CO$_2$ (H$_2$S) MEMBRANE SEPARATIONS AND WGS MEMBRANE REACTOR
MODELING FOR FUEL CELLS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy
In the Graduate School of the Ohio State University

By
Jin Huang, M.S. Ch.E.

****
The Ohio State University
2007

Dissertation Committee:
Professor W. S. Winston Ho, Advisor
Professor L. James Lee
Professor Kurt W. Koelling

Approved by

W. Winston Ho
Advisor
Graduate program in Chemical Engineering
ABSTRACT

Acid-gas removal is of great importance in many environmental or energy-related processes. Compared to current commercial technologies, membrane-based CO₂ and H₂S capture has the advantages of low energy consumption, low weight and space requirement, simplicity of installation / operation, and high process flexibility. However, the large-scale application of the membrane separation technology is limited by the relatively low transport properties.

In this study, CO₂ (H₂S)-selective polymeric membranes with high permeability and high selectivity have been studied based on the facilitated transport mechanism. The membrane showed facilitated effect for both CO₂ and H₂S. A CO₂ permeability of above 2000 Barrers, a CO₂/H₂ selectivity of greater than 40, and a CO₂/N₂ selectivity of greater than 200 at 100 – 150°C were observed. As a result of higher reaction rate and smaller diffusing compound, the H₂S permeability and H₂S/H₂ selectivity were about three times higher than those properties for CO₂. The novel CO₂-selective membrane has been applied to capture CO₂ from flue gas and natural gas. In the CO₂ capture experiments from a gas mixture with N₂ and H₂, a permeate CO₂ dry concentration of greater than 98% was obtained by using steam as the sweep gas. In CO₂/CH₄ separation, decent CO₂ transport properties were obtained with a feed pressure up to 500 psia. With the thin-film composite membrane structure, significant increase on the CO₂ flux was achieved with the decrease of the selective layer thickness.
With the continuous removal of CO₂, CO₂-selective water-gas-shift (WGS) membrane reactor is a promising approach to enhance CO conversion and increase the purity of H₂ at process pressure under relatively low temperature. The simultaneous reaction and transport process in the countercurrent WGS membrane reactor was simulated by using a one-dimensional non-isothermal model. The modeling results show that a CO concentration of less than 10 ppm and a H₂ recovery of greater than 97% are achievable from reforming syngases. In an experimental study, the reversible WGS was shifted forward by removing CO₂ so that the CO concentration was significantly decreased to less than 10 ppm. The modeling results agreed well with the experimental data.
Dedicated to my parents, my brother and Yujun for their love and support
ACKNOWLEDGMENTS

I would like to thank the following people for their help and support in conducting this research:

- Dr. W. S. Winston Ho, my advisor at Ohio State, for his thoughtful guidance, enthusiastic discussion and continuous support and encouragement throughout the five years I have been in the United States. His persistence in pursuing the truth and his hard-working attitude have been, and will be, inspiring my career and life in the past and in the future.

- Dr. L. James Lee, Dr. Kurt W. Koelling, Dr. David Tomasko, and Dr. Barbara Wyslouzil for all their constructive critiques which helped me to improve my work.

- I thank all my colleagues in Dr. Ho’s group: He Bai, Philip Chang, Bishnupada Mandal, Michael Vilt, Chi Yen, Jian Zou, and fellow students in Koffolt Labs who have to remain unnamed here.

Also I would like to thank the following people:

- My friends, both in US and China, for all their encouragements and friendship.

- My parents and my brother for their support and love throughout my studies over the years.
• Yujun for her support, encouragements, patience, and love while writing this thesis.
VITA

April 19, 1977............................................Born in Jianli, Hubei, China
1996.......................................................B.S. Organic Chemical Technology,
                                      Wuhan Institute of Chemical Technology,
                                      Wuhan, China
1999.......................................................M.S. Chemical Engineering,
                                      East China Univ. of Science & Technology,
                                      Shanghai, China
2001 – 2002 ..........................................Graduate Research Associate,
                                      University of Kentucky,
                                      Lexington, KY, USA
2002 – 2006......................................….Graduate Research Associate,
                                      The Ohio State University,
                                      Columbus, OH, USA

PUBLICATIONS


**FIELDS OF STUDY**

Major Field: Chemical Engineering
TABLE OF CONTENTS

Abstract........................................................................................................................................ii
Dedication......................................................................................................................................iv
Acknowledgments.........................................................................................................................v
Vita................................................................................................................................................vii
List of Tables.................................................................................................................................xiii
List of Figures...............................................................................................................................xiv
List of Notations..........................................................................................................................xix

Chapters:

1. Introduction .............................................................................................................................1
   1.1 Membrane Separation Technology..................................................................................1
   1.2 Acid-gas Removal.............................................................................................................3
   1.3 Scope and Objectives of Research....................................................................................4

2. Synthesis of CO\(_2\) (H\(_2\)S)-Selective Membrane..............................................................8
   2.1 Introduction.......................................................................................................................9
      2.1.1 Polymeric Membrane for Gas Separation...............................................................9
      2.1.2 Reaction Mechanism between Amines and Acid Gases........................................12
      2.1.3 Facilitated Transport Membrane for Acid-gas Removal.......................................16
   2.2 CO\(_2\) (H\(_2\)S)-Selective Membrane.....................................................................................21
      2.2.1 Membrane Synthesis and Characterization............................................................21
      2.2.2 Membrane Structure...............................................................................................24
      2.2.3 CO\(_2\) Transport Properties......................................................................................25
      2.2.4 H\(_2\)S Transport Properties......................................................................................27
2.3 Concluding remarks.................................................................29

3. Flue Gas CO$_2$ Removal..............................................................42
   3.1 Introduction...........................................................................43
   3.2 CO$_2$ Capture Experiments..................................................45
   3.3 Modeling Work.................................................................46
   3.4 Results and Discussion.......................................................48
      3.4.1 Transport Properties of CO$_2$-selective Membrane ..........48
      3.4.2 CO$_2$ Removal Capacity.................................................49
      3.4.3 CO$_2$ Capture Performance............................................49
         3.4.3.1 Effect of Feed Inlet Flow Rate.................................50
         3.4.3.2 Effect of Sweep-to-Feed Ratio.................................51
      3.4.4 Modeling Study............................................................51
   3.5 Concluding Remarks..........................................................52

4. High-Pressure CO$_2$ and H$_2$S Removal from Natural Gas..................61
   4.1 Introduction...........................................................................63
   4.2 Experimental.......................................................................67
   4.3 Results and Discussion.......................................................69
      4.3.1 Free-Standing Membrane.................................................69
         4.3.1.1 Effect of Feed Pressure on CO$_2$ Transport Properties...70
         4.3.1.2 Effect of Temperature on CO$_2$ Transport Properties...71
         4.3.1.3 Effect of Permeate Pressure on CO$_2$ Transport Properties...71
      4.3.2 Thin-Film Composite Membrane......................................72
         4.3.2.1 Effect of Membrane Thickness on CO$_2$ Transport Properties...73
         4.3.2.2 Effect of Temperature on CO$_2$ and H$_2$S Transport Properties...74
      4.3.3 Asymmetric Membrane....................................................75
   4.4 Concluding Remarks..........................................................78

5. Other CO$_2$-Selective Membranes..............................................95
   5.1 Introduction...........................................................................97
   5.2 Hybrid Facilitated Transport Membrane..................................99
      5.2.1 Synthesis of Hybrid Membrane.......................................100
      5.2.2 Results and Discussion..................................................101
5.3 Segmented Polyimide Copolymer.................................................................103
5.3.1 Membrane Synthesis and Testing..............................................................103
5.3.2 Results and Discussion..............................................................................104
5.4 Concluding Remarks.....................................................................................106
6. Modeling of CO$_2$-selective WGS membrane reactor for fuel cells..............116
6.1 Introduction....................................................................................................118
6.2 Model Description........................................................................................122
   6.2.1 Molar Balance.........................................................................................125
   6.2.2 Energy Balance......................................................................................126
6.3 Experimental Study of CO$_2$-Selective WGS Membrane Reactor ...............128
6.4 Results and Discussion................................................................................130
   6.4.1 Autothermal Reforming Syngas..............................................................130
      6.4.1.1 Reference Case................................................................................130
      6.4.1.2 Effect of CO$_2$/H$_2$ Selectivity.........................................................132
      6.4.1.3 Effect of CO$_2$ Permeability.............................................................133
      6.4.1.4 Effect of Sweep-to-Feed Ratio.........................................................133
      6.4.1.5 Effect of Inlet Feed Temperature.....................................................135
      6.4.1.6 Effect of Inlet Sweep Temperature..................................................135
      6.4.1.7 Effect of Feed-Side Pressure............................................................136
      6.4.1.8 Effect of Inlet Feed CO Concentration.............................................137
      6.4.1.9 Effect of Catalyst Activity...............................................................137
   6.4.2 Steam Reforming Syngas.........................................................................138
      6.4.2.1 Reference Case................................................................................138
      6.4.2.2 Effect of CO$_2$/H$_2$ Selectivity.........................................................140
      6.4.2.3 Effect of CO$_2$ Permeability.............................................................140
      6.4.2.4 Effect of Sweep-to-Feed Ratio.........................................................141
      6.4.2.5 Effect of Inlet Feed Temperature.....................................................141
      6.4.2.6 Effect of Inlet Sweep Temperature..................................................142
      6.4.2.7 Effect of Feed-Side Pressure............................................................143
      6.4.2.8 Effect of Feed Inlet CO Concentration.............................................143
      6.4.2.9 Effect of Catalyst Activity...............................................................144
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Carbamate stability constants for different amines at 40°C by carbon-13 NMR (Sartori and Savage, 1983)</td>
</tr>
<tr>
<td>3.1</td>
<td>The operating parameters for the CO₂ capture experiments</td>
</tr>
<tr>
<td>5.1</td>
<td>Diols as the option of soft segment</td>
</tr>
<tr>
<td>5.2</td>
<td>The testing results of copolymer membrane</td>
</tr>
<tr>
<td>6.1</td>
<td>The compositions of autothermal reforming syngas and steam reforming syngas</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Facilitated transport mechanism</td>
<td>31</td>
</tr>
<tr>
<td>2.2</td>
<td>Synthesis of the crosslinked PVA with formaldehyde.</td>
<td>32</td>
</tr>
<tr>
<td>2.3</td>
<td>Chemical structures of (a) free polyallylamine and (b) AIBA-K</td>
<td>33</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematic of the gas permeation unit</td>
<td>34</td>
</tr>
<tr>
<td>2.5</td>
<td>Scanning electron microscopic picture of the membrane synthesized</td>
<td>35</td>
</tr>
<tr>
<td>2.6</td>
<td>CO$_2$ permeability vs. temperature</td>
<td>36</td>
</tr>
<tr>
<td>2.7</td>
<td>CO$_2$/H$_2$ selectivity vs. temperature</td>
<td>37</td>
</tr>
<tr>
<td>2.8</td>
<td>CO$_2$/N$_2$ selectivity vs. temperature</td>
<td>38</td>
</tr>
<tr>
<td>2.9</td>
<td>H$_2$S and CO$_2$ permeability vs. temperature</td>
<td>39</td>
</tr>
<tr>
<td>2.10</td>
<td>H$_2$S/H$_2$ and CO$_2$/H$_2$ selectivity vs. temperature</td>
<td>40</td>
</tr>
<tr>
<td>2.11</td>
<td>H$_2$S removal capacity with the circular gas permeation cell (24.6 cm$^2$)</td>
<td>41</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic of the hollow-fiber membrane module</td>
<td>55</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic of gas separation with the CO$_2$-selective membrane</td>
<td>56</td>
</tr>
<tr>
<td>3.3</td>
<td>Exit dry CO$_2$ concentration in the retentate vs. feed flow rate</td>
<td>57</td>
</tr>
<tr>
<td>3.4</td>
<td>Permeate CO$_2$ dry concentration and CO$_2$ recovery vs. feed flow rate</td>
<td>58</td>
</tr>
<tr>
<td>3.5</td>
<td>Permeate CO$_2$ dry concentration and CO$_2$ recovery vs. sweep-to-feed molar ratio</td>
<td>59</td>
</tr>
<tr>
<td>3.6</td>
<td>CO$_2$ concentration (wet) profiles along the length of membrane module</td>
<td>60</td>
</tr>
</tbody>
</table>
4.1 Schematic of gas separation with the CO$_2$ (H$_2$S)-selective membrane.............80
4.2 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. feed pressure at 106°C..........81
4.3 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. feed pressure at 116°C........82
4.4 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. temperature at 150 psia feed pressure.................................................................83
4.5 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. temperature at 500 psia feed pressure.................................................................84
4.6 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. permeate pressure at 106°C and 500 psia feed pressure.................................................................85
4.7 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. permeate pressure at 111°C and 500 psia feed pressure.................................................................86
4.8 CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. permeate pressure at 116°C and 500 psia feed pressure.................................................................87
4.9 CO$_2$ permeance and CO$_2$/CH$_4$ selectivity vs. membrane thickness at 116°C and 150 psia feed pressure.................................................................88
4.10 Total mass transfer resistance, R$_t$, versus membrane thickness....................89
4.11 CO$_2$ and H$_2$S/CH$_4$ selectivities versus operating temperature...............90
4.12 CO$_2$ and H$_2$S permeances versus operating temperature..........................91
4.13 Schematic of the phase inversion process with the delayed demixing (■ denotes the top of the liquid film, ● denotes the bottom of the liquid film, and red lines denote the composition path along the liquid film thickness) ..........92
4.14 The weight reduction of the membrane during the air-drying (23°C, casting gap setting = 10 mil) ........................................................................................................93
4.15 The preliminary data from the asymmetric membranes via the phase inversion process (106°C and 150 psia feed pressure) ..................................94
5.1 CO$_2$/H$_2$ selectivity of PVA membrane and hybrid PVA membrane..............110
5.2 CO$_2$/N$_2$ selectivity of PVA membrane and hybrid PVA membrane..........111
5.3 CO$_2$ permeability of PVA membrane and hybrid PVA membrane.............112
5.4 The thermogravimetric curves for the hybrid PVA membrane and the PVA membrane

5.5 Reaction steps in the synthesis of 2 PMDA/ 1 PEA 2000/ 1 MDA

5.6 FTIR spectra of copolymer, 2 PMDA / 1 PEA 2000 / 1 MDA, after imidization

6.1 Schematic of water-gas-shift hollow-fiber membrane reactor

6.2 Cross-section schematic of the water-gas-shift membrane reactor

6.3 Feed-side CO and CO₂ mole fraction profiles along the length of membrane reactor for autothermal reforming syngas

6.4 Feed-side H₂ mole fraction profiles along the length of membrane reactor for autothermal reforming syngas

6.5 Feed-side and sweep-side temperature profiles along the length of membrane reactor for autothermal reforming syngas

6.6 The effects of CO₂/H₂ selectivity on feed-side exit CO concentration and H₂ recovery for autothermal reforming syngas

6.7 The effect of CO₂ permeability on required membrane area for autothermal reforming syngas

6.8 The effects of sweep-to-feed ratio on feed-side exit CO concentration and H₂ recovery for autothermal reforming syngas

6.9 The effect of inlet feed temperature on required membrane area for autothermal reforming syngas

6.10 Feed-side temperature profiles along the length of membrane reactor for autothermal reforming syngas with different inlet feed temperatures

6.11 The effect of inlet sweep temperature on required membrane area for autothermal reforming syngas

6.12 Feed-side temperature profiles along the length of membrane reactor for autothermal reforming syngas with different inlet sweep temperatures

6.13 The effect of feed-side pressure on required membrane area for autothermal reforming syngas
6.14 Feed-side CO mole fraction profiles along the length of membrane reactor for autothermal reforming syngas with different inlet feed CO temperatures……161

6.15 The effect of catalyst activity on required membrane area for autothermal reforming syngas

6.16 Feed-side CO and CO$_2$ mole fraction profiles along the length of membrane reactor for steam reforming syngas

6.17 Feed-side H$_2$ mole fraction profiles along the length of membrane reactor for steam reforming syngas

6.18 Feed-side and sweep-side temperature profiles along the length of membrane reactor for steam reforming syngas

6.19 The effects of CO$_2$/H$_2$ selectivity on feed-side exit CO concentration and H$_2$ recovery for steam reforming syngas

6.20 The effect of CO$_2$ permeability on required membrane area for steam reforming syngas

6.21 The effects of sweep-to-feed ratio on feed-side exit CO concentration and H$_2$ recovery for steam reforming syngas

6.22 The effect of inlet feed temperature on required membrane area for steam reforming syngas

6.23 Feed-side temperature profiles along the length of membrane reactor for steam reforming syngas with different inlet feed temperatures

6.24 The effect of inlet sweep temperature on required membrane area for steam reforming syngas

6.25 Feed-side temperature profiles along the length of membrane reactor for steam reforming syngas with different inlet sweep temperatures

6.26 The effect of feed-side pressure on required membrane area for steam reforming syngas

6.27 Feed-side CO mole fraction profiles along the length of membrane reactor for steam reforming syngas with different inlet feed CO temperatures

6.28 The effect of catalyst activity on required membrane area for steam reforming syngas
6.29  Retentate CO concentration vs. feed flow rate in the rectangular WGS membrane reactor (Feed gas: 1% CO, 17% CO$_2$, 45% H$_2$, 37% N$_2$, T = 150°C, p$_f$ = 2.0 atm, p$_s$ = 1.0 atm, feed/sweep flow rates = 1/1 (on dry basis), average membrane thickness = 53 μm) ………………………………………………………………………………………………………176

7.1  Extended membrane leaf of a spiral-wound WGS membrane reactor………184
### LIST OF NOTATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p$</td>
<td>heat capacity (J/mol/K)</td>
</tr>
<tr>
<td>$d$</td>
<td>hollow fiber diameter (cm)</td>
</tr>
<tr>
<td>$d_h$</td>
<td>hydraulic diameter (cm)</td>
</tr>
<tr>
<td>$D_A$</td>
<td>diffusion coefficient for gas species, A, (cm$^2$/s)</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>diffusion coefficient for gas-carrier reaction product, (cm$^2$/s)</td>
</tr>
<tr>
<td>$H_{AB}$</td>
<td>Henry’s law constant for gas-carrier reaction product, (atm · cm$^3$/mol)</td>
</tr>
<tr>
<td>$h$</td>
<td>convective heat transfer coefficient (W/cm$^2$/s)</td>
</tr>
<tr>
<td>$H$</td>
<td>height of reactor (cm)</td>
</tr>
<tr>
<td>$\Delta H_r$</td>
<td>heat of reaction (J/mol)</td>
</tr>
<tr>
<td>$J$</td>
<td>permeation flux (mol/cm$^2$/s)</td>
</tr>
<tr>
<td>$k$</td>
<td>reaction rate constant (cm/s)</td>
</tr>
<tr>
<td>$k_a$</td>
<td>gas thermal conductivity (W/cm/s)</td>
</tr>
<tr>
<td>$k_m$</td>
<td>membrane thermal conductivity (W/cm/s)</td>
</tr>
<tr>
<td>$K_T$</td>
<td>reaction equilibrium constant</td>
</tr>
<tr>
<td>$\ell$</td>
<td>membrane thickness (cm)</td>
</tr>
<tr>
<td>$L$</td>
<td>length of reactor or hollow fiber (cm)</td>
</tr>
<tr>
<td>$n$</td>
<td>molar flow rate (mol/s)</td>
</tr>
<tr>
<td>$Nu$</td>
<td>Nusselt number</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure (atm)</td>
</tr>
</tbody>
</table>
\( P \) permeability (Barrer)

Pr Prandtl number

\( r \) volumetric reaction rate \((\text{mol/cm}^3/\text{s})\)

\( R \) ideal gas constant \((\text{atm} \cdot \text{cm}^3/\text{mol}/\text{K})\) (Chapter 6)

\( R \) mass transfer resistance \((\text{s} \cdot \text{cm}^2 \cdot \text{cmHg/ cm}^3\text{(STP)})\) (Chapter 4)

Re Reynolds number

Sc Schmidt number

Sh Sherwood number

\( T \) temperature \((\circ\text{C})\)

\( U_i \) overall heat transfer coefficient \((\text{W/cm}^2/\text{K})\)

\( W \) width of reactor (cm)

\( x \) feed side molar fraction

\( y \) sweep side molar fraction

\( z \) axial position along the length of reactor (cm)

\textit{Greek letters}

\( \alpha \) \(\text{CO}_2/\text{H}_2\) selectivity

\( \gamma \) inlet sweep-to-feed molar flow rate ratio

\( \varepsilon \) porosity of the support layer in the hollow fiber

\( \rho_b \) catalyst bulk density \((\text{g/cm}^3)\)

\textit{Subscripts}

0 initial
f feed side (Chapter 6)

f forward reaction (Chapter 4)

i species

in inside of the hollow fiber

out outside of the hollow fiber

r reverse reaction

s sweep side

t total
1.1 MEMBRANE SEPARATION TECHNOLOGY

During the last half century, membrane separation technology has been used in a wide spectrum of applications in chemical industry and human life, ranging from seawater desalination, gas separation, and artificial kidney to controlled drug delivery. Essentially, a membrane process consists of two bulk phases separated by another phase, membrane. The membrane can be defined as a thin barrier that selectively moderates the diffusion of chemical components in contact with it. The selectivity of a membrane is based on the relative permeation rate of the different components. The separation is realized by allowing one or more components of a mixture to diffuse through the membrane while hindering permeation of other components (Ho and Sirkar, 1992).

People have recognized the membrane phenomena as early as in the middle of 19th century. The pioneering works of Mitchell, Fick, and Graham studied the gas diffusion properties of several different membranes, mainly to illustrate the barrier properties (Tabe-Mohammadi, 1999). However, the development of membrane
separation techniques was very slow in the early stages, due to the insufficient selectivities and low fluxes for the early membrane. The first large-scale application of membranes was the concentration of uranium 235 from 0.17 to 3% in the Manhattan Project during the World War II. In the early 1960s, Loeb and Sourirajan brought a breakthrough to the industrial membrane applications with the introduction of asymmetric membranes by the phase inversion process (Loeb and Sourirajan, 1962; Loeb and Sourirajan, 1964). They successfully produced membranes with a very thin dense top layer (< 0.5 μm) and a relatively thick porous sublayer (50 – 200 μm). The top layer was responsible for the transport rate, while the porous sublayer performed no separation but provided mechanical strength. As the result of an ultra-thin top layer, the first Loeb-Sourirajan reverses osmosis membrane showed a ten times higher flux than that of any membrane then available.

With the development of composite membranes by Ward et al. (Ward et al., 1976) and the coating technique by Henis and Tripodi (Henis and Tripodi, 1980), membrane-based gas separation emerged to be an important industrial membrane application in the 1980s. By using composite structure, the selective and supporting layer could be optimized separately. On the other hand, the coating technique ensured that a leak-free composite membrane was obtained by filling the large pores and defects of the selective layer with a highly permeable polymer. These accomplishments eventually led to the introduction of the PRISM® membrane system by Permea, Inc. (now a division of Air Products) in 1980. Since then, a lot of research has focused on the fundamental and industrial improvement of membrane systems. The current major applications of gas
separation membranes include air separation, hydrogen recovery, and natural gas treatment, etc.

1.2 ACID-GAS REMOVAL

The separation of acid gases (CO$_2$ and H$_2$S) is of great importance in many industrial areas, such as hydrogen production, upgrading of natural gas, greenhouse gas emission reduction, and fuel cell fuel processing. Since CO$_2$ reduces the energy content and is corrosive to the transportation and storage systems in the presence of water, CO$_2$ concentration needs to be reduced to less than 2% to reach the U.S. pipeline specification (Baker, 2002). On the other hand, the increasing public concern over global warming has concentrated on the greenhouse gas emission. It is highly desirable to remove and sequester CO$_2$ from various sources. H$_2$S is a common contaminant in the natural gas or the hydrogen derived from synthesis gas (syngas). For instance, even trace concentrations of H$_2$S (> 10 ppb) in the hydrogen can significantly degrade fuel cell performance by poisoning the anode catalyst. In all of these processes, it is of advantage to remove CO$_2$ or H$_2$S while maintaining other components at the process pressure to avoid recompression.

