>
</tr>
</tbody>
</table>

Cynara-NATCO produced hollow fiber modules using cellulose acetate in 1983, installed and operate two CO₂ separation facilities for the SACROC unit located in West Texas, USA. The plant was initially designed to reduce CO₂ from 45% to 28%, treating 60 000 Nm³/h in 160 modules (5 in. x 2 in.). The plant is still working and today has a capacity of more 120 000 Nm³/h, decreasing the CO₂ content from 80% to less than 10%. Recently, Cynara-NATCO provided a membrane system (16 in. modules) for natural gas sweetening in an offshore platform in the Thailand gulf (830 000 Nm³/h). This is known as the biggest membrane system for CO₂ removal. The plant reduces CO₂ concentration from 36% down to 16%. The 16 inches Cynara module has a 17.5 times higher feed capacity than the flow-rate allowed by a 5 inches module. The last development of 30 inches module however, allows a feed capacity of 62.5 times higher than the smallest one, reducing weight and footprint of more than 90% suitable for offshore and other space-constrained facilities (drioli, et al., 2009)

In gas separation, membrane processes compete directly with other commercial technologies as absorption, adsorption and cryogenic distillation.
However, compared to these conventional technologies membrane processes are often more energy efficient, simpler to operate, and offer a higher reliability resulting in a high on-stream time (Dordtmund and Doshi, 1999).

Furthermore, the environmental impact of membrane processes is relatively low compared to solvent-based processes. There are no hazardous chemicals used that have to be discharged and there is no additional heat required (Jarwaarde, 2007). For offshore operation, membrane processes offer advantages compared to other technologies. Membrane units have a modular design, which results in low weight and space requirements. The modular design makes membrane units easy to scale up, install and to transport. In general, membrane units are designed to be skid-mounted. Table 1.2 tabulates the differences between amine and membrane system for carbon dioxide removal.

Referring to Table 1.1, cellulose acetate, polyimide and polysulfone were primarily used for commercial gas separations. These glassy polymers were chosen due to the fact that they possess high separation factor and good mechanical strength (Drioli, 2010). However, glassy polymeric membranes used for CO\textsubscript{2}/CH\textsubscript{4} separation frequently suffer from CO\textsubscript{2} induced plasticization (Bos et al., 2001). Plasticization of glassy polymers occurs when concentration of CO\textsubscript{2} in the feed stream is high enough to increase free volume and segmental mobility (Bos et al., 1998).

1.3 Problem Statement

While membrane systems for gas separation are proven attractive, it has a major disadvantage when dealing with plasticizing gases such as carbon dioxide. Carbon dioxide has an effect of plasticizing glassy polymers where polysulfone asymmetric hollow fiber membrane is also affected (Kentish et. al, 2010). In case of carbon dioxide/methane separation, carbon dioxide acts as a plasticizer where it reduces the interaction between adjacent segments in the polysulfone polymer. Table 1.2: Comparison of amine and membrane CO\textsubscript{2} removal system (Jarwaarde, 2007).
<table>
<thead>
<tr>
<th>Factor</th>
<th>Amine</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon Loses</td>
<td>Very Low</td>
<td>Loses depending on membrane</td>
</tr>
<tr>
<td>Meet low CO₂ specifications</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>Moderate to high</td>
<td>Low</td>
</tr>
<tr>
<td>Operating cost</td>
<td>Moderate</td>
<td>Low to Moderate</td>
</tr>
<tr>
<td>Maintenance cost</td>
<td>Low to moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Ease of operation</td>
<td>Relatively moderate</td>
<td>Relatively simple</td>
</tr>
<tr>
<td>Environmental effect</td>
<td>Complex</td>
<td>Low</td>
</tr>
<tr>
<td>Pre-treatment cost</td>
<td>Low</td>
<td>Low to Moderate</td>
</tr>
<tr>
<td>Recycle compression</td>
<td>Not used</td>
<td>Depends on condition</td>
</tr>
<tr>
<td>On-site installation</td>
<td>Long</td>
<td>Short for skid-mounted systems</td>
</tr>
</tbody>
</table>

chains. In other words, the existence of carbon dioxide swells the polysulfone membrane during separation process (Bos et al., 1998b). Carbon dioxide induced plasticization depends so much on the amount of sorbed CO₂. At relatively low penetrant concentrations, permeation usually follows the dual sorption model. At this time, the effects of penetrant sorption are mostly reversible over reasonable time periods. However, at high penetrated concentrations, plasticization occurs and the effect is commonly irreversible owing to increased free volume that facilitates molecular motions. This will finally result in increase of the permeability of all gas species (Paul and Horn, 2011).

