

PERPUSTAKAAN UMP



0000087375

POLYVINYLIDENE FLUORIDE AND POLYETHERIMIDE HOLLOW FIBER  
MEMBRANES FOR CARBON DIOXIDE STRIPPING IN GAS-LIQUID  
MEMBRANE CONTACTOR

ROSMAWATI BINTI NAIM

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Gas Engineering)

Faculty of Petroleum and Renewable Energy Engineering  
Universiti Teknologi Malaysia

MARCH 2014

## ABSTRACT

Porous polyvinylidene fluoride (PVDF) and polyetherimide (PEI) hollow fiber membranes were developed for CO<sub>2</sub> stripping in membrane contactor system. The effects of various types of additives (lithium chloride, polyethylene glycol, phosphoric acid, methanol and glycerol) and different concentrations of lithium chloride (LiCl) on the membrane structure and CO<sub>2</sub> stripping performance of PVDF membrane were investigated. Different polymer concentrations of PEI membranes were studied and their effects on membrane structure and CO<sub>2</sub> stripping performance were evaluated. Long term performance of PVDF and PEI membranes were compared and analyzed. The membranes were characterized in terms of gas permeation, contact angle, membrane porosity, liquid entry pressure and tensile strength. Atomic force microscopy (AFM) was used to examine the membrane surface roughness while the membrane morphology was investigated using scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM). Mass transfer resistance of the system was further calculated based on the experimental data. The addition of additives improved the PVDF membrane characteristics in terms of liquid entry pressure and stripping flux. This could be caused by the thermodynamic (polymer-solvent interaction) and kinetic effects (solution viscosity) on the phase inversion process. These effects also contributed to the reduction of membrane pore size, contact angle and gas permeability of PVDF membranes. The CO<sub>2</sub> stripping performance of PVDF with polyethylene glycol (PEG) additive showed the highest stripping flux and efficiency compared to the other membrane samples. The increase in the concentration of LiCl in PVDF membrane produced high stripping fluxes which can be associated to low surface roughness and mass transfer resistance. For PEI membrane, increasing the polymer concentration had significantly enhanced the wetting pressure whilst reducing the gas permeation. From FESEM analysis, PEI hollow fiber membranes showed finger-like structure similar to PVDF membrane but there was variation in thickness of sponge-like layer in the middle of the membrane cross-structure. Comparative study between PVDF and PEI hollow fiber membranes possessed different microstructures with PVDF-PEG membrane achieving the highest stripping flux of  $4.0 \times 10^{-2}$  mol/m<sup>2</sup>s. Although PEI membranes had higher resistance compared to PVDF membranes in terms of liquid entry pressure, both membranes suffered reduction of stripping flux after operating more than 20 hours. However, the percentage of flux reduction during long hour operation for PVDF membrane was 34% higher than PEI membrane. In addition, PVDF membranes demonstrated higher stripping flux compared to PEI membranes. Therefore, highly hydrophobic membranes with reasonable pore sizes and microstructure are preferred in membrane contactor system for CO<sub>2</sub> stripping application.

