

EFFECT OF CO₂-INDUCED PLASTICIZATION AND MEMBRANE
CONFIGURATION ON THE PERFORMANCE OF ASYMMETRIC
POLYSULFONE HOLLOW FIBER MEMBRANE FOR
CO₂/CH₄ GAS SEPARATION

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To my beloved parents

(Encik Yaacob bin Awang Ahmad and Puan Kartini binti Roseley),

My husband

(Nur Shamriman bin Abdul Rahman)

And my siblings

(Yusnaini Yaacob and Muhammad Akmal Yaacob)

Who gave me inspiration, encouragement and valuable support
toward the success of this study.

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ABSTRACT

The present study focuses on the effect of CO₂-plasticization and membrane configuration on the performance of asymmetric polysulfone hollow fiber membrane for CO₂/CH₄ separation. Heat treatment method to suppress plasticization effect and membrane module configurations in series and cascades arrangement for the CO₂/CH₄ gas separation was investigated. The membranes were prepared using polysulfone (Udel P1700) and tested using pure CO₂ and CH₄ and CO₂/CH₄ gas mixture. Gas permeation experiments were conducted for single, two and three-stage configurations. The produced membranes were characterized by pure gas permeation experiments, density measurement, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). In pure gas permeation experiment for both untreated and treated membranes, the pressure-normalized flux of CO₂ decreases with increasing of the membrane stages. In addition, the selectivities of the asymmetric polysulfone hollow fiber membrane showed a more constant trend with increasing feed pressure. Treated membrane exhibited lower pressure-normalized flux than untreated membranes due to skin layer densification which increases the gas transport resistance which lead to the reduction in the CO₂ pressure-normalized flux values. Among all configurations studied, two-stage series configuration showed the most constant trend of selectivity values. The selectivity is slightly below the intrinsic selectivity. However, three-stage cascade configuration produced the highest CO₂/CH₄ selectivity especially when tested at low feed pressure range. Some of the selectivity even surpasses the intrinsic selectivity of polysulfone. Effect of stage cut on feed pressure showed an increasing trend with increasing of CO₂ and CH₄ feed pressure in all configurations. This is due to the increase of the permeation driving force, which causes the passage of larger amounts of more permeable gas through the membrane. This study showed that, three-stage cascade configuration exhibited the smallest stage cut values than other module configurations. Hence, cascade configuration produces higher purity of CO₂ in the permeate stream. In mixed gas permeation experiment, increasing trend of CO₂ pressure-normalized flux was also observed but exhibited lower value due to competition among the penetrant species. As a result, the selectivity and the stage cut achieved are also lower in values. As a conclusion, the results of this work served as a platform in determining the most suitable module configuration to be used for gas separation processes.

