

DEVELOPMENT OF HOLLOW FIBER MEMBRANES FOR CARBON
DIOXIDE ABSORPTION IN GAS-LIQUID MEMBRANE CONTACTORS

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I declare that this thesis entitled “*Development of Hollow Fiber Membranes for Carbon Dioxide Absorption in Gas-Liquid Membrane Contactors*“ is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

Porous asymmetric polyvinylidene fluoride (PVDF) and polysulfone (PSF) hollow fiber membranes were structurally developed to improve gas permeability, wetting resistance and carbon dioxide (CO₂) absorption flux. The membranes were prepared via a wet phase-inversion process and used in gas-liquid membrane contactors for CO₂ absorption. Phase-inversion behavior of the polymer solutions was studied by plotting the ternary phase diagrams of polymer/solvent-additive/water. The effect of different non-solvent additives on the structure and performance of the PVDF and PSF membranes was investigated. The membranes structure was examined in terms of gas permeation, critical water entry pressure (CEP_w), collapsing pressure, overall porosity, contact angle, mass transfer resistance and field emission scanning electronic microscopy (FESEM). The CO₂ absorption performance of the membranes was investigated and compared with the commercial polypropylene (PP) and polytetrafluoroethylene (PTFE) hollow fiber membranes. In addition, the effect of different operating conditions on the physical and chemical CO₂ flux of the PVDF membrane was also investigated. The results showed that the PSF membranes have a thicker skin layer with smaller pore sizes and lower surface porosity compared to the PVDF membranes. The PVDF membranes demonstrated low mass transfer resistance and high wetting resistance. Therefore, the hydrophobic PVDF membranes indicated an improved structure, which considerably increased the CO₂ flux compared to the PSF membranes and symmetric PP and PTFE commercial membranes. A maximum CO₂ flux of 8.20×10^{-4} mol./m².s was achieved at the absorbent flow rate of 310 ml/min, which was approximately 110 % higher than CO₂ flux of the PTFE membrane at the same operating conditions. In case of physical absorption with distilled water, a significant increase in the CO₂ flux was observed as the pressure increased and the temperature decreased. However, in the case of chemical absorption with 1M sodium hydroxide (NaOH) solution, the CO₂ flux was significantly increased by increasing temperature, where the reaction rate was dominant. Moreover, it was found that the operation remains stable at the same gas and liquid pressure without bubble formation in the liquid phase when the liquid contacts the skin layer of the membrane. Results of the long-term study demonstrated that after a certain initial CO₂ flux reduction the membrane performance maintained constant over 150 h operation. Therefore, it can be concluded that the porous hydrophobic membrane with developed structure can be a promising alternative for CO₂ removal from the gas streams.