## ABSTRAK

Membran gentian geronggang polivinilidin florida berliang (PVDF) dan polieterimida (PEI) dibangunkan untuk penyingkiran karbon dioksida (CO<sub>2</sub>) dalam system penyentuh bermembran. Pengaruh pelbagai bahan tambah (litium klorida, polieterlina glikol, asid fosforik, metanol dan gliserol) dan pelbagai kepekatan litium klorida (LiCl) pada struktur membran dan prestasi penyingkiran CO<sub>2</sub> pada membran PVDF telah dikaji. Pelbagai kepekatan polimer untuk membran PEI telah dikaji dan kesan terhadap struktur membran dan prestasi penyingkiran CO<sub>2</sub> telah dianalisa. Prestasi jangka panjang membran PVDF dan PEI telah dibandingkan dan dianalisa. Membran ini telah dicirikan dari segi penelapan gas, sudut sesentuh, keliangan membran, tekanan masukan cecair dan kekuatan tegangan. Mikroskopi daya atom (AFM) telah digunakan untuk menganalisa kekasaran permukaan membran manakala struktur membran telah dianalisa melalui mikroskopi imbasan elektron (SEM) dan mikroskopi imbasan elektron pemancaran medan (FESEM). Rintangan pengangkutan jisim bagi sistem ini telah dikira berdasarkan data eksperimen. Penambahan bahan tambah telah menambahbaik sifat membran PVDF dari segi tekanan masukan cecair dan fluks penyingkiran. Ini berkait rapat dengan kesan termodinamik (interaksi polimer-pelarut) dan kinetik (kepekatan larutan) ke atas proses fasa balikan. Kesan-kesan ini juga menyumbang kepada pengurangan saiz liang membran, sudut sesentuh dan ketelapan gas. Prestasi penyingkiran CO<sub>2</sub> oleh membran PVDF dengan bahan tambah polieterlina glikol (PEG) menunjukkan fluks penyingkiran CO<sub>2</sub> dan keberkesanan penyingkiran yang tertinggi berbanding dengan sampel-sampel membrane lain. Peningkatan kepekatan LiCl pada membran PVDF, meningkatkan prestasi fluks penyingkiran dan ini berkait dengan kekasaran permukaan dan rintangan pengangkutan jisim yang rendah. Bagi membran PEI, peningkatan kepekatan polimer telah meningkatkan secara ketara tekanan kebasahan sementara menurunkan kebolehtelapan gas. Analisa FESEM membran gentian geronggang PEI menunjukkan struktur berjejari serupa dengan membran PVDF tetapi terdapat variasi ketebalan bagi lapisan berspan di tengah-tengah belahan struktur membran. Kajian perbandingan antara membran gentian geronggang PVDF dan PEI menunjukkan struktur mikro yang berlainan dengan membran PVDF-PEG mencatatkan fluks penyingkiran CO<sub>2</sub> yang tertinggi  $4.0 \times 10^{-2} \text{ molm}^{-2}\text{s}^{-1}$ . Walaupun membran PEI mempunyai rintangan yang lebih tinggi dari segi tekanan masukan cecair berbanding membran PVDF, operasi jangka panjang menunjukkan kedua-dua membran mengalami penurunan fluks penyingkiran selepas 20 jam. Namun, kejatuhan peratus fluks semasa operasi jangka panjang bagi membran PVDF adalah lebih tinggi berbanding membran PEI iaitu sebanyak 34%. Tambahan pula, membran PDVF menunjukkan fluks penyingkiran lebih tinggi berbanding dengan membran PEI. Oleh itu, membran yang sangat hidrofobik dengan saiz keliangan dan struktur mikro yang lebih bersesuaian diberi keutamaan dalam sistem penyentuh bermembran bagi aplikasi penyingkiran CO<sub>2</sub>.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENTS	iv
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	xiii
	LIST OF FIGURES	xv
	LIST OF ABBREVIATIONS	xviii
	LIST OF SYMBOLS	xix
	LIST OF APPENDICES	xxi
1	INTRODUCTION	1
	1.1 Research Background	1
	1.2 Problem Statement	4
	1.3 Objectives of the Study	6
	1.4 Research Scopes	7
	1.5 Rationale and Significance of the Study	8
	1.6 Organization of the Thesis	10
2	LITERATURE REVIEW	11
	2.1 Introduction to Membrane Contactors	11
	2.2 Advantages and Disadvantages of Membrane Contactor	14
	2.2.1 Advantages	14

2.2.2	Disadvantages	15
2.3	Basic Principles of Membrane Contactor	15
2.4	Mass Transfer Theory in Membrane Contactor	17
2.5	Membrane Characteristics	20
2.5.1	Polymer Membrane	20
2.5.1.1	Polytetrafluoroethylene (PTFE) Membrane	22
2.5.1.2	Polypropylene (PP) Membrane	24
2.5.1.3	Polyvinylidene fluoride (PVDF) Membrane	25
2.5.1.4	Polyetherimide (PEI) Membrane	26
2.5.2	Membrane Wetting	28
2.5.3	The Potential of Membrane Wetting	29
2.5.4	Membrane Wetting Prevention	31
2.6	Liquid Absorbent for Membrane Contactor	33
2.7	CO <sub>2</sub> Absorption in Water	37
2.8	CO <sub>2</sub> Reaction in Alkanolamine	40
2.9	CO <sub>2</sub> Stripping Performance in Membrane Contactors	43
2.10	Recent Development and Future Direction	49
2.10.1	Recent Development	49
2.10.2	Future Direction	53
<b>3</b>	<b>METHODOLOGY</b>	<b>55</b>
3.1	Research Design	56
3.2	Materials	56
3.3	Membrane Preparation	59
3.3.1	Polymer Dope Preparation	59
3.3.2	Hollow Fiber Spinning	59
3.3.3	Hollow Fiber Post-Treatment	61
3.3.4	Hollow Fiber Module Preparation	61
3.4	Characterization Methods	62
3.4.1	Gas Permeation Test	63
3.4.2	Static Contact Angle Measurement	64
3.4.3	Porosity Measurement	64