ABSTRAK

Fokus utama kajian ini adalah ke atas kesan pemplastikan teraruh CO_2 dan konfigurasi membran terhadap prestasi membran gentian geronggang asimetrik polisulfona bagi pemisahan gas CO_2/CH_4 . Kaedah rawatan pemanasan untuk merencat kesan pemplastikan dan modul konfigurasi membran secara bersiri dan menirus untuk pemisahan gas CO_2/CH_4 turut dikaji. Membran disediakan menggunakan polisulfona (Udel P1700) dan diuji menggunakan gas tulen CO_2 dan CH_4 serta campuran gas CO_2/CH_4 . Ujikaji penelapan gas dijalankan untuk konfigurasi satu, dua dan tiga tahap. Membran yang dihasilkan diciri dengan ujian penelapan gas, pengukuran ketumpatan, Mikroskop Elektron Imbasan (SEM), Permeteran Kalori Pengimbasan Kebezaan (DSC) dan Analisis Termogravimetrik (TGA). Dalam ujian penelapan gas tulen bagi kedua-dua membran yang tidak dirawat dan yang dirawat, fluk tekanan ternormal CO_2 menurun dengan peningkatan bilangan membran. Tambahan pula, kememilihan membran gentian geronggang asimetrik polisulfona menunjukkan keadaan tetap dengan peningkatan tekanan masukan. Membran yang dirawat menunjukkan penurunan dalam fluk tekanan ternormal berbanding membran yang tidak dirawat disebabkan penebalan lapisan kulit membran yang meningkatkan rintangan pengangkutan gas yang membawa kepada penurunan nilai fluk tekanan ternormal CO_2 . Di antara kesemua konfigurasi, konfigurasi dua tahap secara bersiri menunjukkan nilai kememilihan yang paling tetap. Kememilihan yang terhasil adalah sedikit rendah berbanding kememilihan intrinsik polisulfona. Walaubagaimanapun, konfigurasi tiga tahap secara menirus menunjukkan kememilihan CO_2/CH_4 yang tertinggi terutamanya apabila diuji pada julat tekanan masukan yang rendah. Terdapat juga kememilihan yang mengatasi kememilihan intrinsik polisulfona. Kesan keratan aras ke atas tekanan masukan meningkat dengan peningkatan tekanan masukan CO_2 dan CH_4 dalam semua konfigurasi. Ini adalah disebabkan peningkatan daya peresapan yang menyebabkan sejumlah besar gas yang mudah meresap merentasi membran. Kajian ini menunjukkan yang konfigurasi tiga-tahap secara menirus menunjukkan nilai keratan aras yang terkecil berbanding konfigurasi yang lain. Oleh itu, konfigurasi menirus menghasilkan ketulenan CO_2 yang tinggi dalam aliran peresapan. Bagi ujikaji gas campuran, fluk tekanan ternormal CO_2 didapati meningkat tetapi menunjukkan nilai yang lebih rendah disebabkan saingan di antara kumpulan gas. Hasilnya, nilai kememilihan dan keratan aras yang terhasil juga adalah rendah. Kesimpulannya, keputusan ujikaji ini bertindak sebagai satu cara untuk menentukan konfigurasi modul yang paling sesuai untuk kegunaan proses pemisahan gas.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE PAGE	i
	DECLARATION	ii
	DEDICATIONS	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SYMBOLS	xviii
	LIST OF APPENDICES	xxi
1	INTRODUCTION	
	1.1 Membrane for Gas Separation	1
	1.2 Problem Statement	5
	1.3 Research Objectives	6
	1.4 Scope of Thesis	7
2	LITERATURE REVIEW	
	2.1 Membrane Process for Gas Separation	8
	2.1.1 Membrane Gas Separation System	9
	2.1.2 Advantages of Membrane Technology	11
	2.1.3 Configurations of Membrane	12
	2.1.4 Polymeric Membranes	19

2.2	Gas Transport Mechanism in Polymers	24
2.2.1	Solution-Diffusion Model	29
2.2.2	Dual-Mode Sorption Model	31
2.2.3	Molecular Model	34
2.3	Asymmetric Membrane Formation	36
2.3.1	Phase Inversion Process	36
2.3.2	Dry/Wet Phase Inversion	40
2.3.2.1	Dry Phase Separation	42
2.3.2.2	Wet Phase Separation	43
2.4	Gas Polymer Interactions	43
2.5	CO ₂ -Induced Plasticization on the Properties of Glassy Polymers	46
2.5.1	Plasticization in Dense Membranes	51
2.5.2	Plasticization in Asymmetric Membrane Films	55
2.5.3	Plasticization in Asymmetric Hollow Fiber Membranes	57
2.6	Glass Transition Temperature, T _g	59
2.7	Suppression of CO ₂ -Plasticization	60
2.7.1	Cross-Linking Method	61
2.7.2	Heat Treatment Method	62
2.7.3	Blending Method	64
3	METHODOLOGY	
3.1	Research Design	67
3.2	Materials Selections	68
3.2.1	Polysulfone	68
3.2.2	Solvents	69
3.2.3	Gases	70
3.3	Fabrication of Asymmetric Hollow Fiber Membrane	70
3.3.1	Turbidimetric Titration Method	70
3.3.2	Preparation of Multi Component Polymer Dope	71
3.3.3	Membrane Fabrication using Dry/Wet Spinning Process	72