Currently, the principal technologies for acid-gas removal include chemical and/or physical absorption, physical adsorption, membrane separation, and cryogenic distillation. Compared to other technologies, membrane-based CO$_2$ capture has the advantages of low energy consumption, low weight and space requirement, simplicity of installation / operation, and high process flexibility.
For a gas separation membrane process, its economics is primarily determined by the membrane’s transport properties, or its permeability and selectivity for one or more components in a gas mixture. Preferably, membranes should exhibit high selectivity and high permeability simultaneously. However, current commercial membranes usually suffer for a tradeoff between selectivity and permeability, which hinder the large-scale application in the industry. For example, in natural gas treatment, the current largest gas separation application, the membrane process only occupies about less than 1% in the market (Baker, 2002).

1.3 SCOPE AND OBJECTIVES OF RESEARCH

In this study, CO$_2$ (H$_2$S)-selective polymeric membranes with high permeability and high selectivity have been studied based on the facilitated transport mechanism. A novel membrane was synthesized by incorporating amines into hydrophilic polymeric networks. The membranes are selective to CO$_2$ and H$_2$S preferentially versus unreactive gases, such as, H$_2$, N$_2$, and CH$_4$, since CO$_2$ permeates through the amine-containing membranes by the facilitated transport mechanism owing to its reaction with the amine. H$_2$S, as a more reactive acid gas, has shown about three times higher transport properties than CO$_2$. The details about the preparation and characterization of this membrane are discussed in Chapter 2.

This CO$_2$ (H$_2$S)-selective membranes could be also used for acid gas removal from many industrial gas streams, such as flue gas and natural gas. The CO$_2$ capture from CO$_2$/N$_2$ gas mixture was performed successfully with steam as the sweep gas.
Chapter 3 presents the experimental study of CO\(_2\) capture with the described facilitated transport membrane. The effects of feed flow rate and sweep-to-feed molar ratio on membrane separation performance were investigated. A one-dimensional isothermal model was established to examine the performance of a hollow fiber membrane module composed of the described CO\(_2\)-selective membrane.

Removal of CO\(_2\) from the CO\(_2\)/CH\(_4\) mixture was conducted for natural gas applications. Unlike CO\(_2\)/H\(_2\) and CO\(_2\)/N\(_2\) separation, CO\(_2\)/CH\(_4\) separation needs to be carried out under relatively high feed pressure, e.g., 500 – 1000 psia, considering the real pressure at the natural gas wellhead. Chapter 4 discusses the study of membrane transport properties under high pressures. Due to the highly selective reaction between amine carriers and CO\(_2\), high CO\(_2\) permeability and high CO\(_2\)/CH\(_4\) selectivity were achieved simultaneously under a feed pressure of up to 500 psia. An optimum temperature of the membrane transport properties was identified as a result of the enhanced reaction rate with sufficient water retention and with the reduced CH\(_4\) solubility in the membrane. The effects of process parameters, namely, temperature, feed pressure, and permeate pressure, were investigated. Furthermore, thin film composite (TFC) membranes and asymmetric membranes were prepared to further improve the CO\(_2\) flux. With the configuration of TFC membrane, the effect of membrane thickness on the CO\(_2\) flux was studied and H\(_2\)S transport properties were investigated. Similar to the previous results, H\(_2\)S showed 2 – 3 times higher transport properties than CO\(_2\) and demonstrated a wide operating temperature range.

In Chapter 5, two new types of membrane with interesting morphology were studied. Decent CO\(_2\) transport properties at high temperatures are very desired for the
CO₂-selective WGS membrane reactor due to the requirement of the WGS catalyst. To address this problem, a variety of silica were incorporated into the organic polymer network to form the inorganic domain. The experiments demonstrated that better transport properties at high temperatures were obtained from hybrid inorganic-organic membranes. Block copolymers comprising of both hard segment and soft segment have been studied as a candidate for CO₂ removal from natural gas or flue gas. Also the Chapter 5 presents the synthesis of a family of novel copolyimides and their transport properties. These copolymers have microphase-separated structure. The rubbery polyester domains offer high chain mobility and strong affinity to the polar or quadrupolar gases, such as CO₂, while the glassy polyimide domains provide mechanical strength and the ability to form film.

One of the potential applications for this novel membrane would be water-gas-shift (WGS) membrane reactor for fuel cell hydrogen purification. Typically, H₂ is produced by the reforming process, followed by WGS reaction, which convert CO and generate more H₂.

\[
CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \quad \Delta H_r = -41.1 \text{ kJ/mol} \quad (1.1)
\]

In principle, a membrane reactor can be used to improve the performance of this reversible, exothermic reaction with the \textit{in-situ} separation of products. It is possible to overcome thermodynamic constraint and increase the CO conversion significantly.

To demonstrate the potential of CO₂-selective WGS membrane reactor, we have developed a one-dimensional non-isothermal model to simulate this complex process with the combination of reaction and separation. Chapter 6 focuses on the description and results of this model. The membrane reactor was in the configuration of hollow-fiber
module. The modeling results have shown that H₂ enhancement (>54% H₂ for the autothermal reforming of gasoline with air on a dry basis) via CO₂ removal and CO reduction to 10 ppm or lower are achievable for syngases. With this model, we also elucidated the effects of system parameters, including CO₂/H₂ selectivity, CO₂ permeability, and sweep/feed flow rate ratio, on the membrane reactor performance. Using the membrane synthesized, we have obtained <10 ppm CO in the H₂ product in WGS membrane reactor experiments. The experimental data agreed well with the model predictions.

In Chapter 7, important conclusions of this work are summarized with recommendations for future research on membrane-based acid gas removal.
SUMMARY: Compared to conventional separation technologies, membrane based acid-gas separation has shown many unique advantages. However, better transport properties are required to realize large-scale applications. With the aid of carrier complexation reaction, the facilitated transport membrane has shown the potential to achieve both high permeability and high selectivity simultaneously. A novel membrane was synthesized by incorporating amino groups into a polymer matrix. The membranes showed facilitated effect for both CO$_2$ and H$_2$S. A CO$_2$ permeability of above 2000 Barrers, a CO$_2$/H$_2$ selectivity of greater than 40, and a CO$_2$/N$_2$ selectivity of greater than 200 at 100 – 150°C were observed. In addition, these membranes showed very high H$_2$S transport properties. As a result of higher reaction rate and smaller diffusing compound, the H$_2$S permeability and H$_2$S selectivity to H$_2$ were about three times higher than those properties for CO$_2$. 

CHAPTER 2

SYNTHESIS OF CO$_2$ (H$_2$S)-SELECTIVE MEMBRANE
2.1 INTRODUCTION

2.1.1 Polymeric Membrane for Gas Separation

Over the last few decades, membrane separation processes have been extensively applied in many industrial areas. Compared to the conventional separation processes, they generally have the advantages of low energy consumption, steady-state operation and absence of moving parts (Ho and Sirkar, 1992). As a relatively young membrane technology, membrane based gas separation processes are both cost effective and environmentally friendly. In recent years, they have proved the potential as better alternatives to traditional separation processes, such as cryogenic distillation, absorption, and pressure swing adsorption (PSA) (Spillman, 1989; Koros and Fleming, 1993).

By a general definition, membranes are thin barriers that allow selective permeation of certain components. For gas separation process, membranes are primarily prepared with polymeric material, even if some inorganic membranes, such as ceramic, glass and metallic ones, also exist. Gas transport through a nonporous polymeric membrane is usually described by the solution-diffusion mechanism (Zolandz and Fleming, 1992). The permeability of a polymeric membrane to a gas component $i$, $P_i$, is defined in terms of the steady-state flux and the thickness-normalized pressure driving force. It can be calculated by:

$$P_i = \frac{J_i}{\Delta P_i / \ell}$$  \hspace{1cm} (2.1)

The common unit of permeability is Barrer ($1 \text{ Barrer} = 10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{ cm/cm}^2 \cdot \text{ s} \cdot \text{ cm Hg} = 0.76 \times 10^{-17} \text{ m}^3 \text{ (STP)} \cdot \text{ m/m}^2 \cdot \text{ s} \cdot \text{ Pa}$).
If the diffusion process follows Fick’s law and the downstream pressure is much less than the upstream pressure, the permeability is given by (Zolander and Fleming, 1992):

\[ P_i = D_i \times S_i \]  

(2.2)

where \( D_i \) and \( S_i \) are the average diffusivity and the solubility coefficients for the membrane, respectively. The ideal selectivity of a membrane for gas \( i \) over gas \( j \) is defined as the ratio of their pure gas permeabilities:

\[ \alpha_{ij}^* = \frac{P_i}{P_j} = \frac{D_i}{D_j} \left( \frac{S_i}{S_j} \right) \]  

(2.3)

where \( D_i/D_j \) is the diffusivity selectivity and \( S_i/S_j \) is the solubility selectivity. Diffusivity selectivity is kinetic in nature and depends strongly on the size-sieving ability of the polymer matrix, while solubility selectivity is thermodynamic in nature and determined by the relative condensability of the penetrants and the polymer-penetrant interaction.

Extensive research work has been done on the relationship between the chemical structure of polymer and gas permeation properties (Kim et al., 1988; Piroux et al., 2002a; Piroux et al., 2002b; Wind et al., 2002; Burns and Koros, 2003; Wind et al., 2004). Because of their excellent thermal and mechanical properties and better selectivity performance, polyimides are more promising candidates for use as gas separation membranes than the conventional glassy polymers such as cellulose acetate and polysulfone. Different types of polyimides have been studied for separation of mixed gas pairs, such as \( \text{O}_2/\text{N}_2 \), \( \text{H}_2/\text{CH}_4 \), \( \text{CO}_2/\text{CH}_4 \), \( \text{CO}_2/\text{N}_2 \), \( \text{H}_2\text{O}/\text{CH}_4 \), and the mixtures of olefin/paraffin. However, the application of polyimide membranes for gas separation is limited by its low gas permeability. In addition, the polyimide membrane with pure
solution-diffusion mechanism is not suitable for removing CO\(_2\) from H\(_2\) rich syngas since H\(_2\) has a smaller kinetic diameter than CO\(_2\) (Kim et al., 1988). Another problem occurring with glassy polymeric membranes is the membrane plasticization at high CO\(_2\) partial pressure. In general, plasticization is defined as the decrease of membrane selectivity due to the increased polymer-chain mobility in the presence of highly condensable penetrants, such as CO\(_2\), H\(_2\)O, and heavier hydrocarbons. In most current membrane processes, the separation mechanisms are based on solution, diffusion, and / or sieving. With these types of membranes, an increase in selectivity is often accompanied by a decrease in flux, and vice versa (Gottschlich et al., 1988; Robeson, 1991; Ho and Sirkar, 1992).

One way to improve the separation characteristics of solution-diffusion type polymeric membranes is to incorporate facilitated transport mechanism (Ward and Robb, 1967; Way and Noble, 1992). In this type of membrane, either mobile or fixed carrier agents, which can react reversibly with certain gas components, are incorporated. Therefore, the complexation reaction in the membrane creates another transport mechanism in addition to the solution-diffusion mechanism. The gas component of interest dissolves in the membrane firstly, and it can diffuse down its own concentration gradient or diffuse down a concentration gradient of a carrier-gas complex. The second diffusion mechanism is not accessible to the gas component that does not react with carrier agents.

Compared with the conventional membranes based on the solution-diffusion mechanism, facilitated transport membranes have several advantages: (1) they are often highly selective, especially at low concentration driving forces; (2) high permeability can
be achieved when the concentration driving force is low; and (3) they can maintain both high permeability and high selectivity at the same time.

2.1.2 Reaction Mechanism between Amines and Acid Gases

The separation of acid gases is of great importance in many industrial areas, such as hydrogen production, natural gas sweetening, reducing greenhouse gas emission, and fuel cell fuel processing. In all of these processes, it is highly desirable to remove CO₂ or H₂S while maintaining other components at the process pressure to avoid recompression. The typical CO₂ removal technologies include chemical solvent scrubbing, physical solvent scrubbing, pressure or temperature swing adsorption, membranes, and cryogenics. Among these technologies, chemical solvent scrubbing using regenerable alkanolamines is still the standard commercial method for treating industrial gas (Kohl and Riesenfeld, 1979).

Acid-gas scrubbing by absorption with reaction in aqueous amino alcohol solutions consists of two steps: absorption at high feed-gas pressure and low temperature (40–60°C) followed by amine regeneration in one or more strippers at reduced pressure and high temperature (120°C). Amine-based processes are generally used at CO₂ partial pressures in the feed gas up to 100–200 psia. At higher pressures physical absorption in polar organic solvents may be preferred. Physical solvents normally used for acid gas treating processes include chilled methanol (Rectisol® process licensed by Linde Engineering), N-methyl-2-pyrolidone (Purisol® process licensed by Lurgi AG), and dimethylether of polyethylene glycol (Selexol® process licensed by UOP LLC), etc. The
physical solvents have decent good equilibrium loading capacity and their regeneration may require less energy. However, these solvents normally suffer from the co-absorption of hydrocarbons and they are relatively expensive.

The reaction kinetics between CO$_2$ / H$_2$S and amines have been studied extensively mainly for amine absorption processes. The alkanolamines of industrial importance include monoethanolamine (MEA), diethanolamine (DEA), di-isopropanolamine (DIPA), N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP). Based on the chemical structure, they can be divided into primary amines, secondary amines, tertiary amines, and sterically hindered amines.

The reaction between CO$_2$ and the amine can be described with the zwitterions-mechanism, which was originally proposed by Caplow$^{17}$ and reintroduced by Danckwerts.$^{18}$ First, CO$_2$ reacts with primary or secondary amines, RR’NH ($R$: functional group; $R’$: functional group or hydrogen), to form zwitterions, as an intermediate. This reaction is believed to be the rate-controlling step.

$$CO_2 + RR’NH \rightleftharpoons RR’N^+HCOO^-$$  \hspace{1cm} (2.4)

Then zwitterion is deprotonated rapidly by bases such as amine itself and H$_2$O to form the carbamate ion.

$$RR’N^+HCOO^- + RR’NH \rightleftharpoons RR’NCOO^- + RR’NH_2^+$$  \hspace{1cm} (2.5)

$$RR’N^+HCOO^- + H_2O \rightleftharpoons RR’NCOO^- + H_3O^-$$  \hspace{1cm} (2.6)

Combining Equations (2.4) and (2.5), we obtain:

$$CO_2 + 2RR’NH \rightleftharpoons RR’NCOO^- + RR’NH_2^+$$  \hspace{1cm} (2.7)
From this overall equation, it can be seen that the maximum loading is 0.5 mol CO\(_2\)/mol of amine by stoichiometry. Under the high pressure, a certain amount of carbamate hydrolysis may occur to form bicarbonate and regenerate free amines.

\[ RR'NCOO^- + H_2O \rightarrow RR'NH + HCO_3^- \] (2.8)

Since the regenerated free amine can react with additional CO\(_2\), the loading capacity can exceed 0.5.

For tertiary amines \(RR'R''N\) (\(R, R', R''\): functional group), it is impossible to form carbamate, the CO\(_2\)-amine reaction will result in the formation of bicarbonate ion

\[ CO_2 + RR'R''N + H_2O \rightarrow RR'R''NH^+ + HCO_3^- \] (2.9)

This reaction indicates that tertiary amine may catalyze the hydration of CO\(_2\) instead of reacting directly with CO\(_2\) (Versteeg and van Swaaij, 1988; Littel et al., 1990). Therefore, a maximum loading of 1 mol CO\(_2\)/mol of amine may be reached. In spite of this attractive high CO\(_2\) loading, the application of tertiary amines is restricted by the low CO\(_2\)-amine reaction rate. In recent years, the use of mixed amine has been studied to promote the absorption of CO\(_2\) in amine solution (Mandal and Bandyopadhyay, 2005; Mandal and Bandyopadhyay, 2006). Blends of primary and tertiary amines or secondary and tertiary amines have shown the combination of the higher equilibrium capacity of the tertiary amine and the higher reaction rate of the primary or secondary amine. The promotion effect was mainly explained by so-called “shuttle mechanism” (Astarita et al., 1981). The reaction between CO\(_2\) and primary or secondary amine to form carbamate was considered to be instantaneous, and the hydrolysis of carbamate to bicarbonate was assumed to be very slow compared to mass transfer. The formation of carbamate,
therefore, provided an additional parallel path for the diffusion of CO$_2$ from the gas-liquid interface into the liquid bulk.

A sterically hindered amine is defined as a primary amine with the amino group attached to a tertiary carbon atom or a secondary amine with the amino group attached to a secondary or tertiary carbon atom (Sartori et al., 1987). As with tertiary amines, such as MDEA, sterically hindered amines also provide an equilibrium CO$_2$ loading capacity of 1 mol CO$_2$ / mol of amine. In addition, sterically hindered amines will provide much higher CO$_2$-amine reaction rate than tertiary amines.

Introducing steric hindrance by a bulky functional group adjacent to the amino group lowers the stability of the carbamate formed by CO$_2$-amine reaction. As shown in Table 2.1, this lower stability has been verified experimentally by measuring the carbamate stability constant, $K_c$, using carbon-13 nuclear magnetic resonance (Sartori and Savage, 1983).

$$K_c = \frac{[RR'NCOO^-]}{[RR'NH \cdot HCO_3^-]}$$  \hspace{1cm} (2.10)

Reducing carbamate stability allows thermodynamic CO$_2$ loadings to exceed those attainable with conventional, stable-carbamate amines. In addition, the lower stability of carbamate also results in a higher concentration of free amine in the system. Therefore fast amine-CO$_2$ reaction rates are obtained even though the rate constant is reduced due to the steric interference. The final product of CO$_2$-amine reaction is bicarbonate.

$$CO_2 + RNH_2 + H_2O \rightleftharpoons RNH_3^+ + HCO_3^-$$  \hspace{1cm} (2.11)
The reaction mechanism of the CO$_2$ with KHCO$_3$-K$_2$CO$_3$ was presumably similar to that of potassium carbonate promoted by hindered amine described in Equation (2.12) (Sartori and Savage, 1983; Shulik et al., 1996):

$$CO_3^{2-} + CO_2 + H_2O \rightleftharpoons 2HCO_3^-$$  \hspace{1cm} (2.12)

For H$_2$S, the reaction is via proton transfer, and it produces the bisulfide ion.

$$H_2S + RR'NH \rightleftharpoons HS^- + RR'NH_2^+$$  \hspace{1cm} (2.13)

This reaction can be regarded as reversible and instantaneously fast with respect to mass transfer. In other words, H$_2$S-amine equilibrium exists everywhere in the system. In addition, the reactions between H$_2$S and any amines (primary, secondary or tertiary) are the same. This characteristic gives tertiary amines very high H$_2$S vs. CO$_2$ selectivity, considering very low reaction rate between CO$_2$ and tertiary amines.

In the facilitated transport process, these carrier-gas reaction products, i.e., carbamate, bicarbonate and bisulfide ions, will diffuse down their concentration gradient or pass off to the next complex agent. Because of molecular size, bisulfide ion can diffuse through the membrane much faster than the other two complexes, which, together with the fast proton transfer (Cornelissen, 1980), results in much higher permeability.

In addition, a water-swollen condition may provide better facilitation effect than a dry condition. This is due to the fact that CO$_2$ hydration reaction would be enhanced in the presence of amino groups, which work as weak base catalysts. CO$_2$ transport is, therefore, facilitated in the form of bicarbonate (Matsuyama et al., 1996a).

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$ \hspace{1cm} (2.14)
2.1.3 Facilitated Transport Membrane for Acid-gas Removal

Facilitated transport membranes for acid gases removal have been investigated since the 1960s. Like the amine scrubbing process, amines are typically employed to react with CO$_2$ or H$_2$S. Therefore, people could adapt directly amine-gas reaction mechanisms shown above to facilitated transport membranes. However, unlike the amine scrubbing process, membrane separation is a non-equilibrium process combining absorption on the high pressure side and amine regeneration on the low pressure side, which significantly lowers the energy and space requirements. The typical facilitated transport mechanism for CO$_2$ removal is shown in Figure 2.1.

Based on the carrier mobility, facilitated transport membranes can be divided into mobile carrier membranes and fixed carrier membranes. In mobile carrier membranes, the carrier can diffuse in the membrane. Generally, they were prepared by immersing the microporous supports in the carrier solutions or reactive solvent, which was known as immobilized liquid membrane (ILM). Ward and Robb immobilized an aqueous bicarbonate-carbonate solution into a porous support and reported a CO$_2$/O$_2$ separation factor of 1,500 (Ward and Robb, 1967). Meldon et al. investigated the facilitated transport of CO$_2$ through an immobilized alkaline liquid film (Meldon et al., 1977). Their experimental results confirmed that weak acid buffers significantly increased the CO$_2$ transport. For CO$_2$/N$_2$ separation, Dr. Sirkar’s group has proposed to use glycerol carbonate, sodium carbonate/glycerol and dendrimer in the ILM configuration with the microporous substrate of either hydrophilized poly(vinylidene fluoride) (PVDF) or Celgard 2500 polypropylene (Chen et al., 2000; Chen et al., 2001; Kovvali and Sirkar,
2001; Kovvali and Sirkar, 2001). Teramoto et al. proposed a novel facilitated transport membrane module, in which a carrier solution was forced to permeate through a microporous membrane and then was recycled continuously (Teramoto et al., 2001; Teramoto et al., 2002; Teramoto et al., 2003; Teramoto et al., 2004). Improved stability and lower energy consumption than the conventional chemical absorption process were illustrated. Recently, Marzouqi and his coworkers compared the CO$_2$ removal performance of ILMs containing different amine solvents including diethylenetriamine (DETA), diaminoethane (DAE), diethylamine (DEYA), and bis(2-ethylhexyl)-amine (BEHA) (Marzouqi et al., 2005). However, this configuration has two major problems, e.g., the membrane can be dried out at high temperatures and the carrier agents can be lost. The instability issues seriously hindered the industrial application of ILMs.

To improve the membrane stability, ion-exchange membrane was first proposed as the support of ILM by LeBlanc et al. (LeBlanc et al., 1980). When the ionic mobile carriers such as monoprotonated ethylenediamine were immobilized in an ion exchange membrane by the electrostatic force, the washout of carrier would be reduced to some extent. Way et al. studied CO$_2$ facilitated transport through a perfluorosulfonic acid cation-exchange membranes using the same carrier (Way et al., 1987; Way and Nobel, 1989). The authors proposed a reaction equilibrium model similar to the one used for the ILM. The ion-exchange membrane used by Langevin et al. was sulfonated styrene-divinylbenzene in a fluorinated matrix, and a transport model based on the Nernst-Planck equation was developed to interpret the experimental results (Langevin et al., 1993). Yamaguchi and coworkers compared the CO$_2$ facilitated effect of cross-linked polyallylamine membranes and amine functionalized Nafion® membranes (ion-exchange
membranes) (Yamaguchi et al., 1995; Yamaguchi et al., 1996). They have found that although the former membranes had a larger CO$_2$ absorption capacity than the ion-exchange membranes, their facilitation effect of CO$_2$ was very small, which may be due to the low reactive diffusivity. Matsuyama et al. prepared various ion exchange membranes via the plasma graft polymerization and employed different amine moieties as the carriers (Matsuyama et al., 1994; Matsuyama et al., 1996b). They have also blended poly(acrylic acid) with poly(vinyl alcohol) to prepare membranes and introduced monoprotonated ethylenediamine into the membranes by ion-exchange and used it as the carrier (Matsuyama et al., 2001). The major drawbacks for ion-exchange membrane are the troublesome preparation procedure and the loss of carrier in the presence of other ions.