ABSTRAK

Membran tak simetri berliang polivinilidina fluorida (PVDF) dan polisulfona (PSF) gentian geronggang telah dibangun secara fizikal untuk memperbaiki kebolehtelapan gas, rintangan pembasahan dan fluks penyerapan gas karbon dioksida (CO₂). Membran disediakan melalui kaedah fasa balikan basah dan diguna untuk penyerapan CO₂ melalui penyentuh cecair-gas bermembran. Sifat kaedah fasa balikan basah ke atas larutan polimer dikaji dengan melakarkan gambarajah tiga fasa polimer/pelarut-bahan tambah/air. Pengaruh pelbagai bahan tambah bukan pelarut pada struktur dan prestasi penyerapan CO₂ pada membran PVDF dan PSF telah dikaji. Struktur membran ini telah diperiksa dengan kaedah penelapan gas, tekanan kritikal kemasukan air (CEP_w), tekanan runtuh, keliangan keseluruhan, sudut sesentuh air, rintangan pemindahan jisim dan mikroskopi imbasan elektron pemancaran medan (FESEM). Prestasi membran untuk penyerapan CO₂ telah dikaji dan dibandingkan dengan membran gentian bergeronggang polipropilina (PP) dan politetrafluoroetilina (PTFE) komersil. Sebagai tambahan, kesan keadaan operasi yang berbeza ke atas fluks fizikal dan kimia CO₂ untuk membran PVDF telah dikaji. Keputusannya menunjukkan membran PSF mempunyai lapisan kulit yang lebih tebal dengan saiz liang yang lebih kecil dan keliangan permukaan yang lebih rendah berbanding membran PVDF. Membran PVDF menunjukkan rintangan pemindahan jisim yang rendah dan rintangan kebasahan yang tinggi. Oleh itu membran hidrofobik PVDF menunjukkan pembaikan struktur, yang meningkatkan fluks CO₂ berbanding dengan membran PSF yang disediakan serta PP dan PTFE membran komersil simetri. Kadar fluks maksimum 8.20×10^{-4} mol./m².s telah diperolehi dengan air suling sebagai bahan penyerapan cecair pada kadar alir 310 ml/min, iaitu lebih kurang 110% lebih tinggi dari fluks CO₂ membran PTFE. Dalam kes penyerapan fizikal dengan air suling, peningkatan fluks CO₂ yang berkesan telah dapat dicerap melalui peningkatan suhu dan pengurangan tekanan. Akan tetapi, dalam kes penyerapan kimia menggunakan larutan natrium hidroksida (NaOH) 1M, fluks CO₂ telah meningkat dengan peningkatan suhu, di mana kadar tindakbalas adalah tinggi. Tambahan pula, operasi didapati boleh menjadi stabil pada tekanan gas dan cecair yang sama tanpa pembentukan gelembung dalam fasa cecair, apabila cecair bersentuhan dengan lapisan kulit membran. Keputusan dari kajian jangka panjang menunjukkan selepas pengurangan awal fluks CO₂, prestasi membran kekal malar operasi melebihi 150 jam. Oleh itu, dapat disimpulkan bahawa membran hidrofobik berliang dengan struktur yang telah dibangunkan boleh menjadi alternatif yang baik bagi penyingkiran CO₂ dari aliran gas.

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LIST OF ABBREVIATIONS

AFM	:	Atomic force microscopy
CEP _w	:	Critical water entry pressure
DER	:	Dope extrusion rate
DMAc	:	Dimethylacetamide
DMF	:	Dimethylformamide
DMSO	:	Dimethylsulfoxide
FESEM	:	Field emission scanning electron microscopy
NIPS	:	Non-solvent induced phase separation
NMP	:	N-methyl-2-pyrrolidone
PE	:	Polyethylene
PEG	:	Polyethylene glycol
PP	:	Polypropylene
PSF	:	Polysulfone
PTFE	:	Poly(tetrafluorethylene)
PVDF	:	Poly(vinylidene fluoride)
T _g	:	Glass transition temperature
TIPS	:	Thermally induced phase separation

LIST OF SYMBOLS

A	:	surface area (m^2)
C	:	concentration (mol/m^3)
d	:	diameter (m)
D	:	diffusion coefficient(m^2/s), shell side diameter (m)
E	:	enhancement factor (-)
E_{∞}^*	:	modified infinite enhancement factor (-)
Gz	:	Gratez number (-)
H	:	Henry's law constant (-)
Ha	:	Hatta number (-)
Ha^*	:	modified Hatta number (-)
J	:	gas permeance ($mol/m^2 \text{ s pa}$), absorption flux ($mol/m^2 \text{ s}$)
k	:	mass transfer coefficient (m/s)
K	:	overall mass transfer coefficient (m/s)
K_0	:	constant (-)
l	:	membrane thickness (m)
L	:	hollow fiber length (m), pore length (m)
m	:	distribution coefficient (-)
M	:	molecular weight (kg/mol)
n	:	number of fibers (-)
N	:	mass transfer flux ($mol/m^2.s$)
P	:	pressure (pa)
\bar{P}	:	mean pressure (pa)
P_0	:	constant (-)
Q	:	flow rate (m^3/s)
r	:	radius (m)