3.3.4	Hollow Fiber Coating	75
3.3.5	Hollow Fiber Potting	75
3.4	Characterization	76
3.4.1	Pure Gas Permeation Measurements	76
3.4.2	Membrane Configuration Use	83
3.4.3	Network Model	89
3.4.4	Heat Treatment	90
3.4.5	Density Measurements	90
3.4.6	Differential Scanning Calorimetry (DSC)	91
3.4.7	Scanning Electron Microscopy (SEM)	91
3.4.8	Thermogravimetric Analysis (TGA)	92
4	RESULT AND DISSCUSSION	
4.1	Spinning Solution Formulation	94
4.2	Pure Gas Carbon Dioxide and Methane Permeation Behavior in Untreated and Treated Membranes	95
4.3	Mixed Gas Carbon Dioxide and Methane Permeation Behavior in Untreated and Treated Membranes	111
4.4	Effect of Heat Treatment on Fiber Density	137
4.5	Effect of Heat Treatment Process on the Polymer Glass Transition Temperature	138
4.6	Morphology of the Develop Membrane Before and After Heat Treatment Process	140
4.7	Effect of Membrane Weight Loss upon Heat Treatment Process	143
5	CONCLUSIONS AND RECOMMENDATIONS	145
	LIST OF PUBLICATIONS	148
	REFFERENCES	149
	Appendices A-G	159-236

LIST OF TABLES

TABLE NO.	TITLE	PAGE
1.1	Principal gas separation markets, producers and membrane systems	2
1.2	Predicted sales of membrane gas separation in the main target market	3
2.1	Characteristics of different module types	13
2.2	Kinetics sieving dimensions of penetrants based on zeolite sorption cutoff	20
2.3	Summary of types of heat treatment used by previous researchers	65
2.4	Significant suppression methods for gas-plasticization	66
3.1	Summary of spinning conditions	74
3.2	Properties of carbon dioxide and methane	78
4.1	Summary of the solution composition before and after titration	94
4.2	Selectivity comparison of untreated asymmetric polysulfone hollow fibers in series and cascade configurations	105
4.3	Fiber density of untreated and treated asymmetric polysulfone hollow fiber membrane	137

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Typical membrane process for gas separation	9
2.2	Shell side feed hollow fiber module	14
2.3	Spiral wound membrane module	15
2.4	Schematic illustration of the structure of integrally skinned asymmetric membranes	21
2.5	Schematic presentation of mechanism for permeation of gases through membranes	22
2.6	Typical gas sorption isotherm forms for polymeric media	25
2.7	Polymer specific volume as a function of temperature	25
2.8	Solution-diffusion model	31
2.9	Models for the transport of small penetrant molecules in polymers	35
2.10	Schematic phase diagram for ternary consisting of polymer/solvent/nonsolvent	37
2.11	Phase separation by instantaneous and delayed demixing of a polymer solution in a ternary system	39
2.12	Schematic phase diagram for quaternary system consisting of polymer/solvent/nonsolvent/additive	40
2.13	Correlation between the solubility parameter of glassy polymers and the ideal separation factors for CO ₂ /CH ₄ systems	45
2.14	CO ₂ permeation behavior in glassy polymer	48
3.1	Steps of the research	67
3.2	The chemical structure of polysulfone (PSF)	69

3.3	Apparatus for turbidimetric titration	70
3.4	Apparatus for polymer dope preparation	72
3.5	The laboratory scale for dry/wet spinning process	73
3.6	Hollow fiber potting	76
3.7	Schematic diagram of gas permeation testing system	77
3.8	Typical schematic diagram of the membrane module configuration arrangement	84
3.9	Single-stage module configuration	86
3.10	Two stage module configuration in (a) series and (b) cascade configuration	86
3.11	Three-stage module configuration in (a) series and (b) cascade configuration	88
4.1	Pressure-normalized flux of CO ₂ and CH ₄ of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressures	98
4.2	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric hollow fiber membrane in single-stage configuration as a function of feed pressures	98
4.3	Pressure-normalized flux of CO ₂ and CH ₄ of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressures	100
4.4	CO ₂ /CH ₄ selectivity of the untreated and treated asymmetric hollow fiber membrane in two-stage series configuration as a function of feed pressures	100
4.5	Pressure-normalized flux of CO ₂ and CH ₄ of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure	102
4.6	Pressure-normalized flux of CO ₂ and CH ₄ of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure	102