In fixed carrier membranes, in which the reactive carrier agents are covalently bonded to the polymer backbone, CO$_2$ reacts at one carrier site and then hops to the next carrier site along the direction of the concentration driving force via the “hopping” mechanism (Cussler et al., 1989). Yamaguchi et al. developed polyallylamine membranes and compared them with ion-exchange membranes containing amines as the counterions (Yamaguchi et al., 1995). By the plasma graft polymerization, Matsuyama et al. prepared a fixed carrier membrane by grafting 2-($N,N$-dimethyl)aminoethyl methacrylate onto the microporous polyethylene substrate (Matsuyama et al., 1996a). They also tried to blend polyethylenimine and poly(vinyl alcohol) together for the facilitated transport of CO$_2$ (Matsuyama et al., 1999). Heat treatment was found to be beneficial to the increase of CO$_2$ selectivity. Kim et al. reported polyvinylamine membranes prepared by casting polyvinylamine on various microporous support followed with crosslinking (Kim et al., 2004b). A CO$_2$ permeance of 0.014
m³(STP)/m²·bar·h and a CO₂/CH₄ ideal selectivity of > 1000 were demonstrated under the feed pressure of 1–4 bar. They also identified the important role of water as the mobile medium for CO₂ transport. Xomeritakis et al. prepared a sol-gel derived microporous inorganic membrane containing amino groups (Xomeritakis et al., 2005). With the aid of precisely controlled pore size of 4–5 Å, this facilitated transport membrane showed promising CO₂/N₂ selectivities. Other examples for the amine fixed carrier membrane included hydrolyzed polyvinylpyrrolidone membranes (Zhang et al., 2002) and crosslinked polyvinylamine/polyethylene glycol membranes (Yi et al., 2006). Besides amine carriers, Quinn and coworkers used molten salt hydrate or polyelectrolyte, the polymeric analog of salt hydrate, as carriers, a CO₂/H₂ selectivity of 87 and a CO₂ permeance of 6×10⁻⁶ cm³/cm²·s·cmHg were achieved at the ambient temperature (Quinn et al., 1995; Quinn and Laciak, 1997). In the previous study of our group, we reported crosslinked polyvinyl alcohol (PVA) membranes containing dimethylglycine (DMG) salts and polyethylenimine, and found that both CO₂ permeability and CO₂/H₂ selectivity of the membranes increased as temperature increased in the temperature range of 50 – 100°C (Tee et al., 2006). Even though the mobile carrier membranes have shown higher CO₂ transport rates than the fixed-carrier membranes owing to the higher reactive diffusivity, the fixed carrier membranes were considered as the most stable configuration.

Cussler et al. proposed a theory for facilitated transport in fixed carrier membranes based on so-called “Tarzan swing” mechanism (Cussler et al., 1989). According to this theory, the concentration of the complexing agent should be higher than a certain concentration, or percolation threshold, and then the distance between the complexing agents will be short enough to “pass off” a solute molecule from one
complexing agent to the next one. In the other theory, Noble proposed that solute molecules could migrate between complexing agents by moving along the polymer chain (Noble, 1990). A derivation of the effective diffusion coefficient for the solute-carrier complex, which was analogous to facilitated transport in liquid membranes, was developed.

2.2 CO$_2$ (H$_2$S)-SELECTIVE MEMBRANE

The CO$_2$ (H$_2$S)-selective facilitated transport membranes were synthesized by incorporating amine carries into the hydrophilic polymer network. The separation performances of these membranes on CO$_2$ and H$_2$S were studied with a gas permeation unit.

2.2.1 Membrane Synthesis and Characterization

Poly(vinyl alcohol) (PVA) with 99+% hydrolysis [from poly(vinyl acetate)] and a molecular weight of 89,000 – 98,000, potassium hydroxide (KOH) (85+ wt%), formaldehyde (37 wt% solution in water), and 2-aminoisobutyric acid (AIBA) were purchased from Aldrich Chemicals (St. Louis, MO). Poly(allylamine hydrochloride) was from Polysciences, Inc. (Warrington, PA). Deionized water (D.I. water) from Reagent Laboratory, the Ohio State University, was used as the solvent during the membrane preparation. All these chemicals were used as received without further purification.
Two certificated gas mixtures were used as the feed gas. The gas compositions were 20% CO$_2$, 40% H$_2$, 40% N$_2$ and 1% CO, 17% CO$_2$, 45% H$_2$, 37% N$_2$, respectively. The second composition simulated the composition of syngas from the autothermal reforming of gasoline with air. Pre-purified argon (99.998%) was used as the sweep gas in the gas permeation measurements. All of them were obtained from Praxair, Inc. The porous poly(tetrafluoroproethylene) (PTFE) support (thickness = 60 $\mu$m, average pore size = 0.2 $\mu$m, porosity = 80%) was donated by BHA Technologies (Kansas City, MO), and GE E500A microporous polysulfone support (total thickness = 160 $\mu$m, average pore size: 0.05 $\mu$m) was given to us by GE Infrastructure (Vista, CA).

The membrane of PVA-containing amino functional groups in the thin-film-composite structure was prepared by the solution casting method. The crosslinked PVA was prepared by mixing PVA with formaldehyde in water solution at 80°C for 20 hr. A proper amount of KOH was added as catalyst. The amount of formaldehyde was designed to crosslink 60% of the hydroxyl groups of PVA. The crosslinking of PVA with formaldehyde is a condensation reaction, which is shown schematically in Figure 2.2.

Free polyallyamine was prepared by mixing poly(allylamine hydrochloride) with a stoichiometric amount of KOH for overnight in methanol. 2-Aminoisobutyric acid (AIBA) potassium salt (AIBA-K) was synthesized by mixing AIBA with a stoichiometric amount of KOH in water for 30 min. The chemical structures of these compounds are illustrated in Figure 2.3. The designed amounts of these two chemicals were then added into the crosslinked PVA solution as the fixed and mobile carriers, respectively. The resulting solution was centrifuged to remove air bubbles and cast to a uniform thickness
with a stainless steel film applicator (Paul N. Gardner Co.) on the microporous PTFE support or microporous polysulfone support. The membrane was dried first in a fume hood at ambient conditions overnight to remove most of the water, and then further cured in a 120°C furnace for 6 hr to complete the crosslinking reaction. The final composition was 50 wt.% PVA (60 mol.% crosslinked), 10 wt.% AIBA-K, 20 wt.% KOH, and 20 wt.% polyallylamine. The scanning electron microscopic (SEM) images on the cross-section of the membrane prepared were taken using an XL-30 ESEM scanning electron microscope (FEI Company, Hillsboro, OR). The SEM samples were prepared by being freeze-fractured in liquid nitrogen, dried in a vacuum oven, and then coated with gold.

The transport properties of the membrane were measured by using a gas permeation unit, as shown in Figure 2.4. In the experiments, the membrane with the thickness of 30 μm was cut into a circular piece with an effective membrane area of 45.6 cm² and mounted into a circular permeation cell. The ternary gas mixture containing 20% CO₂, 40% H₂ and 40% N₂ at a flow rate of 60 ml/min (at ambient conditions) was used as the feed gas. The total pressure on the feed side was measured by a pressure gauge and set at 2 atm via a back pressure regulator (Tescom, Model 44-2362-24, Elk River, MN). The total pressure of argon sweep gas was set at 1 atm, and the flow rate was 30 ml/min (at ambient conditions).

On both the feed and sweep sides, D.I. water at the flow rate of 0.03 ml/min was pumped into the gas permeation unit by a solvent delivery pump (Varian, Prostar 210, Walnut Creek, CA). Water vapor and each of the dry gases were mixed well in a vessel, respectively. The testing temperature was adjusted with an oven temperature controller (Bemco, Model FTU4.6+50×350C, Simi Valley, CA). After leaving the gas permeation
cell, the water vapor in both the retentate (outlet gas from the feed side) and the permeate (outlet gas from the sweep side) were trapped in water knockout vessels. The dry gas compositions of both gas streams were analyzed using a gas chromatograph (GC) (Agilent, Model 6890N, Santa Clara, CA) equipped with a stainless steel micropacked column (Supelco, 80/100 mesh, Carboxen-1004, Bellefonte, PA) and a thermal conductivity detector (TCD). A counter-current flow configuration was applied to offer the maximum driving force across the membrane, which resulted in the best separation performance.

2.2.2 Membrane Structure

As described above, the facilitated transport membrane consists of hydrophilic polymeric matrix and amine carrier. In this membrane system, poly(vinyl alcohol) (PVA) was chosen as the polymeric matrix, while amine carries such as polyallylamine, AIBA-K, and KHCO$_3$-K$_2$CO$_3$ were incorporated as CO$_2$ (H$_2$S) carriers.

PVA, a 1,3-diglycol polymer with a repeating unit molecular weight of 44, is an excellent hydrophilic membrane material. PVA is named similar to those vinyl polymers which are prepared by the polymerization of vinyl monomers. However, it is actually made from the partial or complete hydrolysis of poly(vinyl acetate), because the corresponding monomer, vinyl alcohol, almost only exists as its rearrangement product acetaldehyde. Besides the high hydrophilicity, PVA has also shown the excellent compatibility with amine carriers and good film-forming ability (Zou and Ho, 2006).
The common PVA is typically *atactic*, i.e., the hydroxyl groups are oriented randomly along the polymer backbone. Like many other vinyl polymers, PVA is semi-crystalline polymer and consists of both crystalline domain and amorphous domain. Glass transition temperature \( (T_g) \) for PVA is typically \( 85^\circ \text{C} \) under the dry condition. However, \( T_g \) will decrease significantly after absorbing certain amount of water. For example, 6% by weight of water would lower \( T_g \) to room temperature.

However, pure PVA is soluble in water, so that either physical method (heat treatment to increase crystallinity) or chemical method (crosslinking) should be used to make PVA membranes water-insoluble. Particularly the latter method can greatly increase the stability of PVA membranes at high temperatures. The acetalation of PVA has attracted a great deal of attention largely because this process is useful in the modification of PVA fibers. The reaction is subject to catalysis by strong acids or bases and can be brought about easily in aqueous solution. The simplest acetal, usually termed a formal, is formed between PVA and formaldehyde. The acetal links are stable in neutral and basic solutions, although the condensation is in principle reversible in acid solutions.

The final membrane could be either a relatively thick free-standing membrane or composite membrane consisting of a thin selective layer and a supporting layer. The scanning electron microscopic picture of the membrane synthesized on a microporous polysulfone support is shown in Figure 2.5. This membrane had a composite structure and contained both active dense toplayer and supporting porous sublayer. As shown in this figure, the nonporous selective membrane was about 20 micron thick, and the microporous substrate was about 80 micron thick.
2.2.3 CO₂ Transport Properties

The transport properties of the gas separation membrane are characterized primarily by permeability and selectivity. The calculation of permeability of a gas species $i$ has been defined earlier in Equation (2.1). The true selectivity between two species, $i$ and $j$, in a gas mixture may be expressed as (Zolandz and Fleming, 1992):

$$a_{ij} = \frac{y_i}{y_j} \frac{x_j}{x_i}$$

(2.15)

Based on the measured gas compositions of both the retentate and the permeate, mass balance was carried out with the assumption of constant argon molar flow rate on the sweep side. The CO₂ permeability and CO₂/N₂ selectivity were then calculated from Equations (2.1) and (2.15), respectively.

Figures 2.6, 2.7 and 2.8 show the CO₂ permeability, CO₂/H₂ selectivity and CO₂/N₂ selectivity as the function of temperature, respectively. As the temperature increased from 100 to 110°C, permeability and both selectivities increased, which could be explained by the higher CO₂-amine reaction rate at the higher temperature and lower H₂ and N₂ solubility in membrane. A CO₂ permeability of 6196 Barrers, a CO₂/H₂ selectivity of 270 and a CO₂/N₂ selectivity of 493 were obtained at 110°C. After the temperature increased to 120°C or higher, permeability and both selectivities gradually dropped. This was because the water content in the membrane decreased with increasing temperature. However, a CO₂ permeability of above 2000 Barrers, a CO₂/H₂ selectivity of about 10 and a CO₂/N₂ selectivity of greater than 40 were still observed at 170°C. It shows that PVA, as a very hydrophilic polymer, is a desirable polymer matrix for the CO₂-selective facilitated transport membrane. Crosslinking is necessary for PVA to hold
membrane structure and maintain enough water content at high temperatures. Polyallylamine, AIBA-K, and KHCO$_3$-K$_2$CO$_3$ (converted from KOH) provide the carriers to facilitate CO$_2$ transport as discussed earlier.

2.2.4 H$_2$S Transport Properties

Similar to CO but in much higher severity, H$_2$S is also a poisonous gas for the fuel cell catalyst. Since sulfur compounds are naturally present in all fossil fuels, small quantities remain after the reforming processes and must be almost completely removed prior to entering the fuel cell. Less than 10 ppb H$_2$S in H$_2$ fuel is required for fuel cell applications. As explained earlier, the CO$_2$-selective membrane synthesized should also show high selectivity to H$_2$S, based on the chemical reaction mechanism.

The H$_2$S transport properties of the membrane were measured using the same gas permeation unit shown previously. To analyze the H$_2$S concentration in the outlet gas streams, an additional sulfur chemiluminescence detector (SCD, Antek instruments L. P., Huston, TX) was installed in the Agilent 6890N GC. H$_2$S gas samples with concentration from 5 ppb to 50 ppm could be measured accurately using different sensitivity ranges. The facilitated transport membrane used in the experiments had the composition of 55 wt.% PVA (100 mol.% crosslinked), 20 wt.% AIBA-K, 10 wt.% KOH, and 15 wt.% polyallylamine. A certificated gas mixture, with the composition of 50 ppm H$_2$S, 1% CO, 17% CO$_2$, 45% H$_2$, and 37% N$_2$, was used as the feed gas. Following the same membrane testing procedure, both CO$_2$ and H$_2$S separation performances were studied at
elevated temperatures. Also, a variety of feed gas rates were applied to study the H$_2$S removal capacity of the membrane at 120°C.

Figures 2.9 and 2.10 illustrate the permeability and selectivity data at different temperatures, respectively. With the increase of temperature, both H$_2$S and CO$_2$ permeabilities decreased due to the reduced water content inside the membrane. At all temperatures, the membrane showed around 3 times higher H$_2$S permeability than CO$_2$ permeability. This could be explained by the fast reaction rate of H$_2$S with amine and small molecular size of bisulfide ion compared with carbamate or bicarbonate. Unlike permeability, the selectivity data showed an optimal temperature. Even though the H$_2$S flux or permeability decreased from 110°C to 120°C, H$_2$ flux was reduced even more because of the much less H$_2$ solubility at a higher temperature. Therefore, the maximum H$_2$S/H$_2$ selectivity was observed at 120°C. At 140°C, a decreased H$_2$S flux caused a significantly lower selectivity. Similarly, H$_2$S/H$_2$ selectivities were around 3 times higher than CO$_2$/H$_2$ selectivities.

Figure 2.11 demonstrates the exit dry H$_2$S concentration as a function of feed flow rate. The temperature was set as 120°C for optimal membrane performance. As can be seen, the exit H$_2$S concentration increased as the feed flow rate increased, which was due to the less residue time in the membrane cell at higher gas flow rates. With a relatively small membrane area (45.6 cm$^2$), H$_2$S was removed from 50 ppm to less than 100 ppb when a 10 cc/min feed flow rate was applied. By a simple calculation, 10 cc/min feed flow rate was corresponded to a gas hourly space velocity of ~ 5800 hr$^{-1}$. This high H$_2$S removal capacity would be advantageous for WGS membrane reactor composed of the
CO₂-selective membrane described. H₂S could be reduced to less than 10 ppb at the entrance section and the sulfur poisoning of WGS catalyst would be avoided afterwards.

2.3 CONCLUDING REMARKS

Polymeric membranes containing amino groups with high CO₂ permeabilities and high CO₂/H₂ and CO₂/N₂ selectivities have been synthesized. With the increase of temperature from 100 to 170°C, transport properties of the membrane increased first due to the higher CO₂-amine reaction rate and lower H₂ and N₂ solubility, and then dropped because of water loss at high temperatures. Membranes showed a CO₂ permeability of above 2000 Barrers, a CO₂/H₂ selectivity of greater than 40, and a CO₂/N₂ selectivity of greater than 200 at 100 – 150°C. In addition, these membranes showed very high H₂S transport properties. The H₂S permeability and H₂S selectivity to H₂ were about three times higher than those properties for CO₂. With a circular permeation cell having a membrane area of 45.6 cm², H₂S was efficiently removed from 50 ppm to less than 100 ppb at a gas hourly space velocity of ~ 5800 hr⁻¹.
<table>
<thead>
<tr>
<th>Amino alcohol</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="MEA structure" /> (MEA)</td>
<td>12.5</td>
</tr>
<tr>
<td><img src="image" alt="DEA structure" /> (DEA)</td>
<td>2.0</td>
</tr>
<tr>
<td><img src="image" alt="AMP structure" /> (AMP)</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

Table 2.1. Carbamate stability constants for different amines at 40 °C by carbon-13 NMR (Sartori and Savage, 1983)
Figure 2.1. Facilitated transport mechanism.
Figure 2.2. Synthesis of the crosslinked PVA with formaldehyde.
Figure 2.3. Chemical structures of (a) free polyallylamine and (b) AIBA-K.
Figure 2.4. Schematic of the gas permeation unit.
Figure 2.5. Scanning electron microscopic picture of the membrane synthesized.
Figure 2.6. CO$_2$ permeability vs. temperature.
Figure 2.7. CO$_2$/H$_2$ selectivity vs. temperature.
Figure 2.8. CO$_2$/N$_2$ selectivity vs. temperature.
Figure 2.9. H$_2$S and CO$_2$ permeability vs. temperature.
Figure 2.10. $\text{H}_2\text{S}/\text{H}_2$ and $\text{CO}_2/\text{H}_2$ selectivity vs. temperature.
Figure 2.11. H\textsubscript{2}S removal capacity with the circular gas permeation cell (45.6 cm\textsuperscript{2}).
SUMMERY: The novel CO$_2$-selective membrane with the facilitated transport mechanism has been applied to the CO$_2$ capture from gas mixtures, especially flue gas. The membrane showed the desired CO$_2$/N$_2$ selectivity of 493 and CO$_2$ permeability of 6196 Barrers at 110°C. With a membrane area of 342.70 cm$^2$, we have demonstrated efficient CO$_2$ removal from 17% to about 100 ppm at a feed gas flow rate of 60 ml/min and to about 1,000 ppm at 120 ml/min. In the CO$_2$ capture experiments from a gas mixture with N$_2$ and H$_2$, a permeate CO$_2$ dry concentration of greater than 98% was obtained by using steam as the sweep gas. The effects of feed flow rate and sweep-to-feed molar ratio on the membrane separation performance were investigated. A one-dimensional isothermal model was established to examine the performance of a hollow fiber membrane module composed of the described CO$_2$-selective membrane. The modeling results show that a CO$_2$ recovery of greater than 95% and a permeate CO$_2$ dry concentration of above 98% are achievable from a 1000 standard cubic feet per minute (SCFM) or 21.06 mol/s flue gas stream with a 2 ft (0.61 m) hollow-fiber module containing 980,000 fibers.
3.1 INTRODUCTION

Flue gas typically refers to the combustion exhaust gas produced at fossil fuel-fired power plants. Even though its composition varies from place to place, it usually consists of mostly N\(_2\) from the combustion air, CO\(_2\) and water vapor. The increasing public concern over global warming has concentrated on the anthropogenic (man-made) emissions of greenhouse gases, especially CO\(_2\). Because the flue gas is responsible for around one-third of total global CO\(_2\) emission (US DOE, 2005), it becomes the major target for CO\(_2\) capture and storage. Besides the desire to reduce greenhouse gas emissions, CO\(_2\) capture from the flue gas is also propelled by the merchant CO\(_2\) market and the renewed interest in enhanced oil recovery (EOR). CO\(_2\) can be used in the industry for carbonated beverages, brewing, firefighting and solvent extraction as a supercritical fluid. Also CO\(_2\) flooding is regarded as the most cost-effective method for enhancing the oil recovery from the depleted fields, which is of increasing interest considering the recent high crude oil price.

Compared with other gas treating applications, such as natural gas sweetening and H\(_2\)-rich syngas purification, the CO\(_2\) recovery from flue gas has its own requirements. For instance, flue gases have very low CO\(_2\) partial pressure because they are typically available at or near ambient pressure with CO\(_2\) concentrations of 4 to 14 %. Also flue gases typically remain high temperatures (200 – 300\(^\circ\)C) when coming out from boilers.

Currently, the principal CO\(_2\) capture technology for the flue gas application is still the amine scrubbing process (Aaron and Tsouris 2005). Due to the low CO\(_2\) partial pressure, only primary amines such as monoethanolamine (MEA) are active enough for
CO₂ recovery. And the hot flue gas must be cooled to around 50°C before entering the scrubber, because otherwise it could cause the solvent degradation and decrease process efficiency.

Compared to the amine scrubbing process, membrane-based CO₂ capture has the advantages of low energy consumption, simplicity of operation, and absence of moving parts. However, today’s commercial polymeric membranes, such as cellulose acetate and polyimide, suffer from low CO₂ permeability and selectivity, since they are based on solution-diffusion mechanism and rely primarily on the subtle size differences of the penetrants to achieve separation. Also, these membranes are not suitable for high-temperature and high-humidity operation, which is required in the direct CO₂ capture from the flue gas in power plants (Koros and Mahajan, 2000; Bredesen et al., 2004). For the specific application of CO₂ capture from the flue gas, it has been reported that a CO₂/N₂ selectivity of greater than 70 and a minimum CO₂ permeability of 100 Barrers are required for the economic operation (Hirayama et al., 1999; Bounaceur et al., 2006). As an alternative to conventional polymeric membranes, facilitated transport membranes have shown better promise to satisfy these goals (Way and Noble, 1992).

As described in Chapter 2, the amine-gas reaction offers an extra transport mechanism for the target gas in the facilitated transport membrane. Therefore, high permeability and high selectivity can be achieved under relatively low driving force (or pressure difference), which is particularly desired for CO₂ removal from the flue gas. In this chapter, the application of the CO₂-selective membrane in flue gas application is investigated systematically. A transport model was established to evaluate the performance of a commercial membrane module using the described membrane.
3.2 CO₂ CAPTURE EXPERIMENTS

The CO₂-selective membrane was prepared by the same procedure described in Chapter 2. Both polyallylamine as the fixed carrier and AIBA-K as the mobile carrier were incorporated in the crosslinked PVA matrix. The final composition was 50 wt.% PVA (60 mol.% crosslinked), 10 wt.% AIBA-K, 20 wt.% KOH and 20 wt.% polyallylamine. The transport properties of the membrane, especially on CO₂/N₂ separation, were measured by using the gas permeation unit described.

To illustrate the CO₂ removal capacity of the flat-sheet membrane, we constructed a rectangular gas permeation cell, which had a larger effective membrane area of 342.70 cm² (19.10 cm × 17.95 cm) and well-defined gas-flow channels on both the feed and sweep sides. The feed gas consisted of 1% CO, 17% CO₂, 45% H₂, and 37% N₂ (on dry basis). The water contents on the feed and sweep sides were approximately 35% and 95%, respectively. A membrane with the same composition as the previous one but a thickness of about 40 μm was used. The retentate CO₂ dry from various feed flow rates ranging from 10 ml/min to 130 ml/min (at ambient conditions), were measured.

The experiments on CO₂ capture from a gas mixture were performed in the circular permeation unit described earlier. Compared to other gases, steam is the more desirable sweep gas in the CO₂ capture process, since steam will condense to become water at ambient conditions and a high-purity CO₂ product can be readily obtained. The ternary gas mixture containing 20 % CO₂, 40 % H₂, and 40 % N₂ was used as the feed gas. Varying gas flow rates were applied to study the effects of process parameters, such as the feed flow rate and the sweep-to-feed molar ratio, on the CO₂ recovery and the
permeate CO₂ purity. The CO₂ recovery was defined as the ratio of the permeate CO₂ molar flow rate to the feed inlet CO₂ molar flow rate. The experimental conditions are listed in Table 3.1. All of the CO₂ capture experiments were performed at 110°C for the optimal membrane transport properties. Feed-side and sweep-side pressures were set at 2 and 1.1 atm, respectively.

3.3 MODELING WORK

Although the CO₂-selective membrane discussed above is still in the laboratory development stage, it is of interest to evaluate the separation performance of the commercial-size membrane module based on the transport data obtained experimentally. In the modeling work, a one-dimensional isothermal model was setup to simulate the CO₂ capture from the flue gas with a hollow fiber membrane module composed of the CO₂-selective membrane described above. The following assumptions were made in the model:

(1) The module is isothermal and operating at a steady state;

(2) The module is operated with a counter-current configuration;

(3) There is no axial mixing;

(4) The pressure drops on both lumen and shell sides are negligible.

Based on the differential volume element on a single hollow fiber along the length direction, as shown in the lower, right side of Figure 3.1, the molar balances for gas species \( i \) on the feed (lumen) side and the sweep (shell) side can be expressed as Equation (3.1) and Equation (3.2), respectively.
\[
\frac{dn_{f_i}}{dz} = -\pi d_{in} J_i \quad (3.1)
\]

\[
\frac{dn_{s_i}}{dz} = -\pi d_{in} J_i \quad (3.2)
\]

where \( J_i \) is expressed as follows:

\[
J_i = P_i \frac{\Delta p_i}{\ell} \quad (3.3)
\]

The feed gas was assumed to be a simulated flue gas mixture containing 9% CO\(_2\), 11% H\(_2\)O, and 80% N\(_2\) at a flow rate of 1000 standard cubic feet per minute (SCFM) or 21.06 mol/s. Pure steam was used as the sweep gas. The operating temperature was assumed to be 110°C, and both feed-side and sweep-side pressures were set at 1 atm considering the real case of the flue gas from power plants. The inlet sweep-to-feed molar flow rate ratio was set at 3.