	3.4.4	Viscosity Measurement	65
	3.4.5	Liquid Entry Pressure (LEPw)	65
	3.4.6	Tensile Test	66
	3.4.7	Atomic Force Microscopy (AFM)	66
	3.4.8	Scanning Electron Microscope (SEM) Analysis	68
	3.4.9	Field Electron Microscope (FESEM)	68
	3.4.10	Immersion Test	69
	3.5	Preparation of CO <sub>2</sub> -Rich DEA Solution	69
	3.6	Stripping Test via Membrane Contactor	70
	3.6.1	Overall Mass Transfer Resistance Measurement	72
<b>4</b>		<b>EFFECT OF NON-SOLVENT ADDITIVES ON THE STRUCTURE AND PERFORMANCE OF PVDF HOLLOW FIBER MEMBRANE CONTACTOR FOR CO<sub>2</sub> STRIPPING</b>	<b>73</b>
	4.1	Overview	73
	4.2	Experimental Design	74
	4.3	Effect of Dope Viscosity on Phase Inversion Behavior of PVDF Hollow Fiber Membrane	75
	4.4	Morphology of PVDF Hollow Fiber Membrane	77
	4.5	Characteristics of the PVDF Hollow Fiber Membrane	79
	4.6	Membrane Stripping Test Performance and Overall Mass Transfer Coefficients	82
	4.7	Summary	89
<b>5</b>		<b>EFFECT OF ADDITIVE CONCENTRATIONS ON THE SURFACE PROPERTIES AND CO<sub>2</sub> STRIPPING PERFORMANCE OF PVDF HOLLOW FIBER MEMBRANE</b>	<b>91</b>
	5.1	Overview	91
	5.2	Experimental Design	92
	5.3	Morphology of Porous PVDF Hollow Fiber Membranes	93
	5.4	Characteristics of PVDF Hollow Fiber Membranes	96
	5.5	Results on Morphological Characterization of Membrane	

	by AFM Analysis	99
5.6	CO <sub>2</sub> Stripping Performance and Overall Mass Transfer Coefficient	105
5.7	Summary	110
<b>6</b>	<b>EFFECT OF POLYMER CONCENTRATIONS AND ADDITIVES ON THE STRUCTURE OF POLYETHERIMIDE HOLLOW FIBER MEMBRANE IN MEMBRANE CONTACTOR FOR CO<sub>2</sub> STRIPPING</b>	<b>112</b>
6.1	Overview	112
6.2	Experimental Design	113
6.3	Structural Analysis of PEI Hollow Fiber Membranes	113
6.4	Structural Analysis of PEI Hollow Fiber Membranes with Various Additives	117
6.5	Characteristics of the PEI Hollow Fiber Membranes	119
6.6	CO <sub>2</sub> Stripping Performance of PEI Hollow Fiber Membranes	120
6.7	Summary	124
<b>7</b>	<b>A COMPARATIVE STUDY ON THE STRUCTURE AND PERFORMANCE OF PVDF AND PEI HOLLOW FIBER MEMBRANE FOR CO<sub>2</sub> STRIPPING</b>	<b>126</b>
7.1	Overview	126
7.2	Experimental Design	127
7.3	Results of Morphology Analysis	128
7.4	Characterization of PVDF and PEI Hollow Fiber Membranes	132
7.5	Performance Test of PVDF and PEI Hollow Fiber Membranes	133
7.6	Summary	137

<b>8</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>138</b>
	8.1 General Conclusions	138
	8.2 Recommendations	140
	<b>REFERENCES</b>	<b>142</b>
	Appendices A-K	158-174



## LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Membrane contactor in summary	13
2.2	Commercial available membrane material for membrane contactor	21
2.3	Surface energy of polymer materials (Mulder, 1991)	32
2.4	Research findings on liquid absorbent employed in membrane contactor system	37
2.5	Results of CO <sub>2</sub> physical absorption test	38
2.6	Research study on CO <sub>2</sub> absorption-stripping process using gas-liquid membrane contactor	47
2.7	Field test/ commercial pilot plant operating on membrane contactor system	51
3.1	Chemical and physical properties of polymer, solvents and additives used in this study	58
3.2	Spinning conditions of the hollow fiber membranes	60
3.3	Specifications of gas-liquid membrane contactor system	71
4.1	Viscosity of polymer dope solution	76
4.2	Hollow fiber membrane characterization results	81
4.3	Mechanical test for hollow fiber membrane	82
4.4	Mass transfer coefficient analysis in stripping membrane contactor	85
4.5	Comparison of stripping flux and overall mass transfer coefficient of membrane in-house made and commercial membranes	87
5.1	Characteristics of PVDF hollow fiber membrane	97
5.2	Mean, maximum and minimum sizes of the nodular aggregates	