4.7	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure	104
4.8	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure	104
4.9	Effect of stage cut on feed pressure in single-stage configuration of untreated and treated membrane (a) CO ₂ and (b) CH ₄	106
4.10	Effect of stage cut on feed pressure in two-stage series configuration untreated and treated membrane (a) CO ₂ and (b) CH ₄	108
4.11	Effect of stage cut on feed pressure in three-stage series configuration untreated and treated membrane (a) CO ₂ and (b) CH ₄	109
4.12	Effect of stage cut on feed pressure in three-stage cascade configuration untreated and treated membrane (a) CO ₂ and (b) CH ₄	110
4.13	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressure at 10 LPM	112
4.14	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressure at 20 LPM	112
4.15	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressure at 30 LPM	113
4.16	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressure at 10 LPM	114
4.17	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressure at 20 LPM	114
4.18	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in single-stage configuration as a function of the feed pressure at 30 LPM	115

4.19	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in single-stage configuration of untreated and treated membrane at 10 LPM	116
4.20	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in single-stage configuration of untreated and treated membrane at 20 LPM	116
4.21	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in single-stage configuration of untreated and treated membrane at 30 LPM	117
4.22	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressure at 10 LPM	118
4.23	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressure at 20 LPM	118
4.24	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressure at 30 LPM	119
4.25	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressure at 10 LPM	120
4.26	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressure at 20 LPM	120
4.27	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in two-stage series configuration as a function of the feed pressure at 30 LPM	121
4.28	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in two-stage series configuration of untreated and treated membrane at 10 LPM	122
4.29	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in two-stage series configuration of untreated and treated membrane at 20 LPM	122
4.30	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in two-stage series configuration of untreated and treated membrane at 30 LPM	123

4.31	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure at 10 LPM	125
4.32	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure at 20 LPM	125
4.33	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure at 30 LPM	126
4.34	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure at 10 LPM	127
4.35	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure at 20 LPM	127
4.36	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage series configuration as a function of the feed pressure at 30 LPM	128
4.37	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in three-stage series configuration of untreated and treated membrane at 10 LPM	129
4.38	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in three-stage series configuration of untreated and treated membrane at 20 LPM	129
4.39	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in three-stage series configuration of untreated and treated membrane at 30 LPM	130
4.40	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure at 10 LPM	131
4.41	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure at 20 LPM	131

4.42	Pressure-normalized flux of CO ₂ /CH ₄ gas mixture of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure at 30 LPM	132
4.43	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure at 10 LPM	133
4.44	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure at 20 LPM	133
4.45	CO ₂ /CH ₄ selectivity of untreated and treated asymmetric polysulfone hollow fiber membrane in three-stage cascades configuration as a function of the feed pressure at 30 LPM	134
4.46	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in three-stage cascades configuration of untreated and treated membrane at 10 LPM	135
4.47	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in three-stage cascades configuration of untreated and treated membrane at 20 LPM	135
4.48	Effect of CO ₂ /CH ₄ gas mixture stage cut on feed pressure in three-stage cascades configuration of untreated and treated membrane at 30 LPM	136
4.49	Fiber density of the untreated and treated asymmetric polysulfone hollow fiber membrane	138
4.50	Effect of heat treatment on the glass transition temperature of asymmetric polysulfone hollow fiber membrane	139
4.51	Scanning electron microscopy pictures of asymmetric polysulfone hollow fiber membrane before and after different heat treatments. Left: partial cross section of membrane, right: skin surface (x250). (a1 and a2: untreated membrane, b1 and b2: treated membrane at 70°C for 2 min, c1 and c2: treated membrane at 70°C for 5 min)	141
4.52	Scanning electron microscopy pictures of asymmetric polysulfone hollow fiber membrane before and after different heat treatments. Left: partial cross section of membrane, right: skin surface (x500). (d1 and d2: untreated membrane, e1 and e2: treated membrane at 70°C for 2 min, f1 and f2: treated membrane at 70°C for 5 min)	142

4.53	Thermogravimetric analysis of asymmetric polysulfone hollow fiber membranes at different heat treatments	144
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LIST OF SYMBOLS