The \textit{bvp4c} solver in Matlab\textsuperscript{®} was used to solve the above differential equations of the boundary value problem. During the calculations, the hollow fiber number was adjusted to satisfy a constraint of CO\(_2\) recovery, i.e., \( > 95\% \). In addition, a similar flat-sheet model was applied to simulate the CO\(_2\) removal experiments with the rectangular cell described earlier. The same geometric dimensions and process parameters as the experimental ones were used.
3.4 RESULTS AND DISCUSSION

3.4.1 Transport Properties of CO$_2$-selective Membrane

The schematic of CO$_2$ separation in the permeation cell is shown in Figure 3.2. As having been shown in Figures 2.6 and 2.8, the membrane showed decent CO$_2$ transport properties at temperatures higher than 100°C. As the temperature increased from 100°C to 110°C, both permeability and selectivity increased, which could be explained by the higher CO$_2$/amine reaction rate but lower N$_2$ solubility in the membrane at the higher temperature. A CO$_2$ permeability of 6196 Barrers and a CO$_2$/N$_2$ selectivity of 493 were obtained at 110°C. After the temperature increased to 120°C or higher, both permeability and selectivity gradually dropped since the water content in the membrane decreased with the increase in temperature. However, CO$_2$ permeability of above 2000 Barrers and CO$_2$/N$_2$ selectivity of greater than 40 were still observed at 170°C, which demonstrated that PVA, as a very hydrophilic polymer, was a desirable polymer matrix for the CO$_2$-selective facilitated transport membrane. Crosslinking was necessary for PVA to hold the membrane structure while maintaining enough water content at the high temperatures. AIBA-K, polyallylamine and KHCO$_3$-K$_2$CO$_3$ (converted from KOH) provided selective carriers to facilitate CO$_2$ transport as discussed earlier.

Almost all of the CO$_2$ facilitated transport studies reported in the literature were carried out at around ambient temperature. The decent transport properties of this CO$_2$-selective membrane at the high temperatures would be more desirable to CO$_2$ capture
from the flue gas, since steam could be used as the sweep gas and operating at higher temperatures would reduce the energy loss from cooling the flue gas.

3.4.2 CO₂ Removal Capacity

A rectangular gas permeation cell was used to study the CO₂ removal capacity. The well-defined gas-flow channels of this cell allowed us to compare the experimental data with the results from the one-dimensional modeling, which assumed no axial mixing. CO₂ removal experiments were carried out using the rectangular cell at 120°C with different feed and sweep flow rates.

As seen in Figure 3.3, the membrane removed CO₂ in the retentate from 17% to about 10 ppm at a feed gas flow rate of 60 ml/min (at ambient conditions) and to 1,000 ppm at 120 ml/min (at ambient conditions). Such effectiveness in CO₂-removal could be attributed to the high CO₂ permeability demonstrated in Figure 2.6. The modeling results based on real experimental parameters are also shown in Figure 3.3. The experimental data have agreed well with the modeling results. This suggests that the one-dimensional model can accurately describe the gas permeation process in the rectangular cell.

3.4.3 CO₂ Capture Performance

Although flue gases from different sources might have various compositions, N₂, CO₂, and water vapor are generally the major components accounting for over 90% of the gas stream. After mixing the dry feed gas with the water vapor in the vessel in the
experimental setup, the total feed gas composition used was about 12% CO₂, 24% H₂, 24% N₂, and 40% H₂O, which would provide a close estimation to the CO₂ capture from the real flue gas. Using the circular permeation cell with an effective membrane area of 45.60 cm², we demonstrated the CO₂ removal capacity of the CO₂-selective membrane. The enhancing effect of the sweep gas on the separation performance was also verified experimentally.

3.4.3.1 Effect of Feed Inlet Flow Rate

In order to study the effect of the feed molar flow rate on the membrane separation performance, the CO₂ capture experiments were carried out with four different flow rates while the feed gas composition and the sweep-to-feed ratio were kept constant (refer to Exp. 1 – 4 in Table 3.1). As shown in Figure 3.4, the permeate CO₂ dry concentration of greater than 98% were achieved for a feed flow rate as high as 11.57×10⁻⁵ mol/s. Furthermore, if we deducted the H₂ portion from the permeate, the CO₂ dry concentration would be greater than 99%. Obviously the high CO₂/N₂ selectivity accounted for this high permeate CO₂ purity. Slightly increasing permeate CO₂ dry concentration was observed with the increase of the feed flow rate. This was due to the fact that a higher steam flow rate was more favorable for keeping a high water content in the membrane, which was favorable for the facilitated transport mechanism. The CO₂ recovery dropped as the feed flow rate increased, which was understandable, considering that the residence time of the gas mixture in the permeation cell was reduced as the feed inlet flow rate increased.
3.4.3.2 Effect of Sweep-to-Feed Ratio

The impact of the sweep gas on the CO$_2$ capture was investigated by using four sweep water rates while the feed gas and water flow rates on the feed side were kept constant. As shown in Table 3.1, from Exp. 5 – 8, the inlet sweep-to-feed molar flow rate ratios were 0.5, 1, 1.5, and 2, respectively. Figure 3.5 illustrates the effect of sweep-to-feed ratio on the permeate CO$_2$ dry concentration and the CO$_2$ recovery. The permeate CO$_2$ dry concentrations were all above 95% and did not change significantly with the increase of the sweep-to-feed ratio. The slightly declining trend was presumably due to the case that a slightly larger amount of CO$_2$ was absorbed in the water knockout when a higher water flow rate on the sweep side was used. The CO$_2$ recovery increased significantly as the sweep-to-feed ratio increased from 0.5 to 1.5. A higher sweep-to-feed ratio resulted in a lower CO$_2$ concentration on the sweep side and then a higher CO$_2$ permeation driving force. Beyond the ratio of 1.5, the higher sweep-to-feed ratio did not show a higher CO$_2$ recovery, which suggested that the excessively higher steam rate on the sweep side would not significantly increase the permeation driving force since the sweep-side CO$_2$ concentration was already sufficiently low.

3.4.4 Modeling Study

As a common type of commercialized membrane modules, the hollow fiber membrane module has shown excellent mass transfer performance due to its large surface area per unit volume (Ho and Sirkar, 1992). In the calculations, hollow fibers were
assumed to have a length of 61 cm (about 2 ft.), an inner diameter of 0.1 cm, and a porous support with a porosity of 50% and a thickness of 30 μm. The membrane assumed had a thickness of 5 μm, a CO₂/N₂ selectivity of 500, and a CO₂ permeability of 6000 Barrers. These values of the CO₂/N₂ selectivity and the CO₂ permeability were based on the experimental data as shown earlier.

Based on the calculations, 980,000 hollow fibers with the given dimensions were needed to recover above 95% CO₂ from the 1000 SCFM or 21.06 mol/s flue gas containing 9% CO₂. Figure 3.6 shows the profiles of the CO₂ wet concentration on both feed and sweep sides along the length of the countercurrent hollow fiber membrane module. The modeling results demonstrated that this membrane module could reduce the feed-side CO₂ concentration (on the wet basis) from 9% to 0.487%. The calculated permeate CO₂ concentration (on the dry basis) and CO₂ recovery were 98.25% and 95.06%, respectively. Since it is well known that there is no significant scale-up effect for the membrane module, simply adding the hollow fiber number or membrane area would result in a predictable capacity increase, if a larger amount of the flue gas needs to be processed. With a further study on the membrane stability, CO₂ capture with such hollow fiber membrane modules could provide a viable and economic approach for reducing CO₂ emission from flue gas.

3.5 CONCLUDING REMARKS

The membrane-based CO₂ capture using the novel facilitated transport CO₂-selective membrane was studied. The membrane synthesized by incorporating free
polyallylamine and AIBA-K as the amine carriers into the crosslinked PVA network showed the highest CO$_2$/N$_2$ selectivity of 493 and the highest CO$_2$ permeability of 6196 Barrers at 110°C. With a larger effective membrane area of 342.70 cm$^2$, we have removed CO$_2$ in the retentate from 17% to about 100 ppm at a feed gas flow rate of 60 ml/min and to about 1,000 ppm at 120 ml/min. The experimental data have agreed well with the modeling results. In the CO$_2$ capture experiments, the permeate CO$_2$ dry concentration of greater than 98% was achieved by using steam as the sweep gas. Also studied were the effects of inlet feed flow rate and sweep-to-feed ratio on the separation performance. As the feed flow rate increased, the permeate CO$_2$ dry concentration slightly increased, and the CO$_2$ recovery decreased owing to the reduced residence time. Increasing sweep-to-feed ratio enhanced the permeation driving force and resulted in the higher CO$_2$ recovery, while the permeate CO$_2$ dry concentration did not change significantly.

We have developed a one-dimensional isothermal model to evaluate the separation performance of a hollow fiber module composed of the described CO$_2$-selective membrane. From the modeling results, a 2-ft hollow fiber module containing 980,000 fibers was sufficient to recover above 95% of CO$_2$ and obtain a permeate CO$_2$ concentration of larger than 98% (on the dry basis) from a 1000 SCFM or 21.06 mol/s flue gas stream containing 9% CO$_2$. 
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Feed side</th>
<th></th>
<th>Sweep side</th>
<th></th>
<th>Sweep-to-feed molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry gas flow rate (ml/min*)</td>
<td>Water flow rate (ml/min)</td>
<td>water flow rate (ml/min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>40</td>
<td>0.02</td>
<td>0.050</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>0.03</td>
<td>0.075</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>0.04</td>
<td>0.100</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.05</td>
<td>0.125</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>0.04</td>
<td>0.050</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>0.04</td>
<td>0.100</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>80</td>
<td>0.04</td>
<td>0.150</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>0.04</td>
<td>0.200</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

*At ambient conditions.

Table 3.1. The operating parameters for the CO₂ capture experiments.
Figure 3.1. Schematic of the hollow-fiber membrane module.
Figure 3.2. Schematic of gas separation with the CO$_2$-selective membrane.
Figure 3.3. Exit dry CO$_2$ concentration in the retentate vs. feed flow rate.
Figure 3.4. Permeate CO$_2$ dry concentration and CO$_2$ recovery vs. feed flow rate.
Figure 3.5. Permeate CO$_2$ dry concentration and CO$_2$ recovery vs. sweep-to-feed molar ratio.
Figure 3.6. CO$_2$ concentration (wet) profiles along the length of membrane module.
SUMMARY: Acid-gas removal from natural gas is currently the largest industrial gas treatment market. Considering the conditions of raw natural gas, this process requires high operating pressure. In this chapter, the performance of CO$_2$ (H$_2$S)-selective facilitated transport membranes on the removal of CO$_2$ and H$_2$S from natural gas was investigated. For dense free-standing membranes, decent CO$_2$ permeability and CO$_2$/CH$_4$ selectivity were obtained with a feed pressure up to 500 psia. With the increase of feed pressure, CO$_2$ transport properties reduced due to the carrier saturation and the reduction of water retention in the membrane. The membranes showed the optimum transport properties at ~ 106°C as a result of the enhanced reaction rate with sufficient water retention and with the reduced CH$_4$ solubility in the membrane. Because of the increased water content in the membrane due to the increase of permeate pressures at 111°C and 117°C, CO$_2$ permeability was improved significantly. High-flux membranes were studied by preparing the thin-film composite membrane and the asymmetric membrane. With the thin-film composite membrane structure, a significant increase on the CO$_2$ flux was achieved with the decrease of the selective layer thickness. Similar to the previous
results, H$_2$S showed 2 – 3 times higher transport properties than CO$_2$ and demonstrated a wide operating temperature range. The preliminary results on the asymmetric membrane via the phase inversion process were also reported.
4.1 INTRODUCTION

Natural gas is one of the principle energy sources in the world. It can be used for many of our daily needs and activities including power generation, hydrogen production, natural gas vehicles, and residential use, etc. The composition of raw natural gas varies substantially from location to location. The major component of natural gas is methane (CH$_4$). It also contains significant amounts of heavier gaseous hydrocarbons, such as ethane (C$_2$H$_6$), propane (C$_3$H$_8$) and butane (C$_4$H$_{10}$). In addition, undesirable impurities, such as nitrogen, water, carbon dioxide and hydrogen sulfide, can also be present. The removal of CO$_2$ and H$_2$S from natural gas is essential because CO$_2$ reduces the energy content and both are corrosive to the transportation and storage systems in the presence of water. To reach the US pipeline specification, CO$_2$ and H$_2$S concentrations need to be reduced to less than 2% and 4 ppm, respectively (Baker, 2002).

The typical CO$_2$ removal technologies include chemical solvent scrubbing, physical solvent scrubbing, pressure or temperature swing adsorption, membranes, and cryogenics. Among these technologies, chemical solvent scrubbing using regenerable alkanolamines is still the standard commercial method for treating natural gas containing up to about 200 psia CO$_2$ partial pressure (Kohl and Riesenfeld, 1979).

Since Monsanto launched the first commercial application in 1980, gas separation membranes have proven to be better alternatives to traditional separation processes (Spillman, 1989; Koros and Fleming, 1993). Compared to the conventional amine scrubbing process, membrane-based gas separation processes have the advantages of low
energy consumption, low capital cost, excellent weight and space efficiency, and superior process simplicity.

Current state-of-the-art gas separation polymeric membranes for natural gas CO\textsubscript{2} removal are primarily made of cellulose acetate or polyimide (Zolandz and Fleming, 1992; Ho and Sirkar, 1992). In principle, CO\textsubscript{2} is more permeable than CH\textsubscript{4} for a given polymeric membrane because CO\textsubscript{2} has a smaller kinetic diameter and is a more condensable gas than CH\textsubscript{4}. Therefore, CO\textsubscript{2} would permeate through the membrane preferentially due to both higher diffusivity and higher solubility. CO\textsubscript{2}/CH\textsubscript{4} selectivities of 12 − 15 for cellulose acetate and 20 − 25 for polyimide under normal operating conditions were reported in the literature (Baker, 2002). However, since they are based on solution-diffusion mechanism and rely primarily on the size-sieving ability to achieve separation, these glassy polymeric membranes suffer from a tradeoff between CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} selectivity (White et al., 1995; Meisen and Shuai, 1997; Koros and Mahajan, 2000; Wind et al., 2004). Another problem associated with glassy polymeric membranes is the membrane plasticization at high CO\textsubscript{2} partial pressure. In general, plasticization is defined as the decrease of membrane selectivity due to the increased polymer-chain mobility in the presence of highly condensable penetrants, such as CO\textsubscript{2}, H\textsubscript{2}O, and heavier hydrocarbons. To improve the plasticization resistance, many studies have been carried out to modify the structure of current commercial membranes via crosslinking or heat treatment (Bos et al., 1998; Wind et al., 2002; Wind et al., 2004). With these treatments, higher CO\textsubscript{2}/CH\textsubscript{4} selectivity under high CO\textsubscript{2} partial pressure was achieved at the cost of lower CO\textsubscript{2} permeability.
In addition to the size-sieving glassy polymers, which show selectivity mainly based on the diffusivity difference between each component, researchers also proposed polar amorphous polymers as the membrane materials (Okamoto et al., 1995; Lin and Freeman, 2004; Lin and Freeman, 2005; Lin et al., 2005, Lin et al., 2006). Due to the strong affinity of the polar ether linkage to the polar molecules such as H₂S and H₂O as well as the quadrupolar molecules such as CO₂, this type of rubbery polymer could show very high solubility selectivity and avoid the possible CO₂ plasticization. However, to achieve desirable CO₂ transport properties, they had to drop the temperature to −20°C (Lin et al., 2006), which is not common for the practical operating conditions of natural gas.

Due to the limited membrane performance, currently the membrane process only occupies less than 1% of the worldwide market for the natural gas separation equipment, which is estimated to be $5 billion/year (Baker, 2002). To expand the market share of the membrane process, polymeric membranes having higher selectivity without permeability loss are required. As an alternative to conventional polymeric membranes, facilitated transport membranes have shown better promise to exhibit excellent transport properties (Ward and Robb, 1967; Way and Noble, 1992; Ho and Sirkar, 1992). In this type of membrane, either mobile or fixed carrier agents, which can react reversibly with certain gas components, are incorporated. The reaction in the membrane creates another transport mechanism for the target gas component in addition to the solution-diffusion mechanism. Therefore, high selectivity and high permeability can be obtained at the same time.
Phase inversion is a process transforming a polymer from a liquid state to a solid state in a controlled manner. Since the first integrally skinned asymmetric membrane was invented by Loeb and Sourirajan in the 1960s, the phase inversion process has become a standard process to prepare asymmetric membranes. In this type of membrane, there are two structurally distinct layers, including a thin, dense and selective layer and a thick porous layer mainly to provide the mechanical strength. Because the permeation rate increases proportionally to the decrease of the active layer thickness, an asymmetric membrane would show a much higher permeation rate than a dense membrane with the similar total thickness.

The common phase inversion techniques include solvent evaporation, precipitation by controlled evaporation, thermal precipitation, precipitation from the vapour phase and immersion precipitation. However, the majority of the commercially available membranes are prepared by immersion precipitation. In this process, a polymer solution is cast on a suitable support, e.g., a glass plate, and immersed in a coagulation (nonsolvent) bath. Since they are miscible with each other, solvent and nonsolvent start to exchange by diffusion. After a certain amount of time, the solution becomes thermodynamically unstable and liquid-liquid demixing occurs. At a certain stage during demixing, the liquid phase having the high polymer concentration will solidify so that a solid matrix is formed.

Based on the time required for the solid matrix formation, there are two types of demixing process. In instantaneous demixing, the porous membrane is formed immediately after immersion in the coagulation bath. While in delayed demixing, it takes much a longer time to form the ultimate membrane. In principle, the delayed demixing
process would result in a relatively dense top layer, which is suitable for the gas separation process.

In this study, the transport properties of the CO$_2$ (H$_2$S)-selective membranes were characterized under high feed pressures. Also the effects of membrane structure and process parameters on the membrane performance were investigated. Furthermore, thin film composite (TFC) membranes and asymmetric membranes were prepared to further improve the CO$_2$ flux. With the configuration of TFC membrane, the effect of membrane thickness on the CO$_2$ flux was studied, and H$_2$S transport properties were investigated.

4.2 EXPERIMENTAL

The membrane of PVA containing amino functional groups was prepared by the solution casting method. In the membrane composition, we used the crosslinked PVA as the hydrophilic matrix and free polyallylamine and AIBA potassium salt (AIBA-K) as amine carriers, respectively. The preparation of the membrane solution has been described earlier in Chapter 2. A typical membrane composition was 50 wt.% PVA (60 mol.% crosslinked), 11.7 wt.% AIBA-K, 18.3 wt.% KOH and 20 wt.% Polyallylamine.

The resulting solution was centrifuged to remove air bubbles and then cast in a uniform thickness with a stainless steel film applicator (Paul N. Gardner Co.) on a clean and horizontally leveled glass plate to prepare a free-standing membrane. The membrane film was separated from the glass plate after ~ 3 hr drying in a fume hood. After sitting in the fume hood overnight, the membrane was cured in a 120°C furnace for 6 hr to complete the crosslinking reaction. By varying the chemical amounts used for solution
preparation, the membranes with different compositions were prepared. The membrane thicknesses were between 50 μm and 80 μm.

A small membrane thickness was essential to achieve high CO\textsubscript{2}/H\textsubscript{2}S flux by reducing the mass transfer resistance in the membrane. For free-standing membranes, it was possible to make a defect-free membrane with a thickness of ~ 25 μm. However, it was difficult to handle a thinner polymer film (< 15 μm) due to the self-clinging phenomenon. To reduce the active membrane thickness, thin film composite (TFC) membranes and asymmetric membranes were prepared.

For TFC membranes, GE E500A microporous polysulfone support (thickness: about 50 μm excluding non-woven fabric support, average pore size: 0.05 μm) donated by GE Infrastructure (Vista, CA) was used. The GE E500A support was soaked in water for overnight before being mounted under slight tension on a glass plate uniformly. Then, the PVA/amine solution with a weight concentration of ~ 8% was cast on the support with a gap setting of less than 5 mils. Special care was taken during the casting process to make a uniform and defect-free surface. The membrane was then dried first in a fume hood at ambient conditions overnight to remove most of water and then further cured in a 120°C furnace for 6 hr to complete the crosslinking reaction.

Asymmetric membranes consisting of a thin active layer on the top and a microporous supporting structure were prepared via the phase inversion process. The aqueous membrane solution containing partially cross-linked PVA and amine carriers was cast on a glass plate following the same procedure of the free-standing membrane. After air-drying in a fume hood for a short time, the partially dried membrane was soaked in a coagulation bath for a certain amount of time. The resulting membrane was opaque
after the phase inversion process. It was then peeled off from the glass plate and cured in a 120°C furnace for 6 hr to complete the crosslinking reaction.

In the gas permeation experiments, two certificated gas mixtures from Airgas, Inc.: (1) 50% CO\textsubscript{2}, and 50% CH\textsubscript{4} and (2) 1% H\textsubscript{2}S, 49% CO\textsubscript{2}, and 50% CH\textsubscript{4}, were used as the feed gas. Pre-purified argon (99.998%) from Praxair, Inc. was used as the sweep gas for the ease of gas chromatograph (GC) analysis in the gas permeation measurements. The similar procedure described in Chapter 2 was applied in experiments. A back pressure regulator was used to control the feed-side pressure up to 500 psia.

The schematic of gas separation with the CO\textsubscript{2} (H\textsubscript{2}S)-selective membrane in the permeation cell is shown in Figure 4.1. Based on the measured gas compositions of both retentate and permeate streams, mass balance was carried out with the assumption of constant argon molar flow rate on the permeate side. The permeability and selectivity were then calculated by Equations (2.1) and (2.15), respectively.

4.3 RESULTS AND DISCUSSION

4.3.1 Free-Standing Membrane

Free-standing membranes with the thickness ranging from 35 to 90 μm were tested using the permeation unit. The gas mixture consisting of 50% CO\textsubscript{2} and 50% CH\textsubscript{4} was used as the feed gas. Various process parameters, such as feed pressure, operating temperature and sweep side pressure, were studied for their effects on the CO\textsubscript{2} removal performance.
4.3.1.1 Effect of Feed Pressure on CO₂ Transport Properties

Figures 4.2 and 4.3 show the effects of feed pressure on the CO₂ transport properties of the membrane at 106°C and 116°C, respectively. At both temperatures, CO₂ permeability decreased significantly with the increase of feed pressure. This was attributed to two reasons. First, unlike the traditional polymeric membrane, the CO₂ flux through the facilitated transport membrane not only depended on the CO₂ partial pressure difference across the membrane, but also was governed by the reactions between CO₂ and amine carriers. Under a high CO₂ partial pressure on the feed side, the amine carriers could have been all reacted. Therefore, the CO₂ flux would not increase as the feed pressure increased. This is so called “carrier saturation” phenomena. The second reason was that the water vapor amount carried by the feed gas into the membrane compartment was reduced under high feed pressures at a given temperature. Based on the facilitated transport mechanism, water is of great importance for the reactions.

On the other hand, the CH₄ flux increased as the feed pressure increased because the CH₄ permeation followed the solution-diffusion mechanism only. Consequently, decreasing CO₂/CH₄ selectivity with feed pressure was observed. Also can be seen in the figures, there was no plasticization occurred, i.e., the CO₂ permeability did not increase at a high feed pressure like glassy polymers, such as cellulose acetate and polyimide. That was because the crosslinked PVA was a rubbery polymer, the sorption of CO₂ in the membrane would not change the membrane structure significantly.
4.3.1.2 Effect of Temperature on CO₂ Transport Properties

Figures 4.4 and 4.5 illustrate the relationships between membrane transport properties and temperature. As can be seen, similar trends were observed under the feed pressures of both 150 psia and 500 psia. The CO₂ permeability increased with increasing temperature up to 106°C and then dropped at higher temperatures. As mentioned earlier, the CO₂ flux through the facilitated transport membrane depended strongly on the amine-CO₂ reaction. Higher temperatures resulted in higher reaction rates and, in turn, a higher CO₂ flux. However, the water content in the membrane reduced at higher temperatures. The temperature of 106°C appeared to be optimal for the case under consideration.