	on the inner and outer surface of PVDF hollow fiber membranes	102
5.3	Pore sizes of PVDF hollow fiber membranes	103
5.4	Mean surface roughness of PVDF hollow fiber membranes	104
5.5	Overall mass transfer coefficient in CO <sub>2</sub> stripping membrane contactor	109
6.1	Polymer dope composition and viscosity	113
6.2	Characterization results of PEI hollow fiber membranes	119
7.1	Polymer dope composition and viscosity	127
7.2	Results of characterization test of PVDF and PEI hollow fiber membrane	132
E.1	Properties of liquid absorbent, mix gas and membrane	166
F.1	N <sub>2</sub> permeance of PVDF hollow fiber membranes with various additives	167
G.1	CO <sub>2</sub> flux of PVDF hollow fiber membranes	168
H.1	N <sub>2</sub> permeance of PEI hollow fiber membranes at different concentration	169
I.1	CO <sub>2</sub> flux of PEI hollow fiber membranes	170
I.2	CO <sub>2</sub> flux of PEI hollow fiber membranes at different temperatures	171
J.1	Calculation of liquid, gas and membrane mass transfer coefficient with various additives	172

## LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Membrane market potential	4
2.1	Schematic of (a) CO <sub>2</sub> absorption and (b) CO <sub>2</sub> stripping mechanism through a gas-liquid membrane contactor	16
2.2	Resistance to the mass transport offered by the gas, membrane and the liquid in membrane contactor system.	17
2.3	Chemical structure of PTFE	22
2.4	Chemical structure of polypropylene	24
2.5	Chemical structure of polyvinylidene	26
2.6	Chemical structure of polyetherimide	26
2.7	Molecular structure of typical amine group gas treating processes	41
3.1	Research design on PVDF and PEI hollow fiber membrane	57
3.2	Schematic diagram of spinning equipment	60
3.3	Schematic of hollow fiber membrane modules (a) gas permeation and liquid entry pressure (b) stripping test module	62
3.4	The cutting technique used for AFM studies of the internal surface of hollow fiber membranes (Rafat <i>et al.</i> , 2006)	67
3.5	Schematic flow diagram of experimental CO <sub>2</sub> stripping via membrane contactor system	72
4.1	FESEM micrograph of PVDF membrane with various non-solvent additives (a) LiCl (b) phosphoric acid (c) PEG-400 (d) methanol (e) glycerol (f) plain	78
4.2	N <sub>2</sub> permeance of prepared PVDF hollow fiber membranes	79
4.3	Effect of liquid velocity on CO <sub>2</sub> stripping flux for PVDF membrane with various non-solvent additives	83

4.4	Stripping efficiency of PVDF membrane at absorbent flow rates of 110 ml/min	84
4.5	Effect of operating time on the performance of PVDF/PEG-400 membrane ( $M_{DEA} = 1.0 \text{ kmol m}^{-3}$ , $v_l = 80 \text{ ml/min}$ , $v_g = 500 \text{ ml/min}$ , $T = 80^\circ\text{C}$ )	89
5.1	SEM morphology of plain PVDF hollow fiber membranes; (a) cross section (b) inner layer (c) outer surface (d) inner surface.	94
5.2	SEM morphology of PVDF-3% LiCl hollow fiber membranes; (a) cross section (b) inner layer (c) outer surface (d) inner surface	95
5.3	SEM morphology of PVDF-5% LiCl hollow fiber membranes (a) cross section (b) inner layer (c) outer surface (d) inner surface	96
5.4	$\text{N}_2$ permeance of PVDF hollow fiber membrane vs. mean pressure	97
5.5	AFM images for outer surface of different PVDF hollow fiber membrane (S1: plain, S2: 3% LiCl, S3: 5% LiCl) prepared at: (S1a-S3a) 1 $\mu\text{m}$ scan (S1b-S3b) 1 $\mu\text{m}$ scan (3D images)	100
5.6	AFM images for inner surface of PVDF hollow fiber membrane (S1- plain, S2- 3% LiCl, S3- 5% LiCl) prepared at; (S1a-S3a) 2 $\mu\text{m}$ scan and (S1b-S3b) 1 $\mu\text{m}$ scan (3D images)	100
5.7	Probability density function curves for (a) inner surface (b) outer surface; generated from the pore sizes measured from the AFM images of the PVDF membranes	104
5.8	Effect of liquid velocity on $\text{CO}_2$ stripping flux of the membrane	106
5.9	Effect of liquid velocity on stripping efficiency and outlet liquid concentration	107
6.1	FESEM micrograph of PEI hollow fiber membrane (a) 13% PEI, (b) 14% PEI, (c) 15% PEI, (d) 16% PEI	115
6.2	FESEM micrograph of PEI hollow fiber membrane (a) before and (b) after immersion in aqueous DEA solution (1.0 M, 25 $^\circ\text{C}$ for 12 days)	116
6.3	FESEM micrograph of PEI hollow fiber membranes with various additives	118
6.4	Effect of liquid velocity on $\text{CO}_2$ stripping flux for PEI hollow	