A	-	Membrane surface area (cm^2)
A_1	-	Effective surface area of dense skin region
A_2	-	Porous surface area
b	-	Hole affinity constant, atm^{-1}
C	-	Solubility, cc (STP)/ cc polymer
C_A	-	Concentration of component A
C_D	-	Henry's law isotherm
C_H	-	Langmuir's isotherm
C_H'	-	Hole saturation constant, cc (STP)/cc polym
d	-	Average pore diameter
$d\mu_i/dx$	-	Gradient in chemical potential of component i
D_A	-	Diffusion coefficient
J_i	-	Flux of component i
J_{vi}	-	Volumetric flux of i across the membrane
k_D	-	Henry's law dissolution constant, cc (STP)/cc polym atm
K_i	-	Total effective pressure-normalized flux
l	-	Thickness of active layer
l_r	-	Pore length
L	-	Thickness of the selective layer
L_i	-	Coefficient of proportionality
LPM	-	Liter per minute
m	-	Mean hydraulic radius or mean pore size
m^2/m^3	-	Surface to volume ratio unit
M	-	Molar mass (g/mol) of the monomer unit
M	-	Molecular weight (g mol^{-1})
N	-	Avogadro constant
p	-	Pressure, atm

p_A	-	External partial pressure of A
p_f	-	CO ₂ average partial pressure in the feed absolute pressures
p_r	-	CO ₂ average partial pressure in the reject absolute pressures
p_{if}	-	Partial pressure of i on the feed side of the membrane
p_{ip}	-	Partial pressure of i on the permeate side of the membrane
p_{ds}	-	Downstream pressure of the gas
p_{us}	-	Upstream pressure of the gas
\bar{p}	-	Mean pressure
P	-	Pressure-normalized flux of i in the membrane polymer
P_A	-	Pressure-normalized flux of gas A in a membrane material
P_1	-	Intrinsic pressure-normalized flux of the membrane material
P_2	-	Effective pressure-normalized flux characteristic of pore
P/l_i	-	Pressure-normalized flux
Q	-	Volumetric flow rate (cm ³ (STP) s ⁻¹ or mol s ⁻¹)
Q_i	-	Total gas flux for permeant i
Q_p	-	Permeate flow rate (cm/s)
s	-	Second
S	-	Stage cut
S_A	-	Solubility coefficient
R	-	Gas constant
T	-	Temperature (K)
T_c	-	Critical temperature
T_g	-	Glass transition temperature
\bar{v}_i	-	Mean molecular speed of permeant i
V	-	Total molar volume of the monomer unit (cm ³ /mol)
V_e	-	Equilibrium volume of densified glass
V_g	-	Actual glassy specific volume
V_w	-	Van der Waals volume
V_0	-	Volume occupied by the chains (cm ³ /mol)
wt%	-	Weight percentage
w/w	-	Weight per weight
x	-	CO ₂ mole fractions in the retentate stream
x_f	-	CO ₂ mole fractions in the feed streams

y	-	CO ₂ mole fraction in the permeate stream
α	-	Selectivity
Å	-	Angstrom
°C	-	Degree Celsius
°C/min	-	Degree Celsius per minute
δ	-	Numerical factor for a particular system
δ^-	-	Negative charge
δ^+	-	Positive charge
ρ	-	Density of the film (g/cm ³)
Δp	-	Pressure difference (bar or cmHg)
γ_i	-	Chemical potential
$\gamma_i c_i$	-	Solvent activity
µm	-	Micrometer
ρ	-	Viscosity (N s m ⁻²)
τ	-	Tortuosity factor

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Spinning Process Calculation	159
B	Pressure-Normalized Flux and Selectivity of Pure Gas	160
C	Stage Cut of Pure Gas	183
D	Experimental Results of Mixed Gas	208
E	Simulation Results of Mixed Gas	220
F	Skin Layer Thickness and Density Measurements	232
G	Differential Scanning Calorimeter	234

CHAPTER 1

INTRODUCTION

1.1 Membrane for Gas Separation

Membrane separation processes is a well-established technology. The process essentially involves contacting one side of a semi-permeable gas separation membrane with a feed gas mixture containing at least the gas whose enrichment is desired, along with one or more other gases. The membranes divide a separation chamber into a high-pressure side into which the feed gas mixture is fed at a low-pressure side. A pressure differential is maintained across the membrane under conditions such that at least one of the gases in the feed gas mixture selectively permeates through the membrane from the high-pressure side to the low-pressure side of the membrane. Then the gas mixture which is relatively enriched in the first group of gases and depleted in the second different group of gases is removed from the low-pressure side of the membrane. While, gas depleted in the first group of gases is removed from the high-pressure side of the membrane (Stern *et al.*, 1997).