The CO₂/CH₄ selectivity showed a minimum at 85°C. The decrease in the selectivity with increasing temperature at lower temperatures was presumably due to the increasing CH₄ diffusivity in the membrane. However, at temperatures above 85°C, the CO₂ flux increased remarkably due to higher reaction rates while the CH₄ flux reduced owing to a reduction of its solubility in the membrane with increasing temperature. Consequently, the CO₂/CH₄ selectivity exhibited a significant improvement at temperatures above 85°C and a minimum at this temperature.

4.3.1.3 Effect of Permeate Pressure on CO₂ Transport Properties

In an attempt to improve the CO₂ transport properties under the feed pressure of 500 psia, the effect of permeate pressure was investigated. Figures 4.6, 4.7, and 4.8 present the experimental results. With the increase of permeate pressure, the CO₂
permeability increased significantly at 111°C and 116°C but did not change much at 106°C. Since a higher permeate pressure resulted in a higher water partial pressure on the permeate side, water transfer across the membrane was then decreased with the reduced driving force. It was very important for the membrane to maintain enough water content for enhancing the diffusion of solutes and the reaction of CO$_2$ with the carriers in the membrane. At 106°C, the effect was not apparent because the water content in the membrane presumably already reached the maximum. However, the higher water content in the membrane could cause a more swollen membrane structure, which enhanced the CH$_4$ flux and thus decreased the CO$_2$/CH$_4$ selectivity. Therefore, an optimal permeate pressure was chosen for the tradeoff between permeability and selectivity. In addition, a high permeate CO$_2$ pressure may be attractive for natural gas purification process to integrate with the following CO$_2$ sequestration step.

4.3.2 Thin-Film Composite Membrane

Thin-film composite membranes with the thickness ranging from 2.5 to 21 μm were tested using the permeation unit. Both gas mixtures with and without H$_2$S were used as the feed gas. The effects of membrane thickness and sweep side water rate were studied. To provide a clearer indication about the achievable flux, permeance, which is defined as the pressure normalized flux, was presented in this section. The common unit for permance is GPU (Gas Permeation Unit, 1 GPU = 10$^{-6}$ cm$^3$(STP)/cm$^2$•s•cmHg).
4.3.2.1 Effect of Membrane Thickness on CO$_2$ Transport Properties

In principle, the transfer of CO$_2$ across the facilitated transport membrane consists of three steps, namely the reaction of CO$_2$ and amine on the feed side, the diffusion of the reaction products through the membrane, and the desorption (reverse reaction) of CO$_2$ on the sweep side. Therefore, the relationship between flux $J$ and partial pressure difference can be expressed as (Ho and Dalrymple, 1994):

$$ \frac{P_f - P_s}{J} = \frac{1}{k_e H_A|_{p_f}} + \frac{1}{k_r H_A|_{p_r}} + \frac{l}{D_A H_A + D_{Ab} H_{Ab}|_{p_f}} $$

(4.1)

In this equation, the term on the left-hand side is the total mass transfer resistance. On the right-hand side, the first term is the mass transfer resistance due to the reaction; the second term is the mass transfer resistance due to the reverse reaction; while the third term is contributed by the diffusion step. If we use $R_t$, $R_f$ and $R_r$ to represent the three resistances and let $P = D_A H_A + D_{Ab} H_{Ab}|_{p_f}$, Equation (4.1) become

$$ R_t = R_f + R_r + \frac{l}{P} $$

(4.2)

where $P$ is the “true” permeability excluding the interfacial reaction resistances. From Equations (4.1) and (4.2), the flux can be expressed as:

$$ J = (p_f - p_s) \left[ R_f + R_r + \frac{l}{P} \right] = \Delta p \left[ R_f + R_r + \frac{l}{P} \right] $$

(4.3)

From the CO$_2$ transport data with different membrane thicknesses, the total resistance $R_t$ was calculated as the partial pressure difference divided by the CO$_2$ flux. Figure 4.9 illustrates the plot of the total mass transfer resistance as a function of membrane thickness at the feed pressure of 150 psia and 106°C. As shown in this figure, the data
points follow approximately a straight line. Based on Equation (4.2), the slope of the plot is the reciprocal of the “true” permeability, while the intercept at a membrane thickness of zero is the combination of mass transfer resistances due to the forward and reverse reactions. This is different from the plot for the conventional solution-diffusion membrane without facilitated transport, which has the total mass transfer resistance of zero at a membrane thickness of zero.

As can be seen, the combined mass transfer resistances due to reactions, \( R_f + R_r \), were relatively small for a thick membrane (less than 20% of the total mass transfer, \( R_t \), for a membrane thickness of 80 μm). However, it became the majority of \( R_t \) as the membrane thickness reduce to less than 5 μm. Meanwhile, the mass transfer resistance for CH₄ without facilitated effect would decrease proportionally with the decrease of membrane thickness. Therefore, the CO₂/CH₄ selectivity decreased as the membrane thickness decreased, which is demonstrated in Figure 4.10.

4.3.2.2 Effect of Temperature on CO₂ and H₂S Transport Properties

To investigate the membrane separation performance for H₂S, a ternary gas mixture consisting of 1% H₂S, 49% CO₂, and 50% CH₄ was used as the feed gas. The permeance and selectivity versus CH₄ for both CO₂ and H₂S were characterized at different temperatures with the same gas / water flow rates.

Figures 4.11 and 4.12 show the plots of permeance and selectivity versus CH₄ as a function of operating temperature. As shown in the figure, the CO₂ permeance decreased gradually as the temperature decreased from 106 to 75°C, owing to the lower CO₂-amine
reaction rate at a lower temperature. Meanwhile, the H$_2$S permeance did not change much when the temperature decreased from 106 to 85°C. As discussed in Chapter 2, this was presumably due to the fact that H$_2$S reacts with amine faster than CO$_2$ as the former reaction is via the faster proton transfer and that the bisulfide ion, HS$^-$, diffuses faster than the carbamate ion.

On the other hand, the CH$_4$ flux increased as the result of a higher solubility in the membrane at a lower temperature. Consequently, both CO$_2$/CH$_4$ and H$_2$S/CH$_4$ selectivity decreased with the decrease of temperature. However, sufficient selectivities of 90 for H$_2$S/CH$_4$ and 30 for CO$_2$/CH$_4$ were still observed at 75°C.

The incorporation of 1% H$_2$S in the feed gas did not affect the membrane performance as evidenced by the comparable CO$_2$ transport properties. When H$_2$S came in contact with amine, it first dissociated into the bisulfide ion, HS$^-$, which was considered to be very fast compared to the diffusion rate. It was reported that H$_2$S would not dissociate further into the sulfide ion, S$_2^{2-}$, except in strong hydroxide solutions. Since almost all of KOH would be converted into KHCO$_3$, a much weaker base, after exposing to CO$_2$, it is unlikely H$_2$S would dissociate into S$_2^{2-}$ under the operating conditions we had. This might account for why H$_2$S did not show any deteriorative effect in the experiments.

4.3.3 Asymmetric Membrane

In our experiments, the aqueous membrane solution containing partially cross-linked PVA and amine carriers was cast on a glass plate following the same procedure used before. After air-drying in a fume hood for a certain amount of time, the partially
dried membrane was soaked in a nonsolvent bath. The nonslovents used in experiments included isopropyl alcohol (IPA), tetrahydrofuran (THF), and dimethylformamide (DMF). The membrane film would gradually change from transparent to opaque. The resulting membrane was then removed from the glass plate followed by the typical curing process. The schematic for the phase inversion process is demonstrated in Figure 4.13. In this figure, line 1 represents the air-drying step causing the increase of the top part concentration, line 2 refers to the composition path right after the immersion, line 3 shows the composition profile after a certain amount of time, and line 4 indicates the final composition path.

In general, solvent/nonsolvent system, solution concentration or viscosity, membrane film thickness, air-drying time, and nonsolvent bath immersion time are several key process parameters affecting the final membrane morphology. The research efforts were spent on identifying the effects of these parameters and finding the optimal operation conditions for achieving asymmetric membrane structure with a thin dense toplayer.

The air-drying process was studied by recording the weight reduction with time. The results are illustrated in Figure 4.14. As demonstrated in the figure, it showed two stages in this air-drying process. The majority of the solvent was removed relatively fast within about 2.5 hr. After that, the sample weight decreased slowly to the final weight. To achieve an ideal asymmetric structure in the phase inversion process, a short air-drying time should be used. If the air-drying time were too short, a relative porous toplayer would form. While if a long air-drying time was applied, the dense top layer would hinder the solvent-nonsolvent exchange.
A key issue with the phase inversion process of PVA/amine solution was that the solvent/nonsolvent exchanging rate was not fast enough when a room-temperature nonsolvent bath was applied. To enhance the solvent/nonsolvent exchange rate, increasing the temperature of the coagulation bath and changing the PVA/amine solution composition was attempted. Lowering PVA/amine solution concentration was also helpful to speed up the solvent/nonsolvent exchanging rate. A membrane cast with a solution concentration of 14.5% was observed to complete phase inversion faster than a membrane cast with a solution concentration of 18%. However, pin holes formed during the phase inversion when a solution with the concentration of < 12% was used.

Based on the experimental work, the best process parameters for the PVA/amine composition included: a gap setting of 9 mil (or 228.6 μm), an IPA bath at 55°C, a solution concentration of 12 – 14%, and an air-drying time and immersion time of 1 min and 20 – 25 min, respectively. Figure 4.15 shows the preliminary data obtained from the asymmetric membranes prepared via the phase inversion process. As seen in the figure, these membranes appeared to show the tradeoff between CO₂ permeance and CO₂/CH₄ selectivity. The transport properties were close to the results of the dense membrane with the similar thickness shown in Figure 4.9. This might be due to the fact that the operating temperature was higher than the glassy transition temperature of PVA. Therefore, the porous structure formed during the phase inversion process might collapse under high feed pressures.
4.4 CONCLUDING REMARKS

CO\(_2\) (H\(_2\)S)-selective facilitated transport membranes were synthesized for the acid gas removal from natural gas. For dense free-standing membranes, the CO\(_2\) permeability of greater than 440 Barrer and the CO\(_2\)/CH\(_4\) selectivity of higher than 135 were achieved at a feed pressure of 150 psia, or a CO\(_2\) partial pressure of 75 psia. Under a feed pressure of 500 psia, or a CO\(_2\) partial pressure of 250 psia, the permeability and selectivity obtained were 88.83 Barrers and 30.59, respectively. With the increase of feed pressure, CO\(_2\) transport properties reduced due to the carrier saturation and the reduction of water retention in the membrane. The temperature of 106°C was found to be optimal for the membrane performance due to the high reaction rates of CO\(_2\) with amine carriers and the low CH\(_4\) solubility in the membrane. Increasing permeate pressure improved the CO\(_2\) permeability by deterring the water transfer through the membrane but decreased the selectivity. High-flux membranes were attempted with the efforts to prepare the thin-film composite membrane and the asymmetric membrane. By using a microporous polysulfone support, thin-film composite membranes with a very thin selective layer were successfully synthesized. The decrease of the selective layer thickness significantly improved the CO\(_2\) flux due to the decrease of diffusion resistance within the membrane. H\(_2\)S showed 2 – 3 times higher permeability and selectivity (vs. CH\(_4\)) than CO\(_2\). Also the membrane could maintain high H\(_2\)S flux in a wider temperature range, e.g, 85 – 106°C. Asymmetric membranes with a thin selective toplayer and a thick porous support layer were prepared via the phase inversion process. However, they did not show a higher CO\(_2\) flux than the dense membranes with the similar total thickness. A probable reason was
that the operating temperature was too high (higher than the glass transition temperature of PVA) to maintain the porous structure of PVA.
Figure 4.1. Schematic of gas separation with the CO$_2$ (H$_2$S)-selective membrane.
Figure 4.2. CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. feed pressure at 106°C.
Figure 4.3. CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. feed pressure at 116°C.
Figure 4.4. CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. temperature at 150 psia feed pressure.
Figure 4.5. CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. temperature at 500 psia feed pressure.
Figure 4.6. CO₂ permeability and CO₂/CH₄ selectivity vs. permeate pressure at 106°C and 500 psia feed pressure.
Figure 4.7. CO$_2$ permeability and CO$_2$/CH$_4$ selectivity vs. permeate pressure at 111°C and 500 psia feed pressure.
Figure 4.8. CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} selectivity vs. permeate pressure at 116\textdegree C and 500 psia feed pressure.
Figure 4.9. Total mass transfer resistance, $R_t$, versus membrane thickness.
Figure 4.10. CO\textsubscript{2} permeance and CO\textsubscript{2}/CH\textsubscript{4} selectivity vs. membrane thickness at 116°C and 150 psia feed pressure.
Figure 4.11. CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> selectivities versus operating temperature.
Figure 4.12. CO$_2$ and H$_2$S permeances versus operating temperature.
Figure 4.13. Schematic of the phase inversion process with the delayed demixing (■ denotes the top of the liquid film, ● denotes the bottom of the liquid film, and lines denote the composition paths along the liquid film thickness).
Figure 4.14. The weight reduction of the membrane during the air-drying (23°C, casting gap setting = 10 mil).
Figure 4.15 The preliminary data from the asymmetric membranes via the phase inversion process (106°C and 150 psia feed pressure).
CHAPTER 5

OTHER CO₂-SELECTIVE MEMBRANES

SUMMERY: Hybrid organic-inorganic materials have the potential to show synergetic properties by combining the advantages from both organic and inorganic domains. Hybrid membranes were synthesized based on the sol-gel process and the CO₂ (H₂S)-selective polymeric membrane for the purpose of enhancing the thermal stability of the membrane. The hybrid membrane showed better CO₂ transport properties than the PVA membrane without inorganic domain at temperatures higher than 160°C. The decent high-temperature performance is of great importance for CO₂-selective WGS membrane reactor.

Based on the molecular design, segmented polyimide copolymers were synthesized by a two-step procedure. This type of copolymer had microphase-separated structure. The rubbery adipate or polyether domain offered high chain mobility and strong affinity to the polar or quadrupolar molecules, while the glassy polyimide domain provided mechanical strength and the ability to form a thin film. The permeation experiments demonstrated the tradeoff between permeability and selectivity with the increase of temperature. A high relative humidity improved the affinity to CO₂ and
improving CO₂ permeability. Due to the higher weight percentage of soft segment, the copolymer with longer soft segment showed better CO₂ transport properties. In addition, the more polar and hydrophilic ether soft segment illustrated better performance than the ester soft segment.
5.1 INTRODUCTION

Hybrid organic-inorganic materials have attracted wide interest in recent years by offering extraordinary synergetic properties (Uragami et al., 2002; Merkel et al., 2002; Li and Liu, 2003; Kim et al., 2004a; Sanchez et al., 2005; Peng et al., 2005). The sol-gel process is the key technology in the synthesis of organic-inorganic hybrids. In this process, a precursor is used to generate an inorganic material chemically through polymerization rather than through melting and reforming an existing ceramic (Iler, 1979). One of the major advantages of this process is the mild reaction conditions under which it occurs, which is preferred in making hybrid materials because of low decomposition temperature of organics. The resulting hybrids would combine the desirable properties of an organic polymer phase for toughness, ductility and processability and of an inorganic phase for good thermal stability, water retention and mechanical strength. Some of their applications include optical filters, electrical materials, biomaterials, coatings, membranes, tunable solid-state lasers, shape-selective catalysts, chemical sensors, molecular sieves, catalyst supports, and selective adsorbents.

Based on the type of interfacial interaction between the organic and inorganic domains, the organic-inorganic hybrid materials can be divided into two groups. The first type of hybrids has extensive hydrogen bonding, van der Waals contacts, or electrostatic forces between the two domains. In the second type, inorganic and organic components are linked by covalent or ionic bonds (Eckert and Ward, 2001).
A typical sol-gel reaction is illustrated in Equations (5.1) to (5.3). In general, the sequence of steps begins with hydrolysis of an alkoxide to generate a silanol group (SiOH) and alcohol.

\[ \equiv Si - OR + H_2O \rightleftharpoons \equiv Si - OH + ROH \]  
\[ \text{(5.1)} \]

Once silanols are present, they can react by condensation with other hydrolyzed silicon sites to generate siloxanes and water.

\[ \equiv Si - OH + HO - Si \rightleftharpoons \equiv Si - O - Si \equiv + H_2O \]  
\[ \text{(5.2)} \]

Alternatively, a reaction between a silanol and an unhydrolyzed silicon can produce a siloxane and alcohol (ROH).

\[ \equiv Si - OR + HO - Si \rightleftharpoons \equiv Si - O - Si \equiv + ROH \]  
\[ \text{(5.3)} \]

where \( R \) is an alkyl group, \( C_nH_{2n+1} \). In general, all three reactions are reversible, depending on the conditions under which the reaction is performed. They are also usually carried out in the presence of a catalyst, which can be an acid, a base, or fluoride ions. Many factors influence these reactions beyond just the reaction temperature and reactant concentrations. The pH and the type of solvent are especially important in determining the reaction pathway and the kinetics of the reaction.

Block copolymers comprising of both hard segment and soft segment have been studied by some researchers as candidates for CO\textsubscript{2} removal from natural gas or flue gas. The hard segments are usually amide or imide moiety. For instance, the commercial product poly(ether block amide), PEBAX\textsuperscript{®} from Arkema, Inc., comprises of polyamide as the hard segment and polyether as the soft segment. The type of copolymer has microphase-separated structure. The rubbery polyether domain offers high chain mobility and strong affinity to the polar molecules such as H\textsubscript{2}S and H\textsubscript{2}O as well as the quadrupolar
molecules such as CO$_2$. While the glassy polyamide or polyimide domain provides mechanical strength and the ability to form a thin film.

Compared to the size-sieving glassy polymers, which show selectivity mainly based on the diffusivity difference between each component, this type of rubbery copolymers could show very high solubility selectivity and avoid the possible CO$_2$ plasticization (Okamoto et al., 1995; Lin and Freeman, 2004; Lin and Freeman, 2005; Lin et al., 2005, Lin et al., 2006).

In this study, hybrid membrane based on the sol-gel process and the CO$_2$ (H$_2$S)-selective polymeric membrane was studied in aim to enhance the thermal stability of the membrane. Also, a two-step procedure was applied to synthesize segmented polyimide copolymers. Copolymer membranes with a variety of molecular designs were prepared and characterized to explore their potentials on CO$_2$ separation.

5.2 HYBRID FACILITATED TRANSPORT MEMBRANE

As stated in previous chapters, CO$_2$-selective membranes have been prepared by incorporating amino groups in polymer networks. However, these membranes could not maintain desirable CO$_2$ transport properties at temperatures higher than 170$^\circ$C. For the application of CO$_2$-selective WGS membrane reactor, membranes with better thermal stability would be more advantageous. For this purpose, hybrid membranes were studied by incorporating various types of silica into the PVA/amine system. As an example, a hybrid membrane containing sulfonated phenyltriethoxysilane (PTEOS) was discussed below.
5.2.1 Synthesis of Hybrid Membrane

Following the same procedure described previously, the PVA/amine solution containing cross-linked PVA, AIBA-K and Polyallylamine was prepared. Sulfonated phenyltriethoxysilane (PTEOS) was prepared by sulfonating PTEOS with chlorosulfonic acid. Two stoichiometric amount of chlorosulfonic acid was dropwise added into PTEOS under rigorous stirring. The mixture was then stirred at room temperature for 24 hrs to complete the sulfonation of the phenyl groups. After sulfonation, a measured amount of sulfonated PTEOS was added dropwise into the prepared PVA/amine solution. After 1-hr mixing, the stirring speed was reduced to remove the air bubbles in the solution. The resulting solution was cast on the BHA-Tech PTFE porous support. The membrane was dried in the fume hood for overnight to remove most of the solvent and then cured in a 120°C oven for 12 hrs. The final composition was 40 wt.% PVA (60 mol.% crosslinked), 10 wt.% sulfonated PTEOS, 10 wt.% AIBA-K, 20 wt.% KOH and 20 wt.% polyallylamine.

The CO₂ transport properties of the hybrid membranes were tested using the same gas permeation unit described earlier. A certificated gas, with a composition of 20% CO₂, 40% H₂ and 40% N₂, was used as the feed gas. The thermal stability of membranes was evaluated by thermogravimetric analysis (Perkin-Elmer, Pyris 1, Shelton, CT). The TGA measurements were carried out under a nitrogen atmosphere at a heating rate of 10°C/min from 30 to 800°C.
5.2.2 Results and Discussion

The comparison of separation performance and thermal stability between the hybrid PVA membrane and the PVA membrane is illustrated in the following figures. The composition for the hybrid PVA membrane was 40 wt.% PVA (60% HCHO Crosslinked), 10 wt.% AIBA-K, 20 wt.% KOH, 20 wt.% Polyallylamine, and 10 wt.% sulfonated PTEOS, and that for the PVA membrane was 50 wt.% PVA (60% HCHO Crosslinked), 10 wt.% AIBA-K, 20 wt.% KOH, and 20 wt.% Polyallylamine.

Figures 5.1 and 5.2 present the CO$_2$/H$_2$ selectivity and the CO$_2$/N$_2$ selectivity as a function of temperature. For both membranes, they showed similar trends on selectivities. The best CO$_2$ transport performance was observed between 110°C and 120°C. At the same conditions, CO$_2$/N$_2$ selectivity was typically 2 – 3 times higher than CO$_2$/H$_2$ selectivity due to the larger molecular size of N$_2$. With the increase of temperature, both selectivities dropped, which could be explained by the lower water content inside the membrane at higher temperatures, resulting in dropping the facilitated effect of the amine carriers. At temperatures lower than 160°C, the PVA membrane demonstrated generally higher selectivities than the hybrid PVA membrane. However, at temperatures higher than 160°C, the selectivities of the hybrid membrane became larger than those of the PVA membrane.

The CO$_2$ permeabilities of the PVA membrane and the hybrid PVA membrane as a function of temperature are shown in Figure 5.3. Similar to the curves of selectivities, the PVA membrane demonstrated higher permeability up to 160°C. At temperatures higher than 160°C, the hybrid PVA membrane showed larger permeability. This
confirms that the presence of inorganic domain might be helpful to maintain CO\textsubscript{2} transport properties at high temperatures, e.g., > 160\textdegree C. This is very advantageous for CO\textsubscript{2}-selective WGS membrane reactor because the optimal working temperature for the commercial low-temperature WGS catalyst is between 160\textdegree C and 220\textdegree C. The higher the reaction temperature, the higher the WGS reaction rate.

When a certain amount of water is absorbed into a polymer, the water molecules generally attach to the polar functional groups in the polymer chain. Since PVA is a more hydrophilic component than the silica derived from sulfonated PTEOS, the PVA membrane might hold more water than hybrid membrane at low temperatures and show better transport performance. However, the micro cavity structure formed by the inorganic domain would be beneficial to maintaining water at the temperatures higher than 160\textdegree C. Additionally, since it is a highly polar group, the sulfonated group in the polymeric membrane could be helpful to improve water retention in the membrane at high temperatures, which has also been proven in the study of fuel cell proton exchange membranes in our group. Typically, PVA might have two effects on the silica particles in the hybrid solution. First, PVA would constrain the growth of the SiO\textsubscript{2} particles and then control the silica particle size. Second, the hydroxyl groups on PVA might combine with Si-OH on the silica particle surface by hydrogen-bonding or possible covalent bonding (Iler, 1979; Uragami et al., 2002; Xu et al., 2004).

Figure 5.4 shows the comparison of the thermal stability between the hybrid PVA membrane and the PVA membrane. As illustrated in Figure 16, there are two stages of degradation for the PVA membrane. The first stage, referred to the removal of hydroxyl group on PVA and amine group on polyallylamine, occurred at 220\textdegree C. The second stage
at 410°C was attributed to the decomposition of the polymer backbone. For hybrid PVA membrane, the temperature of the first degradation stage was shifted to ~ 250°C. Much less weight loss was observed between 300 – 400°C on the hybrid PVA membrane than the PVA membrane. This suggests that the incorporating of silica improved the thermal stability with the strong interaction between the organic and inorganic domains.