R	:	gas constant (J/mol K), reaction rate ($\text{mol/m}^3 \text{ s}$)
Re	:	Reynolds number (-)
Sc	:	Schmidt number (-)
Sh	:	Sherwood number (-)
\overline{Sh}	:	average Sherwood number (-)
T	:	temperature (K)
t	:	time (s)
u	:	velocity (m/s)
\overline{U}	:	average velocity (m/s)
w	:	fiber mass (g)
x	:	pore length wetted by liquid (m), wetting ratio (-)

Greek letters

α	:	constant (-)
γ	:	surface tension (N/m)
δ	:	pore length (m)
ε	:	surface porosity (m^{-1}), porosity (-)
θ	:	contact angle
μ	:	gas viscosity (kg/m s)
ρ	:	density (g/cm^3)
τ	:	tortuosity (-)
ν	:	kinematic viscosity (m^2/s), stoichiometric coefficient (-)
φ	:	packing density (-)
Ω	:	dimensionless function of temperature (-)

Subscripts

<i>A</i>	:	component
<i>B</i>	:	component
<i>b</i>	:	bulk
<i>e</i>	:	equivalent, free surface
<i>f</i>	:	fiber
<i>g</i>	:	gas
<i>h</i>	:	hydraulic
<i>i</i>	:	inner, interface, component
<i>l</i>	:	liquid
<i>lm</i>	:	log mean
<i>m</i>	:	membrane, molecular diffusion, partial reaction order
<i>n</i>	:	number of fibers, partial reaction order
<i>o</i>	:	outer, overall, outlet
<i>p</i>	:	polymer, pore
<i>s</i>	:	inner module

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CHAPTER 1

INTRODUCTION

1.1. Research Background

It is important to develop techniques which would reduce acid gases like carbon dioxide (CO_2), hydrogen sulfide (H_2S) and other sulfuric and nitric components (SO_x and NO_x) arising from the combustion of fossil fuels, present in natural gas, industrial gas and domestic processes effluent gas. Due to the environmental, economical and operational impacts of acid gases they should be removed from the gas streams. CO_2 is the primary component of greenhouse gases, which more than one-third of its emission comes from combustion of fossil fuels in power plants worldwide. It has been associated with global climate change (Herzog et al. 2000). In addition, presence of CO_2 in natural gas can cause pipeline corrosion, reduction in the heating value, increasing transport energy and CO_2 is also able to solidify in cryogenic process (Atcharyawut et al. 2007). Several conventional devices such as gas absorption columns, adsorption systems and cryogenic process have been developed for CO_2 removal from gas streams.

In recent years, an alternative technology that overcomes the disadvantages of conventional gas absorption is non-dispersive gas-liquid contact via a porous membrane. By using a suitable membrane configuration such as a hollow fiber, the gas and liquid can contact on the gas-liquid interface at the mouth of each membrane

pore. Mass transfer occurs by diffusion across the interface, just as in conventional contacting device. Furthermore, as opposed to more conventional applications such as microfiltration, ultrafiltration and reverse osmosis, the driving force for separation is a concentration rather than a pressure gradient; indeed only a very small pressure drop across the membrane is required to ensure that the gas-liquid interface remains immobilized at the mouth of the membrane pores. The membrane gas absorption process offers several advantages over conventional contacting devices such as: high surface area per unit contactor volume, independent control of gas and liquid flow rates without any flooding, loading, weeping, foaming or entrainment problems, known gas-liquid interfacial area, small size, modular, and easy to scale up or down (Gabelman and Hwang, 1999).