Many researchers have studied the effect of CO₂ induced plasticization in glassy polymers. Paul et al., (1985) studied extensively on effect of CO₂ sorption for poly(methyl methacrylate) and poly(vinylidene fluoride). A study upon polystyrene, polycarbonate, poly(vinyl chloride) and poly(ethylene terephthalate) was also conducted by Paul et al. (1985) to investigate the effect of CO₂ induced plasticization. Ismail and Lorna (2003) conducted extensive studies on plasticization.
of polysulfone by CO$_2$. Bos et al. (1998a) studied a series of polymers including plasticization upon polysulfone, polyethersulfone, polyetherimide, cellulose acetate and cellulose triacetate. Numerous studies on plasticization of polyimides have been conducted by Nagai et al. (2007), Krol et al. (2001), Dong et al. (2010), Wind et al. (2001), Koros et al. (2010) and Bos et al. (1998b).

Swelling of membranes shall be eliminated, as it destructs the membrane structure (Kentish et. al, 2010). This will lead to increment of carbon dioxide and methane permeation thus leading to lower selectivity and greater hydrocarbon loss (Paul and Horn, 2011).

Heat treatment or thermal annealing has been proposed by many researchers as an approach to suppress CO$_2$ induced plasticization. Ismail and Lorna (2003) heat up polysulfone at different constant temperatures and different duration of heating time. Ismail and Yaacob (2005), conducted heat treatment upon polysulfone hollow fiber membranes at constant moderate low temperatures. Nagai et al. (2008), studied the effect of thermal annealing at constant temperature for suppression of CO$_2$ induced plasticization on polyimides. Done et al. (2010), used constant temperature to suppress CO$_2$ induced plasticization upon polyimide. Paul et al. (2010) investigated the effect of constant temperature heat treatment upon polysulfone for suppression of CO$_2$ induced plasticization.

Although the above mentioned works conducted by various researchers uses different type of polymer membranes, they do have one thing in common that is using constant temperature heating in order to suppress CO$_2$ induced plasticization. In previous studies, most heat treatment employed the constant heating technique. In this study, two types of heating will be used namely constant temperature heating and progressive heating which is rarely studied in previous works by other researchers. This study will investigate the difference of permeation trend and morphology of the result of two different style of heating technique.
1.4 Objectives of Research

Based on the background and problem statement stated above, the objectives of this study are stated below:

a) To prepare asymmetric polysulfone hollow fiber membrane for carbon dioxide removal.

b) To investigate the effect of thermal treatment on the prepared asymmetric polysulfone hollow fiber membranes.

c) To characterize the separation performance of the prepared treated and untreated asymmetric polysulfone hollow fiber membrane using analytical techniques and permeation test.

d) To determine the preferable heating technique and heating temperature upon the treated membranes that gives the best separation performance from within the test temperatures.

1.5 Scope of Research

In order to reach the objectives, a few scopes have been drawn:

a) Determine the concentration of polymer, solvent and non-solvent used using turbidimetric titration method.

b) Prepare the asymmetric hollow fiber membrane using phase inversion technique.

c) Conducting thermal treatment upon prepared asymmetric hollow fiber membranes using different temperature and method.

d) Characterize the treated and untreated membranes that have been developed.

e) Test the performance of the treated and untreated membrane for carbon dioxide/methane separation at different operating conditions.

f) Determining the preferred heating technique and temperature upon the treated membranes that gives the best CO₂/CH₄ separations.
REFERENCES


Dortmundt, D., Doshi, K., (1999) “Recent Development in CO2 Removal Membrane Technology”, UOP, LLC.