5.3 SEGMENTED POLYIMIDE COPOLYMER

5.3.1 Membrane Synthesis and Testing

The copolymer synthesis experiment consisted of two steps, end-capping reaction and chain-extension reaction (Ho et al., 1991; Ho et al., 1996). During the end-capping reaction, one mole of diol reacted with two moles of dianhydride to make a pre-polymer. Then, such pre-polymer reacted with diamine to finish the chain extension. Figure 5.5 shows the synthesis step of an example using pyromellitic dianhydride (PMDA) / Polyethylene adipate (PEA) / methylene dianiline (MDA) (with molar ratio 2:1:1). The resulting copolymer composition comprised the hard segment of polyamic acid and the soft segment of oligomeric aliphatic polyester. The copolymer solution was cast on a microporous PTFE support. After drying in a fume hood overnight, the membrane was imidized in an oven at 220°C, by which the amic acid linkage was converted into imide linkage. The molecular weight of copolymer should be larger than 25,000 to get membrane with desirable mechanical strength. To systematically study the effect of
molecular structure on the transport properties, several batches of copolymers with different soft segments were synthesized, as shown in Table 5.1.

In the two-step synthesis procedure, the success for the end-capping step was essential to obtain a high molecular weight copolymer. The optimal reaction conditions were identified to be 180°C oil bath with a N\textsubscript{2} purge for both PEA 1000 and PEA 2000 as the soft segments. For poly(2,2-dimethyl propylene) adipate (PDPA), more severe reaction conditions, 200°C oil bath with a N\textsubscript{2} purge, were needed for the end-capping step. For polyethylene glycol (PEG) or polypropylene glycol (PPG) as the soft segment, it seemed that it was very difficult for them to react with PMDA in the end-capping step. However, when using the mixture of PEA and PEG as the diol part, the reaction occurred. This might be due to the transesterification mechanism at the presence of ester linkages in PEA.

The chemical structure of the synthesized copolymer was characterized by Nicolet 470 Fourier transform infrared (FTIR) spectrometer with an attenuated total reflectance (ATR) accessory (Thermo Electron Co., Waltham, MA). The CO\textsubscript{2} transport properties of the copolymer membrane were tested following the same procedure described earlier. Certificated gases with two compositions: (1) 20% CO\textsubscript{2}, 40% H\textsubscript{2}, and 40% N\textsubscript{2} and (2) 50% CO\textsubscript{2} and 50% CH\textsubscript{4}, were used as the feed gas. The feed pressure was set at 29.4 psia and various water rates were applied.

5.3.2 Results and Discussion

The Fourier transform infrared (FTIR) spectrum of the copolymer, 2 PMDA / 1 PEA 2000 / 1 MDA, after imidization are depicted in Figure 5.6. As can be seen, the
symmetric and asymmetric absorption peaks of the imide carbonyl group were observed around 1782 and 1722 cm\(^{-1}\). The absorption of C-N-C in the five-membered imide ring was observed around 1387 cm\(^{-1}\). The bending vibration of the 5-member imide ring was observed around 725 cm\(^{-1}\). The broad band around 1100 cm\(^{-1}\) could be attributed to the ester or ether linkages, which existed extensively in the soft segment.


As can be seen, these copolymer membranes showed similar trends on the effects of temperature and relative humidity on CO\(_2\) permeability and selectivity. As temperature increased, the CO\(_2\) permeability usually increased while the selectivity decreased. There was only the solution-diffusion mechanism taking effect in the membranes. At higher temperatures, the membrane structure could become more open due to the increased polymer chain mobility. The addition of water at 60\(^\circ\)C or higher temperatures increased the CO\(_2\) permeability significantly without deteriorating the CO\(_2\)/N\(_2\) and CO\(_2\)/N\(_2\) selectivity. The presence of water in the membrane facilitated CO\(_2\) transport, since CO\(_2\) could dissolve in water and diffuse through the membrane in the form of bicarbonate ion.

The molecular structure influenced the membrane transport properties greatly. With the decrease of soft segment length from a molecular weight of 2000 to 500, both permeability and selectivity decreased. This indicated that the amount of polar soft
segment was very critical to the affinity of copolymer membranes to CO\textsubscript{2}. Membrane H2004-2-303 contained a copolymer with both PEA 2000 and PEG 2000 as the soft segment (molar ratio 1:1). Compared to PEA 2000 copolymer membrane H2004-2-283, the membrane with PEG showed better CO\textsubscript{2} transport properties at both 25\textdegree C and 60\textdegree C. A possible reason for this higher CO\textsubscript{2} selectivity could be that the polar ether groups in PEG chain are more hydrophilic and show higher affinity to CO\textsubscript{2} than the ester groups in PEA chain.

5.4 CONCLUDING REMARKS

The hybrid organic-inorganic membranes were prepared by incorporating silica derived from alkoxydisilanes into PVA polymer matrix. The hybrid membrane demonstrated better thermal stability than the PVA membrane without the inorganic phase. Even though the PVA membrane performed better at relative low temperature, the hybrid membrane showed superior CO\textsubscript{2} transport properties at temperatures higher than 160\textdegree C. CO\textsubscript{2}/H\textsubscript{2} selectivity of larger than 10 was obtained at 180\textdegree C. The decent high-temperature performance is very important for CO\textsubscript{2}-selective WGS membrane reactor.

Segmented polyimide copolymers were synthesized by a two-step procedure. The permeation experiments showed that these membranes followed the solution-diffusion mechanism. There existed a tradeoff between permeability and selectivity with the increase of temperature. A high relative humidity was beneficial to enhancing the affinity to CO\textsubscript{2} and improving CO\textsubscript{2} permeability. Since the membrane demonstrated the selectivity mainly on the affinity of polar soft segment to CO\textsubscript{2}, the polymer molecular
structure had significant effects on the membrane performance. With the increase of the length or the weight percentage of soft segment in the whole copolymer chain, CO$_2$ transport properties were enhanced considerably. On the other hand, the soft segment containing ether moieties showed better performance than the soft segment consisting of ester moieties, which may be explained by the higher polarity with the ether moieties.
<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular Weight (g/mol)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene adipate (PEA)</td>
<td>1000, 2000</td>
<td>Crompton Co.</td>
</tr>
<tr>
<td>Poly(2,2-dimethyl propylene) adipate (PDPA)</td>
<td>500</td>
<td>Crompton Co.</td>
</tr>
<tr>
<td>Polyethylene glycol (PEG)</td>
<td>1000, 2000</td>
<td>Aldrich, Inc.</td>
</tr>
<tr>
<td>Polypropylene glycol (PPG)</td>
<td>1000, 2000</td>
<td>Aldrich, Inc.</td>
</tr>
</tbody>
</table>

Table 5.1. Diols as the option of soft segment.
<table>
<thead>
<tr>
<th>Membrane No.</th>
<th>T (°C)</th>
<th>Water flow rate (cc/min)</th>
<th>$\alpha$ (CO$_2$/H$_2$)</th>
<th>$\alpha$ (CO$_2$/N$_2$)</th>
<th>CO$_2$ Permeability (Barrers)</th>
<th>CO$_2$ Permeance (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2004-2-283</td>
<td>25</td>
<td>0.00/0.00</td>
<td>5.22</td>
<td>24.28</td>
<td>26.30</td>
<td>1.38</td>
</tr>
<tr>
<td>H2004-2-283</td>
<td>35</td>
<td>0.00/0.00</td>
<td>3.85</td>
<td>23.35</td>
<td>53.52</td>
<td>2.82</td>
</tr>
<tr>
<td>H2004-2-283</td>
<td>60</td>
<td>0.00/0.00</td>
<td>3.63</td>
<td>21.16</td>
<td>70.77</td>
<td>3.72</td>
</tr>
<tr>
<td>H2004-2-283</td>
<td>60</td>
<td>0.01/0.01</td>
<td>3.64</td>
<td>20.35</td>
<td>115.36</td>
<td>6.07</td>
</tr>
<tr>
<td>H2004-2-283</td>
<td>80</td>
<td>0.01/0.01</td>
<td>3.49</td>
<td>16.95</td>
<td>187.24</td>
<td>9.85</td>
</tr>
<tr>
<td>H2004-2-283</td>
<td>100</td>
<td>0.01/0.01</td>
<td>2.64</td>
<td>12.53</td>
<td>212.78</td>
<td>11.20</td>
</tr>
<tr>
<td>H2004-2-283</td>
<td>120</td>
<td>0.01/0.01</td>
<td>1.91</td>
<td>8.16</td>
<td>291.10</td>
<td>15.32</td>
</tr>
<tr>
<td>H2004-2-288</td>
<td>40</td>
<td>0.00/0.00</td>
<td>2.37</td>
<td>22.98</td>
<td>36.76</td>
<td>4.08</td>
</tr>
<tr>
<td>H2004-2-288</td>
<td>60</td>
<td>0.00/0.00</td>
<td>2.47</td>
<td>20.03</td>
<td>56.62</td>
<td>6.29</td>
</tr>
<tr>
<td>H2004-2-288</td>
<td>60</td>
<td>0.01/0.01</td>
<td>2.47</td>
<td>19.96</td>
<td>80.78</td>
<td>8.98</td>
</tr>
<tr>
<td>H2004-2-288</td>
<td>80</td>
<td>0.01/0.01</td>
<td>2.27</td>
<td>15.50</td>
<td>159.48</td>
<td>17.72</td>
</tr>
<tr>
<td>H2004-2-288</td>
<td>100</td>
<td>0.01/0.01</td>
<td>1.77</td>
<td>5.75</td>
<td>247.00</td>
<td>27.44</td>
</tr>
<tr>
<td>H2004-2-288</td>
<td>120</td>
<td>0.01/0.01</td>
<td>1.63</td>
<td>6.28</td>
<td>377.43</td>
<td>41.94</td>
</tr>
<tr>
<td>H2004-2-295</td>
<td>25</td>
<td>0.00/0.00</td>
<td>0.82</td>
<td>8.26</td>
<td>4.41</td>
<td>0.23</td>
</tr>
<tr>
<td>H2004-2-295</td>
<td>60</td>
<td>0.00/0.00</td>
<td>0.71</td>
<td>9.27</td>
<td>6.25</td>
<td>0.33</td>
</tr>
<tr>
<td>H2004-2-295</td>
<td>60</td>
<td>0.01/0.01</td>
<td>0.83</td>
<td>10.96</td>
<td>12.29</td>
<td>0.65</td>
</tr>
<tr>
<td>H2004-2-295</td>
<td>80</td>
<td>0.01/0.01</td>
<td>1.48</td>
<td>14.18</td>
<td>50.92</td>
<td>2.68</td>
</tr>
<tr>
<td>H2004-2-295</td>
<td>80</td>
<td>0.02/0.02</td>
<td>1.86</td>
<td>4.56</td>
<td>155.58</td>
<td>8.19</td>
</tr>
<tr>
<td>H2004-2-303</td>
<td>25</td>
<td>0.00/0.00</td>
<td>7.65</td>
<td>54.26</td>
<td>62.43</td>
<td>6.24</td>
</tr>
<tr>
<td>H2004-2-303</td>
<td>60</td>
<td>0.00/0.00</td>
<td>4.29</td>
<td>23.65</td>
<td>207.29</td>
<td>20.73</td>
</tr>
<tr>
<td>H2004-2-303</td>
<td>80</td>
<td>0.00/0.00</td>
<td>3.20</td>
<td>14.80</td>
<td>248.82</td>
<td>24.88</td>
</tr>
<tr>
<td>H2004-2-303</td>
<td>100</td>
<td>0.01/0.01</td>
<td>2.64</td>
<td>11.55</td>
<td>420.10</td>
<td>42.01</td>
</tr>
<tr>
<td>H2004-2-303</td>
<td>120</td>
<td>0.01/0.01</td>
<td>2.12</td>
<td>8.26</td>
<td>542.52</td>
<td>54.25</td>
</tr>
</tbody>
</table>

Table 5.2. The testing results of copolymer membrane.
Figure 5.1. CO$_2$/H$_2$ selectivity of PVA membrane and hybrid PVA membrane.
Figure 5.2. CO$_2$/N$_2$ selectivity of PVA membrane and hybrid PVA membrane.
Figure 5.3. CO$_2$ permeability of PVA membrane and hybrid PVA membrane.
Figure 5.4. The thermogravimetric curves for the hybrid PVA membrane and the PVA membrane.
Figure 5.5. Reaction steps in the synthesis of 2 PMDA/ 1 PEA 2000/ 1 MDA.
Figure 5.6. FTIR spectra of copolymer, 2 PMDA / 1 PEA 2000 / 1 MDA, after imidization.
CHAPTER 6

MODELING OF CO₂-SELECTIVE WGS MEMBRANE REACTOR
FOR FUEL CELLS

SUMMARY: Water-gas-shift (WGS) reaction is critical to hydrogen purification for fuel cells. Being reversible and exothermic, the WGS reaction in the traditional fixed bed reactor is not efficient. Using a CO₂-selective membrane reactor shifts the reaction towards the product side, which enhances the conversion of CO and increases the purity of the H₂ product at a high pressure. The simultaneous reaction and transport process in the countercurrent WGS membrane reactor was simulated by using a one-dimensional non-isothermal model, and the effect of several system parameters including CO₂/H₂ selectivity, CO₂ permeability, sweep-to-feed molar flow rate ratio, inlet feed temperature, inlet sweep temperature, feed-side pressure, feed inlet CO concentration and catalyst activity were investigated. The syngases from both autothermal reforming and steam reforming were used as the feed gas, while heated air was used as the sweep gas. A published WGS reaction rate expression with the commercial Cu/ZnO catalyst was incorporated into the model. The modeling results show that a CO concentration of less than 10 ppm, a H₂ recovery of greater than 97%, and a H₂ concentration of greater than
54% (on the dry basis) are achievable from autothermal reforming syngas. If steam reforming syngas is used as the feed gas, H$_2$ concentration can be as high as 99.64% (on the dry basis). An experimental study of the CO$_2$-selective WGS membrane reactor was also conducted. By removing CO$_2$, the reversible WGS was shifted forward so that the CO concentration was significantly decreased to less than 10 ppm. The modeling results agreed well with the experimental data.
6.1 INTRODUCTION

Fuel cell is an efficient energy conversion device for both transportation and stationary power generation. It converts chemical energy directly into electrical energy, which is about two times efficiency of the internal combustion engine in terms of gas mileage (Acres 2001; Barnett and Teagan, 1992). On the other hand, fuel cell is also an environmental friendly device; water is the only emission when hydrogen is the fuel.

Although pure hydrogen is a superior fuel-cell fuel, currently there are issues on its storage and distribution (Brown, 2001; Cropper et al., 2004). As a more practical way, hydrogen used in an automotive fuel cell is suggested to be produced by reforming reactions of the available fuels, such as methanol, natural gas, gasoline and diesel. Steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR) are three major reforming processes. In SR, steam reacts with hydrocarbon over a catalyst to form H$_2$, CO and CO$_2$ at around 750 – 800°C since this reaction is strongly endothermic. In POX, the hydrocarbon reacts with a deficient amount of oxygen or air to produce H$_2$, CO and CO$_2$ while a large amount of heat is generated. ATR integrates these two processes together by feeding the hydrocarbon, water, and air together into the reactor at the same time. The SR reaction absorbs most of the heat generated by the POX reaction, and an overall process takes place slightly exothermally.

For transportation fuel cell applications, one of the key issues is the purity of H$_2$. Even a very small amount of CO in the hydrogen, e.g., >10 ppm, will deteriorate the fuel cell performance by poisoning platinum, which works as the electrocatalyst in polymer electrolyte membrane fuel cells (Ahmed and Krumpelt, 2001). Typically, water-gas-shift
(WGS) reaction is used to convert CO in the syngas from the reformer and generate more H₂.

\[ CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H_r = -41.1 \text{ kJ/mol} \quad (6.1) \]

However, WGS reaction is a reversible, exothermic reaction that is thermodynamically unfavorable at elevated temperatures, and it results in a high CO concentration (~1%) and a bulky, heavy reactor with the traditional fixed bed reactor. Generally speaking, a membrane reactor can be used to improve the reaction performance with the in-situ separation of products. It is possible to overcome thermodynamic constraint and increase the CO conversion significantly.

By using palladium or other inorganic H₂-selective WGS membrane reactors, many researchers have achieved high CO conversion values beyond the equilibrium ones or close to 100% (Uemiya et al., 1991; Basile et al., 1996; Xue et al., 1996; CrisCuli et al., 2000; Basile et al., 2001; Giessler et al., 2003; Tosti et al., 2003). However, the difficulty to prepare thin, flawless and durable membranes is still the remaining challenge for the commercial application of this type of membrane reactor (Armor, 1998).

Several modeling studies of membrane reactors were published recently. Ma and Lund developed a two-step microkinetic model for the high-temperature WGS membrane reactor (Ma and Lund, 2003). They found that eliminating the inhibitory effect of CO₂ was more important for better reactor performance than finding a perfect membrane. A modeling analysis of WGS reaction performed by Basile et al. showed that the countercurrent mode of the H₂-selective, Pd/Ag-based membrane reactor could have higher H₂ recovery than the co-current mode because of more uniform driving force (Basile et al., 2003). Process simulations for investigating potential catalyst deactivation
and conversion improvement were also done for the methane steam reforming performed in the H₂-selective membrane reactors based on Pd membranes (Hou et al., 1999; Marigliano et al., 2001; Gallucci et al., 2004a).

Using a CO₂-selective membrane (Ho, 2000; Tee et al., 2006; Zou and Ho, 2006) can shift the WGS reaction to clean up CO and generate more H₂. With the continuous removal of CO₂, CO₂-selective WGS membrane reactor is a promising approach to enhance CO conversion and increase the purity of H₂ under relatively low temperatures (~150°C). In comparison with the H₂-selective membrane reactor, the CO₂-selective WGS membrane reactor is more advantageous because (1) a H₂-rich product is recovered at high pressure (feed gas pressure) and (2) air can be used to sweep the permeate, CO₂, on the low-pressure side of the membrane to obtain a high driving force for the separation.

The WGS catalysts have been studied for long time. A two-stage process is usually used in the industry: Fe₃O₄/Cr₂O₃ catalyst is used for the high-temperature shift (HTS) and Cu/ZnO/Al₂O₃ catalyst is used for the low-temperature shift (LTS). Since the development of Cu/ZnO/Al₂O₃ in the 1960s, the main industrial application of WGS reaction has been H₂ production for ammonia production or for petroleum refining (Rhodes et al., 1995; Choi and Stenger, 2003). However, the requirements on transportation fuel cell applications are fundamentally different from those of industrial uses. The suitable catalysts should be very active and poison-resistant materials, which would result in a small reactor volume, short start-up time and good stability under transient or steady state conditions.

There are many studies focusing on catalyst preparation and the reaction mechanism in the literature for both classical and novel LT-WGS catalysts. The
traditional Cu/ZnO/Al₂O₃ catalyst shows good activity at 200 – 240°C because of the optimal adsorption heat of CO on Cu (about 80 kJ/mol) (Grenoble et al., 1981). The main drawbacks of this catalyst are that it is pyrophoric and highly sensitive to sulfur poisoning. The novel WGS catalysts active at low temperatures are normally based on platinum group metals (PGM) or gold. For many years, Pt/CeO₂ has been proven to be a very active WGS catalyst especially at high temperatures (Mendelovici, 1985; Swartz et al., 2001; Hilaire et al., 2004). However, the activity and stability of these ceria-supported catalysts need to be improved by studying the preparation conditions and formulations. Newly developed Pt-containing catalysts show improved durability over a large range of temperatures (200–500°C) (Ghenciu, 2002). Gold-based catalyst for WGS reaction is a new alternative investigated during the last decade (Fu et al., 2001; Andreeva, 2002; Andreeva et al., 2002, Tabakova et al., 2004). Andreeva reported that Au/Fe₂O₃ has higher activity than Cu/ZnO/Al₂O₃ starting from 120°C (Andreeva, 2002). Additionally, improved stability was obtained from Au/CeO₂ (Fu et al., 2001). The activity and stability of these catalysts, however, are sensitive to the preparation techniques, gold particle size and specific gold-support interaction. Recent research from Fu et al. showed that the active sites in these catalysts are gold or platinum ions strongly associated with the surface oxygen of ceria instead of gold or platinum metal nanoparticles (Fu et al., 2003). This finding may significantly reduce the requirement for the precious metal.

The objectives of this study are, therefore, to propose the concept of CO₂-selective WGS membrane reactor, to develop a one-dimensional non-isothermal model to simulate the reaction and transport process, and to show the effect of several system
parameters including CO₂/H₂ selectivity, CO₂ permeability, and sweep-to-feed molar flow rate ratio on the reactor performance. In addition, the parameters influencing catalyst performance, including inlet feed temperature, inlet sweep temperature, feed-side pressure, inlet feed CO concentration and catalyst activity were also investigated. Both autothermal reforming and steam reforming syngases were used as the feed gas in this work. Finally, CO₂-selective WGS membrane reactor experiments were carried out using a rectangular cell to validate the modeling data.

6.2 MODEL DESCRIPTION

As one of the two main types of commercialized membrane modules, the hollow fiber membrane module has shown excellent mass transfer performance because of its large surface area per unit volume (about 3000 ft²/ft³ for gas separation) (Ho and Sirkar, 1992). In this work, the WGS membrane reactor was configured to be a hollow fiber membrane module with catalyst particles packed inside the fibers. The following assumptions were made in the model:

(1) The hollow fiber module is composed of CO₂-selective facilitated transport membrane;

(2) CO₂ and H₂ are the only two gases permeating through the membrane;

(3) Membrane permeability is fixed and does not change with temperature variation in the module;

(4) There is no temperature variation in the radial direction inside a hollow fiber due to its small dimension;
(5) The module is adiabatic and operating at a steady state;
(6) There is no axial mixing;
(7) The pressure drops on both lumen and shell sides are negligible.

The $\text{CO}_2/\text{H}_2$ selectivity for the membrane is expressed in Equation (6.2). The flux for a permeating gas species is related to the membrane permeability, transmembrane partial pressure difference, and membrane thickness in Equation (6.3).

$$\alpha = \frac{y_{\text{CO}_2}}{x_{\text{CO}_2}} / \frac{y_{\text{H}_2}}{x_{\text{H}_2}}$$  \hspace{1cm} (6.2)

$$J_i = P_i \frac{\Delta p_i}{\ell}$$  \hspace{1cm} (6.3)

The catalyst packed was assumed to be the commercial Cu/ZnO/Al$_2$O$_3$ catalyst for lower-temperature WGS reaction. A number of studies on the reaction kinetics have been published (Moe, 1962; Campbell, 1977; Fiolitakis et al., 1980; Salmi and Hakkarainen, 1989; Keiski et al., 1993; Amadeo and Laborde, 1995). Above 200°C, Campbell’s rate equation is pore-diffusion limited, not chemical-reaction limited. Campbell stated that his reaction rate fitted poorly with experimental data obtained for temperatures less than 200°C (Campbell, 1977). Fiolitakis et al. gave an activation energy of 46 kJ/mol but did not give a reaction rate constant (Fiolitakis et al., 1980). Salmi and Hakkarainen only had data for temperatures greater than 200°C (Salmi and Hakkarainen, 1989). Based on the experimental data of the commercial catalyst (ICI 52-1), Keiski et al. gave two reaction rates for the low-temperature WGS reaction over a range of 160 – 250°C (Keiski et al., 1993). The first was dependent only on CO concentration and gave an activation energy of 46.2 kJ/mol. The second reaction rate was dependent on CO and steam concentrations with a lower activation energy of 42.6
kJ/mol. Because of the proximity of our operation conditions to theirs and the fact that steam is in excess in most of the membrane reactors, Keiski et al.’s first reaction rate expression was chosen for this work. The reaction rate is given by Equation (4).

\[ r_i = 1.0 \times 10^{-1} \frac{\rho_b P_f}{n_i R T_f} \exp(13.39 - \frac{5557}{T_f}) n_{CO}(1 - \frac{n_{f,H_2} n_{f,CO_2}}{K_T n_{f,CO} n_{f,H_2O}}) \]  

(6.4)

where the expression for \( K_T \) (19, 23) is as follows:

\[ K_T = \exp(-4.33 + \frac{4577.8}{T_f}) \]  

(6.5)

The catalyst bulk density, \( \rho_b \), used in this work was 1.395 g/cm\(^3\) (Keiski et al., 1993).