	fiber membranes	121
6.5	Effect of absorbent temperature on CO <sub>2</sub> stripping flux for PEI hollow fiber membranes	123
6.6	Stripping efficiency of various PEI membranes at different liquid flow rates	124
7.1	The structure of PVDF hollow fiber membranes for (a) plain (b) with PEG-400 (1) cross section (2) shell side (3) lumen side	130
7.2	The structure of PEI hollow fiber membranes for (a) plain (b) with PEG-400 (1) cross section (2) shell side (3) lumen side	131
7.3	Effect of liquid velocity on CO <sub>2</sub> stripping flux for PEI and PVDF membrane ( $M_{DEA} = 1 \text{ M}$ , $T = 80 \text{ }^\circ\text{C}$ , $P_l - P_g = 0.2 \times 10^5 \text{ Pa}$ , $\nu_g = 500 \text{ ml min}^{-1}$ )	135
7.4	Long term study of PVDF and PEI membranes ( $M_{DEA} = 1 \text{ M}$ , $T = 80 \text{ }^\circ\text{C}$ , $P_l - P_g = 0.2 \times 10^5 \text{ Pa}$ , $\nu_l = 0.52 \text{ ms}^{-1}$ )	136
7.5	Stripping efficiency of all membranes at absorbent flow rates of 110 ml/min	137
B.1	Photo of gas-liquid membrane contactor system	159

**LIST OF ABBREVIATIONS**

AFM	-	Atomic force microscopy
CO <sub>2</sub>	-	Carbon dioxide
DEA	-	Diethanolamine
DMAc	-	Dimethylacetamide
FESEM	-	Field emission scanning electron microscopy
HCl	-	Hydrochloric acid
H <sub>2</sub> S	-	Hydrogen sulfide
LEP <sub>w</sub>	-	Liquid entry pressure of water
LiCl	-	Lithium chloride
MEA	-	Monoethanolamine
M	-	Molarity
MPa	-	Megapascal
N <sub>2</sub>	-	Nitrogen
NaOH	-	Sodium hydroxide
NMP	-	N-methyl-2-pyrrolidone
PA	-	Phosphoric acid
PEG	-	Polyethylene glycol
PEI	-	Polyetherimide
PP	-	Polypropylene
PSF	-	Polysulfone
PTFE	-	Polytetrafluoroethylene
PVDF	-	Polyvinylidene fluoride
SEM	-	Scanning electron microscopy
SO <sub>2</sub>	-	Sulfur dioxide

## LIST OF SYMBOLS

$K_{ov}$	-	overall mass transfer coefficient (m/s)
$k_g$	-	gas side mass transfer coefficient (m/s)
$k_m$	-	membrane mass transfer coefficient (m/s)
$k_l$	-	liquid phase physical mass transfer coefficient (m/s)
$H$	-	Henry's constant
$E$	-	enhancement factor (dimensionless)
$d_o$	-	fiber outer diameter (m)
$d_i$	-	fiber inner diameter (m)
$d_{lm}$	-	log mean diameter of the fiber (m)
$D_i$	-	diffusivity of species ( $m^2/s$ )
$\delta$	-	membrane thickness (m)
$\varepsilon$	-	membrane porosity (dimensionless)
$\varepsilon_e$	-	effective membrane porosity (dimensionless)
$\tau$	-	membrane tortuosity (dimensionless)
$d_h$	-	hydraulic diameter (m)
$L$	-	length of hollow fiber (m)
$C_i$	-	molarity of solution ( $mol.dm^{-3}$ )
$T$	-	temperature (Kelvin)
$\rho$	-	density ( $g\ cm^{-3}$ )
$V$	-	molar volume of solution ( $cm^3\ mol^{-1}$ )
$x_i$	-	mole fractions of species
$M_i$	-	molecular weights (g/mol)
$\mu_i$	-	viscosity of species (mPa s)
$\Omega$	-	percent mass (%) of solution
$\alpha$	-	CO <sub>2</sub> loading (mol CO <sub>2</sub> / mol amine)
$Re$	-	Reynolds number (dimensionless)