The application of membranes to gas separation problems has grown rapidly since the installation of the first industrial plants in the early 1980s. Membranes have gained an important place in chemical process industries and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. Removal of CO₂ is the only natural gas separation currently practiced on a large scale (more than 200 plants have been installed). Most were installed by Grace (now Kavanaugh-GMS), Separex (UOP) and Cynara. All of these plants used

cellulose acetate membranes in hollow fiber or spiral wound module form. More recently, hollow fiber polyaramide (Medal) and polyimide (Ube) membranes have been introduced due to their higher selectivity (Baker, 2000). A list of the principal gas separation markets, producers and membrane systems is given in Table 1.1.

These market estimates are based on the new membrane equipment produced each year. Currently, only eight or nine polymer materials that are listed above are used to make at least 90% of the total installed gas separation membrane base. Plasticization problems, aging phenomena, low process ability and high cost are the main reasons why only eight to nine different polymers are used in 90% of the commercial applications (Barsema, 2003). The table shows that, to date, two thirds of the total gas separation market is in the separation of hydrogen from ammonia purge gas or syngas. These are clean gas streams, generally free of components that might foul or plasticize the membrane, which means that hollow fiber modules work well. However, the growing application areas are in natural gas treatment and in refining and petrochemical plants. The gas streams often contain high levels of plasticizing and condensable vapors, which degrade membrane performance.

Table 1.1: Principal gas separation markets, producers and membrane systems (Baker, 2000)

Company	Principal membrane material used	Module type	Principal markets/ Estimated annual sales
Permea (Air Products)	Polysulfone	Hollow fiber	Large gas companies; N ₂ /air at US\$75 million per year; and hydrogen separation at US\$25 million per year.
Medal (Air Liquide)	Polyimide/Polyaramide	Hollow fiber	
Generon (MG industries)	Tetra bromo polycarbonate	Hollow fiber	
IMS (Praxair)	Polyimide	Hollow fiber	
Kvaerner	Cellulose acetate	Spiral wound	Mostly natural gas separations at US\$30 million per year.
Separex (UOP)	Cellulose acetate	Spiral wound	
Cynara (Natco)	Cellulose acetate	Hollow fiber	
Parker-Hannifin	Polyphenylene oxide	Hollow fiber	Vapor/gas separation, air dehydration and other at US\$25 million per year
Ube	Polyimide	Hollow fiber	
GKSS Licensees	Silicone rubber	Plate and frame	
MTR	Silicone rubber	Spiral wound	

Therefore, robust membrane modules, which are able to handle ‘upsets’, are required (Baker, 2001).

Developing processes such as CO₂ separation from natural gas, Volatile Organic Compound (VOC) separation from air and nitrogen and recovery of light hydrocarbons from refinery and petrochemical plant purge gases are performed on a commercial scale and in total several hundred plants have been installed. Some predictions of the future for the membrane gas separation market are given in Table 1.2. It seems that the total market will grow, but perhaps not uniformly in all the areas that are shown. Natural gas sales have reached about USD 30 million per year and should increase rapidly, perhaps reaching USD 90 million by 2010.