The temperatures of both feed (lumen) and sweep (shell) sides are affected by the heat of the reaction and the heat transfer through the membrane. The overall heat transfer coefficient \( U_i \) was derived via the series resistance method to include both convective and conductive heat transfer.

\[ U_i = \frac{1}{\frac{1}{h_f} + \frac{d_{in}}{2k_m} \ln(d_{in} + 2\ell) + \frac{1}{2[(1 - \varepsilon)k_m + \varepsilon k_a]} \ln(\frac{d_{out}}{d_{in} + 2\ell}) + \frac{d_{in}}{d_{out}} \frac{1}{h_i}} \]  

(6.6)

In Equation (6.6), the thermal conductivities of the selective membrane layer and the hollow-fiber support layer were assumed to be the same, i.e., \( k_m \), which is true for an integrally skinned membrane. The thermal conductivities, \( k_a \) and \( k_m \), used in this work were \( 3.4 \times 10^{-4} \) and \( 1.7 \times 10^{-3} \) W/cm/s, respectively (Perry and Green, 1997).

The convective heat transfer for the feed (lumen) side can be considered to be that on the inside wall of a packed bed. Due to the small dimension of the lumen, we assumed that the inside heat transfer resistance was negligible and then there was no temperature difference in the radical direction inside the fiber. Many researchers have studied the shell side mass transfer of hollow fiber modules based on either empirical or
fundamental work (Yang and Cussler, 1986; Dahuron and Cussler, 1988; Costello et al., 1993; Wu and Chen, 2000; Lipnizki and Field, 2001). According to the analogy between heat and mass transfer, similar equations can be used for the calculation of heat transfer coefficients by changing $Sh$ to $Nu$ and $Sc$ to $Pr$, respectively. Yang and Cussler’s correlation equation (Yang and Cussler, 1986) was chosen because the module configuration and operation parameters they used were similar to those in this work.

$$h_s = 1.25 \frac{k_a}{d_h^{0.07}} \left( \frac{Re}{L} \right)^{0.93} Pr^{0.33}$$  \hspace{1cm} (6.7)

In addition, because mass transfer and heat transfer occurred simultaneously in the membrane reactor, the energy carried by permeating gases was also taken into account in the model.

Based on the schematic diagram of the WGS hollow-fiber membrane reactor illustrated in Figure 6.1, the molar and energy balances were performed on both feed (lumen) and sweep (shell) sides, respectively.

6.2.1 Molar Balance

*Feed (lumen) Side*

Based on the volume element from $z$ to $z + \Delta z$, the molar balance for gas species $i$ can be expressed as,

\[ \text{In} - \text{Out} + \text{Generation} = \text{Accumulation} \]

or
\[ n_{\beta} \bigg|_{z} - n_{\beta} \bigg|_{z+\Delta z} - \pi d \Delta z J_i + \frac{1}{4} \pi d^2 \Delta z r_i = 0 \]  

(6.8)

Dividing both sides of Equation (8) by \( \Delta z \) and taking the limit as \( \Delta z \to 0 \) give

\[ \frac{dn_{\beta_i}}{dz} = \frac{1}{4} \pi d_{in}^2 r_i - \pi d_{in} J_i \]  

(6.9)

**Sweep (shell) Side**

Similarly, the molar balance on the sweep or shell side is carried out, and the resulting equation is

\[ \frac{dn_{\beta_i}}{dz} = -\pi d_{in} J_i \]  

(6.10)

In addition, the \( \text{H}_2 \) recovery is defined as the ratio of the exit \( \text{H}_2 \) molar flow rate to the combination of the inlet \( \text{H}_2 \) and \( \text{CO} \) molar flow rates. All these flow rates are on the feed, lumen side.

**6.2.2 Energy Balance**

With considering the heat of the reaction, the heat transfer through the membrane, and the energy carried by permeating gases, the energy balance on the volume element of the membrane reactor was carried out from \( z \) to \( z + \Delta z \). Differential equations were obtained by taking the limit as \( \Delta z \to 0 \).

**Feed (lumen) Side**
\[ \frac{d\sum(n_f c_{pf} T_f)}{dz} = \frac{1}{4} \pi d_{in}^2 r_i \Delta H_r T_f - \pi d_{in} (U_i + c_{pcO} J_{CO} + c_{pH_2} J_{H_2}) (T_f - T_s) \]  
\( (6.11) \)

The heat capacities for all the gas species were taken from the literature (Smith, et al., 2001).

**Sweep (shell) Side**

\[ \frac{d\sum(n_{sl} c_{ps} T_s)}{dz} = -\pi d_{in} (U_i + c_{pcO} J_{CO} + c_{pH_2} J_{H_2}) (T_f - T_s) \]  
\( (6.12) \)

The boundary conditions of above differential equations are listed as follows:

At \( z = 0 \),

\[ T_f = 140^\circ C, \quad n_{f,CO} = x_{CO} n_{i0}, \quad n_{f,H_2O} = x_{H_2O} n_{i0}, \]
\[ n_{f,H_2} = x_{H_2} n_{i0}, \quad n_{f,CO} = x_{CO} n_{i0} \]

At \( z = L \),

\[ T_s = 140^\circ C, \quad n_{s,CO} = 0, \quad n_{s,H_2O} = 0, \]
\[ n_{s,H_2} = 5 \times 10^{-7} n_{i0} \gamma, \quad n_{s,CO} = 370 \times 10^{-6} n_{i0} \gamma \]

In this work, \( n_{i0} \) was 1 and 0.635 mol/s for autothermal reforming syngas and steam reforming syngas, respectively. With the compositions of both syngases given in Table 6.1, these flow rates were chosen because a sufficient \( H_2 \) molar flow rate would hence be provided to generate a power of 50 kW via the fuel cell for a five-passenger car (Brown, 2001). Heated air was used as the sweep gas. The concentrations of hydrogen and carbon dioxide in the inlet air were set as 0.5 ppm and 370 ppm, respectively.
The \textit{bvp4c} solver in Matlab\textsuperscript{®} was used to solve the above differential equations of the boundary value problem with the given boundary conditions. During the calculation, the hollow fiber number was adjusted to satisfy the constraint of feed exit CO concentration, i.e., $< 10$ ppm.

6.3 EXPERIMENTAL STUDY OF CO$_2$-SELECTIVE WGS MEMBRANE REACTOR

To demonstrate the potential of the proposed CO$_2$-selective WGS membrane reactor and verify the developed model, the gas permeation unit was modified to carry out membrane reactor experiments. A rectangular gas permeation cell, which had a larger effective membrane area of 342.70 cm$^2$ (19.10 cm $\times$ 17.95 cm) and well-defined gas-flow channels on both the feed and sweep sides, was constructed for the CO$_2$-selective WGS membrane reactor experiments (Zou et al., 2006). For the membrane reactor experiments, a specific amount of the catalyst was loaded onto the top of the membrane for each experiment. One piece of filter paper and one piece of either microporous Teflon support or microporous polysulfone support were used between the catalyst and the membrane to prevent the catalyst from damaging the membrane. The catalyst used in the membrane reactor experiments was Cu/ZnO/Al$_2$O$_3$ low-temperature WGS catalyst (C18-AMT-2) obtained from SÜD-CHEMIE Inc. (Louisville, KY). The catalyst particles were 3/16 by 3/32 inch tablets and were crushed to fractions of about 0.1 – 0.5 mm before loading. About 40 to 45 grams of catalyst were loaded in each experiment. The commercial low-temperature WGS catalyst particles were supplied in the oxide form and needed to be reduced to metallic copper before use.
\[
\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \quad (\Delta H = -80.8 \text{ kJ/mol}) \quad (6.13)
\]

A certificated gas mixture consisting of 1.0% CO, 17% CO\textsubscript{2}, 45% H\textsubscript{2}, and 37% N\textsubscript{2} was used as the feed gas in the membrane reactor experiments. This composition was used to simulate the composition of the autothermal reforming syngas with air. Argon was used as the sweep gas for the ease of gas chromatography analysis. Gas flow rates and water flow rates were controlled by mass flow meters and Varian Prostar 210 pumps, respectively. The compositions for both the retentate and permeate gases were analyzed using an Agilent 6890N gas chromatograph.

The special design of the rectangular cell made the gas flows on both the feed side and the sweep side ideal plug-flows. Therefore, a one-dimensional isothermal model was used to simulate the simultaneous reaction and transport process in this rectangular CO\textsubscript{2}-selective WGS membrane reactor operated at a set temperature. The following assumptions were made in the model:

1. The reactor is isothermal and operating at a steady state;
2. The reactor is operated with a counter-current configuration;
3. There is no mixing along the length of the reactor;
4. The N\textsubscript{2} and CO permeations across the membrane are negligible;
5. The pressure drops on both the feed and sweep sides along the length of the reactor are negligible.

Based on the differential volume element along the length direction, as shown in Figure 6.2, the molar balances for the gas species \(i\) on the feed side and the sweep side can be expressed as Equations (6.14) and (6.15), respectively.

\[
\text{Feed side:} \quad \frac{dn_{i,f}}{dz} = WH \, r_i - W \, J_i \quad (J_i = P_i \frac{\Delta p_i}{\ell})
\]

(6.14)
Sweep side: \[
\frac{dn_{si}}{dz} = -W_i J_i
\] (6.15)

The WGS reaction rate and the equilibrium constant, \(K_T\), expressed by Equations (6.4) and (6.5) were incorporated. And the \textit{bvp4c} solver in Matlab\textsuperscript{®} was used to solve the above differential equations of the boundary value problem.

6.4 RESULTS AND DISCUSSION

6.4.1 Autothermal Reforming Syngas

6.4.1.1 Reference Case

A reference case was chosen with the \(\text{CO}_2/\text{H}_2\) selectivity of 40, the \(\text{CO}_2\) permeability of 4000 Barrers (1 Barrer = \(10^{-10}\) cm\(^3\) (STP) \(\cdot\) cm/cm\(^2\) \(\cdot\) s \(\cdot\) cm Hg), the inlet sweep-to-feed molar flow rate ratio of 1, the membrane thickness of 5 \(\mu\)m, 52,500 hollow fibers (a length of 61 cm, an inner diameter of 0.1 cm, and a porous support with a porosity of 50% and a thickness of 30 \(\mu\)m), both inlet feed and sweep temperatures of 140\(^\circ\)C, a feed gas contained 1% CO, and the feed and sweep pressures of 3 and 1 atm, respectively. Based on this case, the effects of \(\text{CO}_2/\text{H}_2\) selectivity, \(\text{CO}_2\) permeability, and sweep-to-feed ratio on the reactor behavior were then investigated. It should be noted that the values of the \(\text{CO}_2/\text{H}_2\) selectivity and \(\text{CO}_2\) permeability were based on the experimental data obtained from \(\text{CO}_2\)-selective membranes as described in the previous chapters.
Figure 6.3 shows the profiles of the feed-side mole fractions of CO and CO$_2$ along the length of the countercurrent membrane reactor. The modeling results demonstrated that this membrane reactor could decrease CO concentration from 1% to 9.82 ppm along with the removal of almost all the CO$_2$. Figure 6.4 depicts the profiles of feed-side H$_2$ concentrations on the dry and wet bases. As depicted in this figure, the membrane reactor could enhance H$_2$ concentration from 45.30% to 54.95% (on the dry basis), i.e., from 41% to 49.32% (on the wet basis). In this case, the H$_2$ recovery calculated from the model was 97.38%. With the advancement of the high temperature proton-exchange-membrane fuel cell (120 – 160$^\circ$C), it is expected that the constraint of CO concentration can be relaxed to about 50 ppm in the near future. Then, the required hollow fiber number could be reduced significantly to 39,000 based on the modeling results.

The temperature profiles for both feed and sweep sides are shown in Figure 6.5 with a maximum for each profile. Since the overall module was adiabatic, the feed gas was heated by the exothermic WGS reaction. The highest feed-side temperature was 158$^\circ$C at about $z = 15$ cm. Beyond that, the feed-side temperature reduced, and it became very close to the sweep-side temperature at the end of membrane reactor. This was due to the efficient heat transfer provided by the hollow fiber configuration. Higher temperatures enhance WGS reaction rates but are unfavorable for CO conversion. Thus, it is important to use air with appropriate temperature, i.e., 140$^\circ$C as the sweep gas to keep the feed gas within 150 ± 10$^\circ$C.

For comparison, the cases of conventional fixed bed reactor and isothermal conditions were also considered. The case of conventional reactor was calculated by assuming both CO$_2$ and H$_2$ permeabilities to be zero. The exit CO concentration
increased drastically to 1390 ppm, which was very close to the equilibrium CO value at 140°C. The H₂ recovery increased to 99.67% because of no loss due to H₂ permeation. The result strongly showed the advantage of simultaneous CO₂ removal for the reactor performance of achieving <10 ppm CO in the H₂ product. The simulation for the case of isothermal conditions was performed by assuming the temperatures for both feed and sweep sides to be 140°C. The exit CO concentration increased significantly to 23.90 ppm, and the H₂ recovery became 97.41%. This showed that the isothermal case was less favorable than the non-isothermal case with enhanced CO conversion due to a temperature rise for achieving < 10 ppm CO in the H₂ product.

6.4.1.2 Effect of CO₂/H₂ Selectivity

In order to study the impact of CO₂/H₂ selectivity on the membrane reactor performance, α = 10, 20, 40, 60, and 80 were applied in the model while the other parameters for the reference case were kept constant. As shown in Figure 6.6, the feed-side exit CO concentration increased slightly as the CO₂/H₂ selectivity increased. This was due to the fact that the higher selectivity with lower H₂ permeability resulted in a lower H₂ permeation rate or higher H₂ concentration on the feed side, which was unfavorable for the WGS reaction rate. Also shown in this figure, the H₂ recovery increased from 89.85% to 98.68% as the CO₂/H₂ selectivity increased from 10 to 80. This indicated that the higher selectivity decreased the H₂ loss because of the reduction in H₂ permeation through the membrane.
6.4.1.3 Effect of CO$_2$ Permeability

The membrane areas required for the exit feed CO concentration of < 10 ppm in the H$_2$ product were calculated with five different CO$_2$ permeabilities ranging from 1000 to 8000 Barrers while the other parameters for the reference case were kept constant. As demonstrated in Figure 6.7, the required membrane area or hollow fiber number dropped rapidly as permeability increased from 1000 Barrers to 4000 Barrers. Beyond that, it approached an asymptotic value gradually. Increasing CO$_2$ permeability increased the CO$_2$ permeation rate and enhanced the CO$_2$ removal, which shifted the WGS reaction towards the product side. However, after the permeability exceeded about 6000 Barrers, the overall system became reaction controlled. Hence, the influence of the permeability became less significant.

In the literature, similar results of increasing CO or CH$_4$ conversion with the decrease of the membrane thickness have been reported (Uemiya et al., 1991; Gallucci et al., 2004b). From Equation (3), it can be seen that decreasing membrane thickness would have the same effect on the reduction of transport resistance as increasing permeability.

6.4.1.4 Effect of Sweep-to-Feed Ratio

The inlet sweep-to-feed molar flow rate ratios of 0, 0.25, 0.5, 1, 1.5, 2, and 2.5 were used in the calculation while the other parameters for the reference case were kept constant. Figure 6.8 illustrates the effect of sweep-to-feed ratio on feed-side exit CO concentration. As illustrated in this figure, increasing the sweep-to-feed ratio decreased
the exit CO concentration first and then increased it slightly. A higher sweep-to-feed ratio resulted in a lower CO$_2$ concentration on the sweep side and then a higher CO$_2$ permeation driving force. However, it also enhanced heat transfer and then decreased the feed-side temperature, which was unfavorable to the WGS reaction rate. Therefore, an optimal sweep-to-feed ratio of about 1 existed as a result of the tradeoff between the effects on the CO$_2$ permeation rate and the WGS reaction rate. Also illustrated in this figure is the effect of sweep-to-feed ratio on H$_2$ recovery. The sweep-to-feed ratio, particularly for $\gamma = 0.25$ or greater, did not have a significant effect on the H$_2$ recovery. This was due to the fact that the resulting CO concentrations were very low (< 240 ppm for $\gamma = 0.25$ or greater) and did not affect the H$_2$ recovery.

For the extreme case with zero sweep flow, the exit CO concentration increased drastically to 1168 ppm, and the H$_2$ recovery became 98.15%. Lowering a sweep-to-feed ratio (to 0.25 or lower) decreased the CO$_2$ removal and the H$_2$ permeation by reducing their driving forces. This resulted in a lower CO conversion accompanied with a higher CO concentration in the H$_2$ product and a slightly higher H$_2$ recovery. The effect of sweep flow on membrane reactor performance was investigated experimentally by some researchers (Giessler et al., 2003; Gallucci et al., 2004b). Giessler et al. showed a similar trend and maximum CO conversion for their molecular sieve silica membrane reactor (Giessler et al., 2003).
6.4.1.5 Effect of Inlet Feed Temperature

The membrane areas required for the exit feed CO concentration of < 10 ppm in the H₂ product were calculated with seven different inlet feed temperatures ranging from 80 to 200°C, while the other parameters for the reference case were kept constant. As shown in Figure 6.9, the required membrane area or hollow fiber number decreased as the inlet feed temperature increased. It gradually approached an asymptotic value. The feed-side temperature profiles for different inlet feed temperatures are presented in Figure 6.10. The feed-side temperature increased as inlet feed temperature increased, especially at the entrance section. The higher feed-side temperature brought a higher WGS reaction rate, and thus a less reactor or catalyst volume was required. The unfavorable WGS equilibrium at high temperatures was compensated by the simultaneous CO₂ removal.

6.4.1.6 Effect of Inlet Sweep Temperature

In order to study the impact of inlet sweep temperature on the membrane reactor performance, Tₐ₀ = 80, 100, 120, 140, 160, 180 and 200°C were applied in the model while the other parameters for the reference case were kept constant. As demonstrated in Figure 6.11, the required membrane area or hollow fiber number dropped rapidly as the inlet sweep temperature increased from 80°C to 160°C. Beyond 160°C, it only increased slightly. Figure 6.12 depicts the feed-side temperature profiles along the membrane reactor with different inlet sweep temperatures. Increasing the inlet sweep temperature increased the feed-side temperature significantly over a longer reactor length in
comparison with increasing the inlet feed temperature as shown in Figure 6.10. Higher feed-side temperature resulted in higher WGS reaction rate. When the inlet sweep temperature exceeded about 160°C, the WGS reaction equilibrium became less favorable for CO conversion, and the overall system became more mass transfer controlled. Hence, more membrane area was needed to remove the generated CO₂ to achieve < 10 ppm CO in the H₂ product.

6.4.1.7 Effect of Feed-Side Pressure

Figure 6.13 demonstrates the required membrane area for different feed-side pressures. As the pressure increased from 1 atm to 2 atm, the required hollow fiber number decreased drastically from 390000 to 89000. Beyond that, the hollow fiber number continued gradually decreasing. Obviously, the increasing feed-side pressure brought a higher CO₂ permeation driving force, but the pressure of 1 atm would be too small to provide enough driving force. Additionally, for a gas phase reaction, the WGS reaction rate is proportional to the feed-side pressure, \( p_f \), which was evidenced by Equation (6.4). Therefore, higher feed-side pressure would not only increase the mass transfer driving force, but also enhance the reaction rate. However, in the real applications, we need to consider the possible physical damage by the extremely high pressure.
6.4.1.8 Effect of Inlet Feed CO Concentration

The composition of autothermal syngas varies with the different fuel type and reforming conditions. The autothermal syngases containing higher feed inlet CO concentration, e.g., 5% and 10%, were used as the feed gas in the calculation. The complete gas compositions are shown in Table 6.1. Figure 6.14 demonstrates the feed-side CO mole fraction profiles for 1%, 5% and 10% CO. The required hollow fiber numbers for 5% and 10% CO were 51,500 and 52,000, respectively, which were slightly less than that for the 1% CO feed gas in the reference case. This was due to the fact that the module was assumed to be adiabatic and higher CO concentration caused higher reaction heat generation. Therefore, a higher feed-side temperature reduced the membrane area required, even if larger amounts of CO might need a larger reactor volume.

6.4.1.9 Effect of Catalyst Activity

The effect of catalyst activity on the required membrane area was studied by assuming several WGS reaction kinetics based on the Cu/ZnO kinetics equation proposed by Keiski et al. (Keiski et al., 1993). In Figure 6.15, the number on the horizontal x-axis indicates the reaction kinetic rate in terms of the Cu/ZnO kinetics, e.g., 1 represents the Cu/ZnO kinetics, 2 represents a kinetics 2 times the reaction rate of the Cu/ZnO kinetics, etc. As illustrated in this figure, increasing catalyst activity reduced the required membrane area significantly. The higher catalyst activity resulted in a higher reaction
rate, which also increased the CO$_2$ permeation rate because of a higher CO$_2$ partial pressure on the feed-side and thus a higher driving force across the membrane. Hence, with the development of more active WGS catalysts, the membrane reactor would become more compact.

6.4.2 Steam Reforming Syngas

6.4.2.1 Reference Case

For the steam reforming syngas, we chose a reference case with the same system parameter values as those for the autothermal reforming syngas except 31,000 hollow fibers with the same dimensions described earlier. The reduced number of hollow fibers for the steam reforming syngas was due to the fact that this syngas had a higher H$_2$ concentration and thus a lower flow rate than the autothermal reforming syngas. Similarly, the effects of CO$_2$/H$_2$ selectivity, CO$_2$ permeability, and sweep-to-feed ratio on the reactor behavior were investigated for the steam reforming syngas based on the reference case.

Figure 6.16 shows the profiles of the feed-side mole fractions of CO and CO$_2$ along the length of the membrane reactors. The modeling results showed that this membrane reactor could decrease CO concentration from 1% to 9.89 ppm along with the removal of almost all the CO$_2$.

Figure 6.17 depicts the profiles of feed-side H$_2$ concentrations on the dry and wet bases. As depicted in this figure, the membrane reactor could enhance H$_2$ concentration
from 79.58% to 99.64% (on the dry basis), i.e., from 65.1% to 78.69% (on the wet basis). In this case, H₂ recovery was 97.38%. Compared with the outlet gas from the autothermal reforming syngas, a much higher exit H₂ concentration was obtained from the steam reforming syngas. This was attributed to the higher inlet H₂ concentration and no N₂ in the steam reforming syngas. Higher hydrogen concentration is believed to improve fuel cell performance. However, since the steam reforming reaction is strongly endothermic, a large and heavy reactor is needed to meet the heat exchange requirement. With smaller and lighter hardware, the autothermal reforming process is generally considered to be more attractive for on-broad hydrogen generation for the automotive fuel cell system (Ahmed and Krumpelt, 2001).

The temperature profiles for both feed and sweep sides are illustrated in Figure 6.18. As illustrated in this figure, maximum temperatures existed for both feed and sweep sides due to the heat of the WGS reaction generated in the adiabatic module.

For comparison, the cases of conventional fixed bed reactor and isothermal conditions were also considered. For the case of conventional reactor calculated by assuming both CO₂ and H₂ permeabilities to be zero, the exit CO concentration increased drastically to 1393 ppm, and the H₂ recovery became 99.79%. As explained earlier, this poor CO result was due to the fact that the chemical equilibrium restricted the CO conversion without CO₂ removal. For the case of isothermal conditions by assuming the temperatures for both feed and sweep sides to be 140°C, the exit CO concentration increased significantly to 32.94 ppm, and the H₂ recovery became 97.81%. This showed a similar trend described earlier for the autothermal reforming syngas.
6.4.2.2 Effect of CO$_2$/H$_2$ Selectivity

The CO$_2$/H$_2$ selectivity values of 10, 20, 40, 60, and 80 were applied in the model to study the selectivity impact on the membrane reactor performance while the other parameters for the reference case were kept constant. As shown in Figure 6.19, the curves for feed-side exit CO concentration and H$_2$ recovery showed consistent trends with those for the autothermal reforming syngas in Figure 6.6. Both exit CO concentration and H$_2$ recovery increased as the CO$_2$/H$_2$ selectivity increased. As explained earlier, the lower H$_2$ permeation rate from higher selectivity increased the exit CO concentration and the H$_2$ recovery.