<i>Sc</i>	-	Schmidt number (dimensionless)
<i>Sh</i>	-	Sherwood number (dimensionless)



## LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Titration of CO <sub>2</sub> Absorption in Amine Solution	158
B	The Gas-Liquid Membrane Contactor System	159
C	Details Calculation on Mass Transfer Coefficient	160
C.1	Liquid Phase Mass Transfer Coefficient ( $k_l$ )	160
C.2	Gas Phase Mass Transfer Coefficient ( $k_g$ )	161
C.3	Membrane Mass Transfer Coefficient ( $k_m$ )	162
C.4	Henry's Constant (H)	163
C.5	Reynolds Number	163
C.6	Schmidt Number	164
C.7	Graetz Number	164
D	Nitrous Oxide (N <sub>2</sub> O) Analogy	165
E	Characteristics of Liquid Absorbent, Mix Gas and Membrane Properties	166
E.1	Properties of liquid absorbent, mix gas and membrane	162
F	Measured N <sub>2</sub> Permeance of PVDF Hollow Fiber Membranes with Various Additives	167
F.1	N <sub>2</sub> permeance of PVDF hollow fiber membranes with various additives	167
G	Measured CO <sub>2</sub> Flux for PVDF Hollow Fiber Membranes	168
G.1	CO <sub>2</sub> flux for PVDF hollow fiber membranes	168
H	Measured N <sub>2</sub> Permeance of PEI Hollow Fiber Membranes at Different Concentration	169
H.1	N <sub>2</sub> permeance of PEI hollow fiber membranes at different concentration	169
I	Measured CO <sub>2</sub> Flux for PEI Hollow Fiber Membranes	170

I.1	CO <sub>2</sub> flux for PEI hollow fiber membranes	170
I.2	CO <sub>2</sub> flux for PEI hollow fiber membranes at different temperatures	171
J	Calculation of Individual Mass Transfer Coefficient for PVDF Membrane with Various Additives	172
J.1	Calculation of individual mass transfer coefficient for PVDF membrane with various additives	172
K	List of Publications	173

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Current concerns on environmental issues and climate change have promoted scientists and researchers to find effective ways to reduce the amount of CO<sub>2</sub> gas released to the atmosphere as it is commonly associated with greenhouse effects and global warming. A study by environmental agency reported that emissions of CO<sub>2</sub> are increasing yearly due to human activities especially in industrial, transportation, residential, commercial and agricultural fields. Of these activities, fossil fuel combustion for energy generation has contributed about 70-75% of the total CO<sub>2</sub> emissions.

In industrial and natural gas processing, removal of acid gases (mainly CO<sub>2</sub> and H<sub>2</sub>S) is essential as they could cause corrosion in the gas pipeline and reduce the hydrocarbon content hence resulting in a lower energy content of the fuel. These phenomena incurred economical losses in investment and reduction in the efficiency of the system (Kladkaew *et al.*, 2011). Several established technologies in gas separation namely chemical absorption (amine), physical absorption, cryogenic distillation and membrane system have been applied to combat the problem and have produced promising results. The removal of CO<sub>2</sub> by absorption-stripping into aqueous solutions using equipment such as packed bed, spray columns and bubble column has been conventionally used and acknowledged as an effective method to remove CO<sub>2</sub>. For stripping process, Weiland *et al.* (1982) designed and analysed

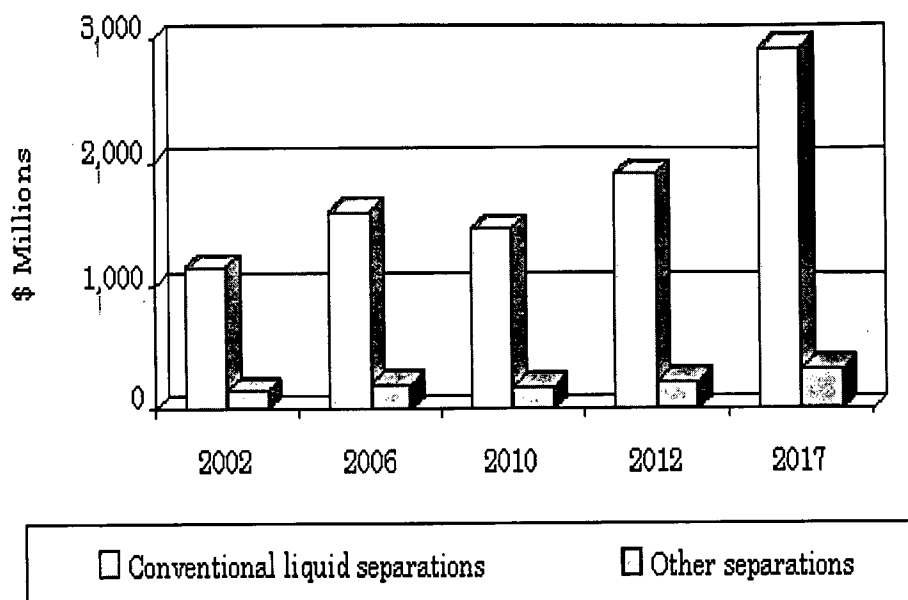
packed column for CO<sub>2</sub> stripping from monoethanolamine in gas purification process. Xu *et al.* (1995) used packed column for CO<sub>2</sub> desorption from aqueous methyldiethanolamine (MDEA) and activated MDEA solutions. However, for a long term operation, this conventional equipment has suffered from significant drawback such as flooding, channelling, entrainment and foaming (Criscuoli and Drioli, 2008). Therefore, alternative technology such as gas-liquid membrane contactor has been identified as a promising option that has potential to replace conventional equipment in CO<sub>2</sub> absorption-stripping process.