CO₂ removal from natural gas has been practiced using cellulose acetate membranes for more than 10 years and the introduction of more selective polyimide membranes has begun and in time is likely to make membrane processes much more competitive with amine absorption. In the area of CO₂/CH₄ separation membranes,

Table 1.2: Predicted sales of membrane gas separation in the main target market (Baker, 2001)

Separation	Membrane market (USD million, 2,000 dollars)		
	2000	2010	2020
Nitrogen from air	75	100	125
Oxygen from air	<1	10	30
Hydrogen	25	60	150
Natural gas			
CO ₂	30	60	100
NGL	<1	20	50
N ₂ /H ₂ O	0	10	25
Vapor/nitrogen	10	30	60
Vapor/vapor	0	20	100
Other	15	30	100
Total	155	340	760

natural gas sweetening, the removal of CO₂ in landfill gas recovery processes and CO₂ removal from fractured wells as well as the removal of CO₂ in enhanced oil recovery applications (EOR) are of interest (Staudt-Bickel and Koros, 1999). CO₂ produced can be injected into adjacent oil fields to enhance oil recovery (Lonsdale, 1982). In order to achieve excellent performance in membrane processes, the process reliability needs to be enhanced to make CO₂ removal technology the ultimate choice in a variety of processing conditions. It is crucial to transport the field gas through the conventional pipeline without catastrophic corrosion problems. Hence, an efficient method to reduce the composition of CO₂ gas is critically in need and membrane gas separation processes was found to be the best solution.

Nowadays, there are wide varieties of acid gas removal technologies available. Membrane separation processes have been shown to be very effective for natural gas processing. An efficient separation of CO₂ and hydrogen sulfide from natural gas can be achieved by selective permeation through polymer membranes (Lee *et al.*, 1995). However, membrane technologies have been chosen for applications that have large flows, have high CO₂ contents or are in remote areas. The removal of CO₂ from off gas and reinjection into the oil field is desirable but the recycle gas must have a CO₂ purity of at least 95%. This minimum level is necessary in order to maintain the solvent power of the CO₂ (Dortmundt and Doshi, 1999). When the CO₂ content of the feed was above 75% CO₂, the separation could be achieved in a single membrane stage. In this case, the compressor was no longer needed (Ho and Sirkar, 1992).

Even though the separation of CO₂/CH₄ using polymeric membranes is growing rapidly, the plasticization of the membrane material is always a problem. This is due to the pressure-normalized flux of the slower gas which is facilitated by the highly soluble, faster gas. This phenomenon is attributed to plasticization effects caused by the high CO₂ solubility or interactions between CO₂ and the polymer material. As the membrane is plasticized the pressure-normalized flux increases significantly but the selectivity for gaseous mixtures decreases (Barsema *et al.*, 2003). A good asymmetric membrane for natural gas separation can be achieved if it possesses the following material and performance characteristics: (1) inherently high

selectivity for CO₂ and CH₄ gas pair and (2) immunity to plasticization induced by CO₂. The CO₂-induced plasticization usually causes a severe deterioration of membrane separation performance in the natural gas application loss (Cao *et al.*, 2003).

An understanding of the plasticization phenomenon is crucial to develop and achieve a high performance membrane in order to make membrane separation application attractive. Therefore, a thorough investigation of CO₂-induced plasticization phenomenon must be carried out in order to reduce the extent of plasticization phenomena in glassy polymer membranes.

1.2 Problem Statement

The problem encountered in the CO₂/CH₄ separation was the swelling of the polymer matrix by the highly sorbed CO₂, which resulted in an increase in CO₂ pressure-normalized flux. This behavior is related to the so-called plasticization effects that occur during the separation process. This phenomenon took place since CO₂ that falls into the category of acid gas such as hydrogen sulfide (H₂S) is commonly found in natural gas streams and hydrocarbon gases at levels as high as 40% to 60% and sometimes up to 80% as hydrocarbon capacities decline, and up to a feed pressure of 60 atm. These extreme operation conditions were the result of the swelling and plasticization of most membrane materials by the CO₂ present in the feed stream (Ho and Sirkar, 1992, Scott, 1998, Staudt-Bickel and Koros, 1999). In other words, degraded the membrane performance. As a result, pressure-normalized flux of CH₄ increases. As it increases more than the pressure-normalized flux of CO₂, the selectivity decreases (Bos *et al.*, 1998). Since plasticization is a major problem that occurs in CO₂/CH₄ separation, it is necessary to develop a membrane that has less plasticization effect besides maintaining the separation performance at elevated pressure conditions.