6.4.2.3 Effect of CO$_2$ Permeability

Five different CO$_2$ permeabilities ranging from 1000 to 8000 Barrers were used in the calculation while other parameters for the reference case were kept constant. The effect of CO$_2$ permeability on the required membrane area for the exit feed CO concentration of < 10 ppm is presented in Figure 6.20. Similar to the autothermal reforming syngas, the required hollow fiber number decreased significantly as CO$_2$ permeability increased. Higher CO$_2$ permeability enhanced the CO$_2$ permeation, which shifted the WGS reaction towards the product side. Therefore, the required membrane area or hollow fiber number was reduced.
6.4.2.4 Effect of Sweep-to-Feed Ratio

The inlet sweep-to-feed molar flow rate ratios of 0, 0.25, 0.5, 1, 1.5, 2, and 2.5 were used in the calculation while the other parameters for the reference case were kept constant. Figure 6.21 illustrates the effect of sweep-to-feed ratio on feed-side exit CO concentration and H₂ recovery. Similar to the autothermal reforming syngas, the exit CO concentration decreased and then increased as the sweep-to-feed ratio increased. A minimum CO value existed at the sweep-to-feed ratio of about 1. A higher sweep-to-feed ratio enhanced the CO₂ permeation but also decreased the feed side temperature. The balance between the two opposite effects resulted in the lowest exit CO concentration. H₂ recovery did not change significantly with different sweep-to-feed ratios, due to the reason explained earlier.

For the extreme case with zero sweep flow, the exit CO concentration increased drastically to 1083 ppm, and the H₂ recovery became 98.12%. As explained earlier, this poor CO result was due to the chemical equilibrium restricting the CO conversion without sufficient CO₂ removal.

6.4.2.5 Effect of Inlet Feed Temperature

The inlet feed temperatures of 80, 100, 120, 140, 160, 180 and 200°C were applied in the model to study the impact of inlet feed temperature on the membrane reactor performance while the other parameters for the reference case were kept constant. As demonstrated in Figure 6.22, the curves for the required membrane area showed
consistent trends with that for the autothermal reforming syngas. The required membrane area decreased as the inlet feed temperature increased. Figure 6.23 shows the feed-side temperature profiles for different inlet feed temperatures. As explained earlier, the higher feed-side temperature from the higher inlet feed temperature increased the WGS reaction rate and decreased the membrane area requirement.

6.4.2.6 Effect of Inlet Sweep Temperature

Seven different inlet sweep temperatures ranging from 80 to 200°C were used in the calculation while other parameters for the reference case were kept constant. The effect of inlet sweep temperature on the required membrane area for the exit feed CO concentration of < 10 ppm is presented in Figure 6.24. Similar to the autothermal reforming syngas, the required hollow fiber number decreased significantly as the inlet sweep temperature increased, and a minimal value existed at ~ 170°C. As shown in Figure 6.25, the higher inlet sweep temperature increased feed-side temperature significantly over most of the reactor length, which increased the WGS reaction rate. When the inlet sweep temperature exceeded about 170°C, the WGS reaction equilibrium became less favorable, and the overall system became more mass transfer controlled. Hence, more membrane area was needed to reduce the feed exit CO concentration to less than 10 ppm.
6.4.2.7 Effect of Feed-Side Pressure

The feed-side pressure of 1, 2, 3, 4, 5, and 6 atm were used in the calculation while the other parameters for the reference case were kept constant. Figure 6.26 demonstrates the required membrane area for different feed-side pressures. Similar to the autothermal reforming syngas, the required hollow fiber number decreased significantly as the feed pressure increased. A higher feed pressure enhanced the CO\textsubscript{2} permeation and also increased the WGS reaction rate as the concentration for gas components increased.

6.4.2.8 Effect of Feed Inlet CO Concentration

To investigate the effect of CO concentration on the performance of membrane reactor, steam reforming syngases with feed inlet CO concentration of 5% and 10% were used in the calculation. The complete gas compositions are shown in Table 6.1. The feed-side CO mole fraction profiles are illustrated in Figure 6.27. The hollow fiber number requirement for 5% and 10% CO syngases were 31,000 and 31,500, respectively. As explained earlier, a higher CO amount in the feed gas needed more reactor volume to convert CO completely, but also generated more WGS reaction heat in the adiabatic module and increased feed-side temperature. The balance between the two opposite effects resulted in similar membrane area requirements for three syngases with different CO concentrations.
6.4.2.9 Effect of Catalyst Activity

Figure 6.28 illustrates the effect of catalyst activity on the required membrane area to satisfy the constraint of feed exit CO concentration. As illustrated in this figure, the membrane area required decreased significantly with the improved catalyst activity, a similar trend to the autothermal reforming syngas. As explained earlier, a higher catalyst activity increased the WGS reaction rate and enhanced the CO$_2$ permeation because of a higher driving force. Therefore, the higher catalyst activity resulted in a small amount of catalyst or a small reactor size.

6.4.3 Membrane Reactor Results

After the catalyst activation, the syngas feed containing 1% CO, 17% CO$_2$, 45% H$_2$, 37% N$_2$ (on the dry basis) was admitted into the membrane reactor. Water was pumped into both sides. For the rectangular membrane reactor experiments, the water concentration of the feed stream was between 40 to 50%, while the water concentration of the sweep steam was kept at 93%. The flow rates of the feed and sweep streams were kept at 1/1 ratio on the dry basis. The actual flow rate ratio of the sweep to the feed was about 8/1, if steam was taken into account. The operating temperature was 150°C, and the feed pressure of the syngas was 2.0 atm.

Figure 6.29 shows the results obtained from this rectangular WGS membrane reactor. As shown in this figure, the CO concentration in the retentate was less than 10 ppm (on the dry basis), for the various feed flow rates of the syngas from 20 to 70 cc/min.
As the feed flow rate increased, the retentate CO concentration increased slightly owing to the reduced residence time. Meanwhile, the H\textsubscript{2} lost due to its permeation through the membrane was very small. Due to the removal of CO\textsubscript{2} and conversion of CO, a H\textsubscript{2} concentration of greater than about 50% was achieved in the retentate. The modeling results are shown by the solid line in the same plot. As also shown in this figure, the data agreed well with the prediction by the isothermal mathematical model described earlier based on the material balances, membrane permeation, and the WGS reaction kinetics for the Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst. In this calculation, we assumed that the membrane had a CO\textsubscript{2} permeability of 6,500 Barrers, a CO\textsubscript{2}/H\textsubscript{2} selectivity of 80, and negligible N\textsubscript{2} and CO permeation, which were reasonable based on the experimental results. The agreement between the experimental data and the modeling prediction also proved the accuracy of the modeling assumptions.

6.5 CONCLUDING REMARKS

The CO\textsubscript{2}-selective WGS membrane reactor was proposed to decrease CO concentration in reforming syngases and obtain high-purity H\textsubscript{2} products. A one-dimensional non-isothermal model was developed to simulate the countercurrent hollow-fiber membrane reactor. Based on the modeling study, a CO concentration of less than 10 ppm, a H\textsubscript{2} recovery of greater than 97%, and a H\textsubscript{2} concentration of greater than 54% (on the dry basis) are achievable from autothermal reforming syngas. If steam reforming syngas is fed into the membrane reactor, a H\textsubscript{2} concentration of greater than 99.6% can be obtained along with a reduced membrane area requirement. Both autothermal reforming
and steam reforming syngases showed similar trends with respect to seven system parameters, \( \text{CO}_2/\text{H}_2 \) selectivity, \( \text{CO}_2 \) permeability, sweep-to-feed ratio, inlet feed temperature, inlet sweep temperature, WGS catalyst activity, and CO inlet feed concentration. As the \( \text{CO}_2/\text{H}_2 \) selectivity increased, the recovery of \( \text{H}_2 \) increased, without affecting the membrane area requirement and the low CO attainment significantly. Higher membrane permeability resulted in the reduction of the required membrane area. Increasing sweep-to-feed ratio enhanced the permeation driving force but decreased the feed side temperature and thus the reaction rate, resulting in a net effect balanced between them and an optimal ratio of about 1. As the inlet feed temperature increased, the membrane area requirement decreased. The increase of inlet sweep temperature resulted in more significant reduction of the required membrane area because feed-side temperature was shifted over a longer reactor length. However, overly high temperatures would be unfavorable to the exothermic and reversible WGS reaction. Increasing catalyst activity made the WGS reaction faster and enhanced the permeation driving force. Therefore, both the WGS reaction rate and the \( \text{CO}_2 \) permeation played an important role on the overall reactor performance. The modeling study showed that the \( \text{CO}_2 \)-selective membrane reactor could be used for syngases with high CO concentrations. A rectangular membrane cell was used to conduct the \( \text{CO}_2 \)-selective WGS membrane reactor experiments. By removing \( \text{CO}_2 \), the reversible WGS was shifted forward so that the CO concentration was significantly decreased to less than 10 ppm. The modeling results based on the experimental conditions agreed well with the experimental data.
<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>H₂O</th>
<th>H₂</th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Autothermal reforming</td>
<td>1%</td>
<td>9.5%</td>
<td>41%</td>
<td>15%</td>
<td>33.5%</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>13.5%</td>
<td>37%</td>
<td>11%</td>
<td>33.5%</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>18.5%</td>
<td>32%</td>
<td>6%</td>
<td>33.5%</td>
<td>0%</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>1%</td>
<td>18.2%</td>
<td>65.1%</td>
<td>15.5%</td>
<td>0%</td>
<td>0.2%</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>22.2%</td>
<td>61.1%</td>
<td>11.5%</td>
<td>0%</td>
<td>0.2%</td>
</tr>
<tr>
<td></td>
<td>10%</td>
<td>27.2%</td>
<td>56.1%</td>
<td>6.5%</td>
<td>0%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

Table 6.1. The compositions of autothermal reforming syngas and steam reforming syngas.
Figure 6.1. Schematic of water-gas-shift hollow-fiber membrane reactor.
Figure 6.2. Cross-section schematic of the water-gas-shift membrane reactor.
Figure 6.3. Feed-side CO and CO$_2$ mole fraction profiles along the length of membrane reactor for autothermal reforming syngas.
Figure 6.4. Feed-side H₂ mole fraction profiles along the length of membrane reactor for autothermal reforming syngas.
Figure 6.5. Feed-side and sweep-side temperature profiles along the length of membrane reactor for autothermal reforming syngas.
Figure 6.6. The effects of CO$_2$/H$_2$ selectivity on feed-side exit CO concentration and H$_2$ recovery for autothermal reforming syngas.
Figure 6.7. The effect of CO$_2$ permeability on required membrane area for autothermal reforming syngas.
Figure 6.8. The effects of sweep-to-feed ratio on feed-side exit CO concentration and H₂ recovery for autothermal reforming syngas.
Figure 6.9. The effect of inlet feed temperature on required membrane area for autothermal reforming syngas.
Figure 6.10. Feed-side temperature profiles along the length of membrane reactor for autothermal reforming syngas with different inlet feed temperatures.
Figure 6.11. The effect of inlet sweep temperature on required membrane area for autothermal reforming syngas.
Figure 6.12. Feed-side temperature profiles along the length of membrane reactor for autothermal reforming syngas with different inlet sweep temperatures.
Figure 6.13. The effect of feed-side pressure on required membrane area for autothermal reforming syngas.
Figure 6.14. Feed-side CO mole fraction profiles along the length of membrane reactor for autothermal reforming syngas with different inlet feed CO temperatures.
Figure 6.15. The effect of catalyst activity on required membrane area for autothermal reforming syngas.
Figure 6.16. Feed-side CO and CO$_2$ mole fraction profiles along the length of membrane reactor for steam reforming syngas.
Figure 6.17. Feed-side H₂ mole fraction profiles along the length of membrane reactor for steam reforming syngas.
Figure 6.18. Feed-side and sweep-side temperature profiles along the length of membrane reactor for steam reforming syngas.
Figure 6.19. The effects of CO$_2$/H$_2$ selectivity on feed-side exit CO concentration and H$_2$ recovery for steam reforming syngas.
Figure 6.20. The effect of CO$_2$ permeability on required membrane area for steam reforming syngas.
Figure 6.21. The effects of sweep-to-feed ratio on feed-side exit CO concentration and H$_2$ recovery for steam reforming syngas.
Figure 6.22. The effect of inlet feed temperature on required membrane area for steam reforming syngas.
Figure 6.23. Feed-side temperature profiles along the length of membrane reactor for steam reforming syngas with different inlet feed temperatures.
Figure 6.24. The effect of inlet sweep temperature on required membrane area for steam reforming syngas.
Figure 6.25. Feed-side temperature profiles along the length of membrane reactor for steam reforming syngas with different inlet sweep temperatures.
Figure 6.26. The effect of feed-side pressure on required membrane area for steam reforming syngas.
Figure 6.27. Feed-side CO mole fraction profiles along the length of membrane reactor for steam reforming syngas with different inlet feed CO temperatures.
Figure 6.28. The effect of catalyst activity on required membrane area for steam reforming syngas.
Figure 6.29. Retentate CO concentration vs. feed flow rate in the rectangular WGS membrane reactor. (Feed gas: 1% CO, 17% CO₂, 45% H₂, 37% N₂, T = 150°C, p_f = 2.0 atm, p_s = 1.0 atm, feed/sweep flow rates = 1/1 (on dry basis), average membrane thickness = 53 μm)
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CO₂ (H₂S)-SELECTIVE POLYMERIC MEMBRANES AND APPLICATIONS

Polymeric membranes containing amino groups with high CO₂ permeabilities and high CO₂/H₂ and CO₂/N₂ selectivities have been synthesized. With the increase of temperature from 100 to 170°C, transport properties of the membrane increased first due to the higher CO₂-amine reaction rate and lower H₂ and N₂ solubility, and then dropped because of the reduction of the water retention in the membrane at high temperatures. Membranes showed a CO₂ permeability of above 2000 Barrers, a CO₂/H₂ selectivity of greater than 40, and a CO₂/N₂ selectivity of greater than 200 at 100 – 150°C. In addition, these membranes showed very high H₂S permeability and selectivity. The H₂S permeability and H₂S selectivity to H₂ were about three times those for CO₂. With a circular permeation cell having a membrane area of 45.6 cm², H₂S was efficiently removed from 50 ppm to less than 100 ppb at a gas hourly space velocity of ~ 5800 hr⁻¹.

The membrane-based CO₂ capture using a new facilitated transport CO₂-selective membrane was studied. The membrane synthesized containing free polyallylamine and
AIBA-K as the amine carriers in the crosslinked PVA network showed good CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity up to 170°C. The highest CO<sub>2</sub>/N<sub>2</sub> selectivity of 493 and the highest CO<sub>2</sub> permeability of 6196 Barrers were observed at 110°C. With a larger effective membrane area of 342.70 cm<sup>2</sup>, CO<sub>2</sub> in the retentate was removed from 17% to about 100 ppm at a feed gas flow rate of 60 ml/min and to about 1,000 ppm at 120 ml/min. The experimental data agreed well with the modeling results. In the CO<sub>2</sub> capture experiments, the permeate CO<sub>2</sub> dry concentration of greater than 98% was achieved by using steam as the sweep gas. Also studied were the effects of inlet feed flow rate and sweep-to-feed ratio on the separation performance. As the feed flow rate increased, the permeate CO<sub>2</sub> dry concentration slightly increased, and the CO<sub>2</sub> recovery decreased owing to the reduced residence time. Increasing sweep-to-feed ratio enhanced the permeation driving force and resulted in the higher CO<sub>2</sub> recovery, while the permeate CO<sub>2</sub> dry concentration did not change significantly.

A one-dimensional isothermal model to evaluate the separation performance of a hollow fiber module composed of the described CO<sub>2</sub>-selective membrane was developed. From the modeling results, a 2-ft hollow fiber module containing 980,000 fibers was sufficient to recover above 95% of CO<sub>2</sub> and obtain a permeate CO<sub>2</sub> concentration of larger than 98% (on the dry basis) from a 1000 SCFM or 21.06 mol/s flue gas stream containing 9% CO<sub>2</sub>.

CO<sub>2</sub> (H<sub>2</sub>S)-selective facilitated transport membranes were synthesized for the acid gas removal from natural gas. For dense free-standing membranes, the CO<sub>2</sub> permeability of greater than 440 Barrer and the CO<sub>2</sub>/CH<sub>4</sub> selectivity of higher than 135 were achieved at a feed pressure of 150 psia, or a CO<sub>2</sub> partial pressure of 75 psia. Under a feed pressure
of 500 psia, or a CO$_2$ partial pressure of 250 psia, the permeability and selectivity obtained were 88.8 Barrers and 30.6, respectively. With the increase of feed pressure, CO$_2$ permeability and selectivity properties reduced due to the carrier saturation and the reduction of water retention in the membrane. The temperature of 106°C was found to be optimal for the membrane performance due to the high reaction rates of CO$_2$ with amine carriers and the low CH$_4$ solubility in the membrane. Increasing permeate pressure improved the CO$_2$ permeability by deterring the water transfer through the membrane but decreased the selectivity. High-flux membranes were attempted with the efforts to prepare the thin-film composite membrane and the asymmetric membrane. By using a microporous polysulfone support, thin-film composite membranes with a very thin selective layer were successfully synthesized. The decrease of the selective layer thickness significantly improved the CO$_2$ flux due to the decrease of diffusion resistance within the membrane. The permeability and selectivity for H$_2$S were 2 – 3 times those for CO$_2$. Also the membrane could maintain high H$_2$S flux in a wider temperature range, e.g., 85 – 106°C. Asymmetric membranes with a thin selective toplayer and a thick porous support layer were prepared via the phase inversion process. However, they did not show a higher CO$_2$ flux than the dense membranes with the similar total thickness. A probable reason was that the operating temperature were too high (higher than the glass transition temperature of PVA) to maintain the integrity of the porous structure.

The hybrid organic-inorganic membranes were prepared by incorporating silica derived from alkoxy silanes into the PVA polymer matrix. The hybrid membrane demonstrated better thermal stability than the PVA membrane without the inorganic phase. Even though the PVA membrane performed better at relative low temperature, the
hybrid membrane showed higher lower CO₂ transport properties at temperatures higher than 160°C. CO₂/H₂ selectivity of larger than 10 was obtained at 180°C. The decent high-temperature performance is very important for CO₂-selective WGS membrane reactor. Segmented polyimide copolymers were synthesized by a two-step procedure. The permeation experiments showed that these membranes followed the solution-diffusion mechanism. There existed a tradeoff between permeability and selectivity with the increase of temperature. A high relative humidity was beneficial to enhancing the affinity to CO₂ and improving CO₂ permeability. Since the membrane exhibited the selectivity mainly due to the affinity of polar soft segment to CO₂, the polymer molecular structure had significant effects on the membrane performance. With the increase of the length or the weight percentage of soft segment in the whole copolymer chain, CO₂ transport properties were enhanced considerably. On the other hand, the soft segment containing ether moieties illustrated better performance than the soft segment consisting of ester moieties, which could be explained by the higher polarity for the ether moieties.

The CO₂-selective WGS membrane reactor was proposed to decrease CO concentration in reforming syngases and obtain high-purity H₂ products. A one-dimensional non-isothermal model was developed to simulate the countercurrent hollow-fiber membrane reactor. Based on the modeling study, a CO concentration of less than 10 ppm, a H₂ recovery of greater than 97%, and a H₂ concentration of greater than 54% (on the dry basis) are achievable from autothermal reforming syngas. If steam reforming syngas is fed into the membrane reactor, a H₂ concentration of greater than 99.6% can be obtained along with a reduced membrane area requirement.
Both autothermal reforming and steam reforming syngases showed similar trends with respect to seven system parameters, CO₂/H₂ selectivity, CO₂ permeability, sweep-to-feed ratio, inlet feed temperature, inlet sweep temperature, WGS catalyst activity, and CO inlet feed concentration. As the CO₂/H₂ selectivity increased, the recovery of H₂ increased, without affecting the membrane area requirement and the low CO attainment significantly. Higher membrane permeability resulted in the reduction of the required membrane area. Increasing sweep-to-feed ratio enhanced the permeation driving force but decreased the feed side temperature and thus the reaction rate, resulting in a net effect balanced between them and an optimal ratio of about 1. As the inlet feed temperature increased, the membrane area requirement decreased. The increase of inlet sweep temperature resulted in more significant reduction of the required membrane area because feed-side temperature was shifted over a longer reactor length. However, overly high temperatures would be unfavorable to the exothermic and reversible WGS reaction. Increasing catalyst activity made the WGS reaction faster and enhanced the permeation driving force. Therefore, both the WGS reaction rate and the CO₂ permeation played an important role on the overall reactor performance. The modeling study showed that the CO₂-selective membrane reactor could be used for syngases with high CO concentrations. A rectangular membrane cell was used to conduct the CO₂-selective WGS membrane reactor experiments. By removing CO₂, the reversible WGS was shifted forward so that the CO concentration was significantly decreased to less than 10 ppm. The modeling results based on the experimental conditions agreed well with the experimental data.
7.2 RECOMMENDATIONS FOR FUTURE WORK

The CO₂ (H₂S)-selective membranes prepared demonstrated good transport properties and showed the right direction on the development of the facilitated transport membranes. To further improve the membrane performance, the future research should be carried out on both polymeric matrix and amine carrier aspects.

Even though cross-linked PVA has proven to be an excellent hydrophilic matrix, it still has some issues under severe working conditions, such as high-temperature or high-pressure applications. Therefore, a more stable polymeric matrix should be researched and studied. Potential candidates include modified polybenzimidazole, segmented polyimide copolymer, and hybrid organic-inorganic material.

A membrane is defined by what it does instead of what it is. It has become apparent that the selection of suitable amine carriers is highly dependent on the real application. To maximize the CO₂ transport properties, an amine system with higher loading capacity, such as sterically hindered amines, would be preferred. Because of faster reaction rate between H₂S and amine carriers, the membranes synthesized have shown a wider operating temperature window for H₂S than CO₂. In other words, the membrane can be used for H₂S separation at lower temperatures. Therefore, more reactive amines with suitable volatility may be chosen for the effective H₂S removal without sacrificing the membrane stability.

As for the membrane structure, efforts should be made to synthesize even thinner based on the thin-film composite membrane. Asymmetric membranes did not demonstrate better transport properties than the dense membrane with the similar
thickness at the temperature above 100°C. However, since the membrane could show good transport properties for H₂S at relatively low temperature, these membranes may be able to demonstrate the advantage of asymmetric structure for H₂S removal.

The future modeling study may focus on developing the reaction and transport model based on another commercial membrane module, the spiral-wound membrane module. Spiral-wound modules are constructed by sealing two membrane sheets together at three edges to form a membrane leaf, which is wrapped around a collection tube. Compared with hollow-fiber modules, spiral-wound modules may be easier to incorporate catalyst particles because of their flat membrane structure. The WGS membrane reactor would be configured to be a spiral-wound membrane module with catalyst particles placed inside the membrane leaves. In general, spiral wound module can be treated as an extended membrane leaf as shown in Figure 7.1. Therefore, a two-dimensional, non-isothermal model will be developed based on moral and energy balances on the volume element of Δx*Δy.
Figure 7.1. Extended membrane leaf of a spiral-wound WGS membrane reactor.

Acres, G. J. K. (2001), Recent advances in fuel cell technology and its applications, *J. Power Sources* 100, 60.


Quinn, R., Appleby, J. B., and Pez, G. P. (1995), New facilitated transport membranes for
the separation of carbon dioxide from hydrogen and methane, J. Membr. Sci. 104,
139.

Quinn, R., and Laciak, D. V. (1997), Polyelectrolyte membranes for acid gas separations,
J. Membr. Sci. 131, 49.

Quinn, R., Laciak, D. V., and Pez, G. P. (1997), Polyelectrolyte-salt blend membranes for

the mechanistic boundary, Catal. Today, 23, 43.

Robeson, L. M. (1991), Correlation of separation factor versus permeability for

Salmi, T., and Hakkarainen, R. (1989), Kinetic study of low-temperature water-gas shift

Sanchez, C., Julian, B., Belleville, P., and Popall, Michael. (2005), Applications of hybrid
organic-inorganic nanocomposites, J. Mater. Chem. 15, 3559.


Sartori, G., Ho, W. S. W., Savage, D. W., Chludzinski, G. R., and Wiechert, S. (1987),

Smith, J. M., Van Ness, H. C., and Abbott, M. M. Introduction to Chemical Engineering

Spillman, R. W. (1989), Economics of gas separation membranes, Chem. Eng. Prog. 85,
41.

Shulik, L. J., Sartori, G., Ho, W. S. W., Thaler, W. A., Milliman, G. E., and Wilbur, J. C.
Technol. 31, 1663.

Tabakova, T., Boccuzzi, F., Manzoli, M., Sobczak, J. W., Idakiev, V., and Andreeva, D.
(2004), Effect of synthesis procedure on the low-temperature WGS activity of

Tabe-Mohammadi, A. (1999), A review of the applications of membrane separation


Zou, J., and Ho, W. S. W. CO$_2$-selective polymeric membranes containing amines in crosslinked poly(vinyl alcohol). Accepted by *J. Membr. Sci.* 2006.