Gas-liquid membrane contactor was employed earlier in 1970's by Esato and Eiseman (1975) for blood oxygenation which consists of hydrophobic microporous PTFE membrane known as Gore-Tex membranes. These membranes were also used in fuel cell system for U.S space program in the late 1960's. Further application of membrane in gas-liquid contactor started to emerge when Feron and Jansen (2002) first introduced CORAL solvent with porous polyolefin membranes for the production of carbon dioxide from flue gas. Since then, membrane contactor technology has been applied in wide range applications such as fermentation, pharmaceuticals, water treatment (Drioli *et al.*, 2005), beverage carbonation (Mackey and Mojonier, 1995) and absorption-stripping process (Gabelman and Hwang, 1999). Some of the prominent advantages of membrane contactor are high area per unit volume, no flooding or entrainment, independent of gas and liquid flow, system easily scale-up and most importantly no moving parts in the system.

Polymer membranes such as polyvinylidene fluoride (PVDF), polytetrafluorethylene (PTFE), polypropylene (PP), polyethylene (PE) and polyetherimide (PEI) are among the prominent polymers applied in gas-liquid contactor application. Due to its favorable properties such as being hydrophobic, compatible in organic solvent, resistant to heat and chemical reaction; having a straightforward process in membrane preparation has made PVDF polymer as a favourite over other commercial polymers. Modification of PVDF hollow fiber membrane by adding non-solvent additives has been reported in the literature and has produced promising outcomes in CO<sub>2</sub> absorption. These include the enhancement of gas permeability (Yeow *et al.*, 2004), high CO<sub>2</sub> absorption flux (Mansourizadeh and

Ismail, 2011a), high wetting pressure (Bakeri *et al.*, 2011) and altering the final membrane structure which turned out to affect CO<sub>2</sub> absorption performance (Atchariyawut *et al.*, 2006). Up to present, experimental results on the applications of polymeric membrane in CO<sub>2</sub> stripping have been scarcely reported (Khaisri *et al.*, 2011; Simioni *et al.*, 2011a). Khaisri *et al.* (2011a) performed CO<sub>2</sub> stripping from loaded aqueous monoethanolamine (MEA) solution by using PTFE hollow fiber membrane. A study on plasma sputtering nylon membrane for CO<sub>2</sub> stripping has been carried out by Simioni *et al.* (2011b) at elevated temperatures up to 100 °C with aqueous potassium carbonate as liquid absorbent. Mansourizadeh and Ismail (2011b) investigated CO<sub>2</sub> stripping from water using PVDF hollow fiber at 60°C. To the best of our knowledge, there is no specific discussion regarding the effects of non-solvent additive on the membrane stripping performance that has been highlighted. Recently, a modified version of PEI hollow fiber membrane incorporated with fluorinated silica (fSiO<sub>2</sub>) inorganic layer was studied by Zhang and Wang (2013) for CO<sub>2</sub> absorption. It was reported that the hydrophobicity of the membrane was significantly increased due to reduction of surface free energy and enhancement of surface roughness generated by the SiO<sub>2</sub> layer.

According to the latest technical market research report by BCC Research, (2012), the total market for membrane used in gas and liquid separations is expected to reach nearly \$3.3 billion in 2017 after increasing at a five-year compound annual growth rate of 8.9%. This can be broken down into two main categories; conventional liquid separations and other separations as shown in Figure 1.1. The conventional liquid separations may include the separation applications such as reverse osmosis, desalination, ultrafiltration, nanofiltration and gas separation. Since the membrane contactor application is an emerging technology, it is expected that 10% out of the total market demand will be contributed by the demand in membrane contactor application.