1.3 Research Objectives

As stated above, the separation of CO₂ from CH₄ customarily takes place in the processes of natural gas treatment, enhanced oil recovery, landfill gas and also in digester gas upgrading and flue gas recovery in order to reduce pipeline corruptions induced by CO₂ as well as to produce high-purity energy products. Polymer membrane based technology is competitive for this kind of application in view of the following facts: (1) the high pressure of feed gas is a ready-made driving force for permeation and (2) CO₂ is more permeable than CH₄ in most membranes. Thus, the enriched CH₄ as the residual stream still retains at a high pressure for other operations without a significant pressure loss (Cao *et al.*, 2003). Many polymers used for the CO₂/CH₄ gas separation show the typical trend of a decreasing pressure-normalized flux with increasing pressure at low feed pressures and an increasing pressure-normalized flux as the CO₂ pressure is further elevated. The increase of pressure-normalized flux with increasing pressure is caused by plasticization (Bos *et al.*, 1998).

From the literature, few researchers reported on asymmetric membrane film, in addition very few researchers report on plasticization in asymmetric hollow fiber membranes. This phenomenon is mainly due to the fact that the dense selective layer of the hollow fibers is very thin and the inception of plasticization in the hollow fibers may occur at a very low feed pressure (Wang *et al.*, 2002a). Many researchers studied polyimide membranes. However, polyimide trade off is not attractive to be used commercially and is expensive compared to polysulfone. On the other hand, the trade-off for polysulfone is favorable for commercial applications. This can help to reduce the cost of using membrane separation systems with condensable gases such as CO₂.

Developing a better membrane that has less plasticization effect besides maintaining the membrane performance is essential for the future application of membrane based gas separation. Not much attention was given to overcoming the plasticization effect in hollow fiber membranes especially on polysulfone. As such, it is necessary to reduce the effect caused by the dissolved CO₂ that will alter the

polymer matrix, resulting in an increase in pressure-normalized fluxes and a reduction of selectivities. From the discussion above, the objectives of this research are:

1. To develop and characterize asymmetric polysulfone hollow fiber membranes.
2. To study the effect of plasticization in asymmetric polysulfone hollow fiber membranes for CO₂/CH₄ gas separation systems.
3. To determine the optimize operating conditions for suppression of plasticization in hollow fiber membranes for CO₂/CH₄ separation system.

1.4 Scope of Thesis

In order to achieve the objective as stated above, the following scopes of work are identified:

1. Fabricating asymmetric polysulfone hollow fiber membrane and membrane modules for testing purposes.
2. Designing and fabricating a high-pressure three-stage gas permeation testing system in order to determine the separation performance of the asymmetric polysulfone hollow fiber membranes.
3. Investigating the plasticization effect using pure CO₂ and CH₄ as well as CO₂/CH₄ mixture permeation experiments.
4. Performing a mild heat treatment process below polysulfone glass transition temperature in order to suppress CO₂-plasticization.
5. Conducting membrane characterizations using density measurement, Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) that can provide an indirect evidence of plasticization.

LIST OF PUBLICATIONS

1. N. Yaacob, A. F. Ismail, Polysulfone Hollow Fiber Membrane System for CO₂/CH₄ Separation: Influence of Membrane Module Configuration on the Separation Performance, Regional Symposium on Membrane Science and Technology (MST 2004), 22nd-24th April 2004, Puteri Pan Pacific Hotel, Johor Bahru.
2. N. Yaacob, A. F. Ismail, Effect of Membrane System Configuration on the Performance of Polysulfone Hollow Fiber Membrane System for CO₂/CH₄ Separation, Symposium of Malaysian Chemical Engineers (SOMChE), 13th-14th December 2004, Universiti Teknologi Petronas, Tronoh.
3. A. F. Ismail, N. Yaacob, Performance of Treated and Untreated Asymmetric Polysulfone Hollow Fiber Membrane in Series and Cascade Module Configurations for CO₂/CH₄ Gas Separation System, Paper submitted to Separation and Purification Technology Journal.
4. A. F. Ismail, N. Yaacob, Experimental and Simulation Analysis of Series and Cascade Module Configuration for Mixed CO₂/CH₄ Gas Separation System, Paper submitted to Journal of Membrane Science.

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