**Figure 1.1:** Membrane market potential (BCC Research LLC., 2012)

## 1.2 Problem Statement

In order to be feasible for CO<sub>2</sub> stripping, the membrane contactor should be equipped with a novel membrane that exhibits high CO<sub>2</sub> transport rates and can prevent the loss of volatile absorbent from the aqueous solutions. The performance of contactor is strongly related to the membrane properties e.g. membrane structure, pore size, porosity, degree of hydrophobicity and breakthrough/wetting pressure which significantly influence the mass transfer process between gas and liquid phases. To date, numerous findings have been reported on the performance of the CO<sub>2</sub> absorber unit. However, there was limited data focusing on detailed stripping operation, despite the fact that stripping and regeneration unit acquire about 80% of the total energy during solvent regeneration, thus responsible for the major cost component in impurity removal process (Chakma, 1997; Tobeisen *et al.*, 2005).

CO<sub>2</sub> stripping by membrane contactor has long been used in various applications such as for removal of volatile organic compounds (VOCs) (Majumdar *et al.*, 2001), lactate extraction (Coelhoso *et al.*, 1997), spring water treatment (Cabassud *et al.*, 2001) and exhaust gas treatment (Falk-Pedersen and Dannstrom,

1997). In such system, a hydrophobic membrane was employed for an efficient contact between gas and liquid phases and the rate of mass transfer process between those phases were determined by the liquid and membrane resistance. The increase in membrane resistance is commonly occur due to the intrusion of liquid absorbent into pore structure and consequently resulted in severe wetting of membrane material. Some of the commercially available membranes (Kosaraju *et al.*, 2005; Simioni *et al.*, 2011a) were found to be wetted more than 70% by liquid absorbent when operated at long hours and at increased temperatures. This condition would in turn reduce the system performance in terms of flux and efficiency.

Although commercial membranes have been diversely used in membrane contactor application, results showed that some of the hydrophobic membrane materials are susceptible to wetting problem after long hour operation. This is unexpected as the membrane has very high contact angle value (more than 90°) and has good chemical resistance against any organic solvent. Hence, having higher contact angle value is not an assurance that the membranes are robust enough to withstand liquid absorbent intrusion through the membrane pores. Therefore, PVDF and PEI membranes were suggested in this study over the commercial membrane based on their good performance reported in the literature (Liu *et al.*, 2011, Bakeri *et al.*, 2012). While PVDF membranes have been a favourite in gas-liquid separation in membrane contactor due to simple and ease of processing steps in phase inversion process, PEI membranes can be tailored made to produce a membrane that has high wetting pressure resistance and high surface hydrophobicity (Zhang *et al.*, 2012). Since the plain PVDF and PEI were expected to have low wetting pressure (Mansourizadeh and Ismail, 2010a) due to macrovoid finger-like structure, it is possible to improve the membrane structure by adding the additives in the polymer solution.

Membrane structure plays an important role in ensuring the efficient flow of gas through the pore structure in mass transfer process. A porous membrane structure with combined finger-like was found suitable for CO<sub>2</sub> absorption in membrane contactor application (Mansourizadeh *et al.*, 2010). This could be done by controlling the spinning variables or adding non-solvent additives to tailor the

membrane structure. The existence of finger-like structure can provide an easy channel for the liquid to permeate and this would reduce the liquid entry pressure of the system. Therefore, an appropriate membrane structure with a trade off between finger-like and sponge-like structure should be developed to achieve high flux and efficiency of stripping process.

From the abovementioned study, it is clearly shown that further study on the enhancement of membrane properties and structure need to be emphasized since the existing membranes are very susceptible to wetting at long operating hours. In addition, the stripping process variables e.g. liquid and flow rates, operating condition, membrane porosity and membrane morphology should be addressed in order to have a good correspondence of their effects on the stripping performance in the membrane contactor system.

### **1.3 Objectives of the Study**

Based on the problem statements addressed, the current study is performed with the following objectives:

- i. To evaluate the effects of various non-solvent additives on the structure of PVDF hollow fiber membrane and CO<sub>2</sub> stripping performance in membrane contactor system.
- ii. To evaluate the effects of additive concentrations on the PVDF hollow fiber membrane surface characteristics and CO<sub>2</sub> stripping performance in membrane contactor system.
- iii. To evaluate the potential of polyetherimide (PEI) hollow fiber membrane in CO<sub>2</sub> stripping via membrane contactor application.
- iv. To evaluate the long term performance of PVDF and PEI hollow fiber membrane in CO<sub>2</sub> stripping via membrane contactor system.