Esato and Eiseman (1975) were the first to employ the microporous membrane as a gas-liquid contacting device using hydrophobic flat Gore-Tex membranes of poly (tetrafluoroethylene) (PTFE) for oxygenation of blood. Removal of CO₂, one of the major greenhouse gases, from gas streams by a membrane contactor has been a research focus since 1980s and for this purpose investigators have considered several factors like absorption solutions, membrane materials and membrane modules to improve the performance of CO₂ removal. Qi and Cussler (1985a,b) were the first to develop the idea of the hollow-fiber contactor using a microporous non-wetted polypropylene hollow fiber membrane for absorption of CO₂ where aqueous sodium hydroxide solution was used as an absorbent. Feron and Jansen (2002) employed porous polyolefin membranes with the novel absorption liquids (CORAL) based on mixtures of salts and amino-acids for removal of carbon dioxide from various feed gases contain different CO₂ concentration. Ren et al. (2006) prepared poly (vinylidene fluoride) (PVDF) hollow fiber membranes to make membrane contactors for CO₂ capture. These hollow fiber membranes were spun with two different dope solutions at different shear rates in order to understand the influences of the rheological characteristics of the dope solution on the membrane structure and the system performance for CO₂ absorption. Applications, advantages and disadvantages of hollow fiber membrane contactors have been discussed in more details by Gabelman and Hwang (1999). Li and Chen (2005) also reviewed absorption of CO₂ using chemical solvents in hollow fiber membrane contactors.

Therefore, the advantages of gas-liquid membrane contactors paved the way for the application of this technology in the removal of acid gases from flue gases, natural gas and various industrial process gas streams, which have led a number of investigators to explore a number of gas separation applications.

1.2. Problem Statement

Membrane gas absorption using microporous hollow fiber polymeric membranes have attracted considerable attention in recent years and exciting results have been reported. However, recent developments in this area are still at the stage of laboratorial scale, and the long-term stability of the membrane has seldom been considered in the literature. In fact, the chemical stability of the membrane material has a considerable effect on its long-term stability. Any interaction between the liquid absorbent and membrane material can possibly influence the membrane integrity and surface structure. Liquid absorbents with high load of acid gases which is normally used in membrane contactors are corrosive in the nature and can make the membrane material less resistance to chemical attack.

In addition, the presence of a membrane adds an additional resistance to the overall mass transfer process compared to conventional absorption devices. In the ideal case, the membrane pores are filled with the gaseous component (non-wetted) resulting into a negligible mass transfer resistance. When the membrane pores are filled with the liquid (wetted), the mass transfer resistance of the membrane becomes significant, resulting into an unviable economical operation (Kreulen et al., 1993a). Thus long-term stable operation of the membrane contactor requires that the pores of membrane remain completely gas filled. The wetting tendency of a membrane-absorbent combination is mainly determined by properties of the membrane, the liquid absorbent and operating conditions.

In general, liquids with low surface tensions tend to wet the membrane more than liquids having higher surface tensions based on Laplace-Young equation. Most of the absorbents used in the acid gases removal are organic in nature and have low

surface tension. On the other hand, water with significant surface tension has a relatively low affinity to CO₂ absorption.

The choice of membrane material and its properties affect phenomena such as absorption and chemical stability under the conditions of actual application. This implies that not only the chemical and thermal properties of the material, but the membrane structure and properties play important roles on the CO₂ flux of the membranes. Among various hydrophobic polymers, polypropylene (PP) and PTFE are the most popular membrane materials that have been fabricated as symmetric hollow fiber membranes for gas absorption process. Indeed, high hydrophobicity of the membranes can reduce wetting tendency of the membrane. However, since porous PTFE and PP membranes are usually provided by stretching and thermal methods, their relatively low porosity restricts a significant increase on absorption flux. Consequently the main advantage of the microporous hollow fiber membrane i.e. a high area to volume ratio can not be fully achieved.

The other hydrophobic polymer like PVDF can be used to prepare asymmetric membranes via phase-inversion method. Since the PVDF has a small critical surface tension about 25 dynes/cm, the penetration of the coagulant (water) into the nascent membrane is restricted during the phase-inversion process. Therefore, the precipitation rate and solidification of the nascent membranes are slow which can cause considerable difficulties in preparing the porous asymmetric PVDF hollow fiber membranes. Moreover, polysulfone has been widely used as a membrane material due to its mechanical strength, thermo-stability, stability against chemicals and relative hydrophobicity. PSF is also an excellent material for spinning hollow fiber membranes with controlled pore size.

Therefore, it is possible to develop porous asymmetric membrane structure with properties such as high surface porosity, small pore size and ultra thin skin layer with low mass transfer resistance, which are favorable for gas absorption applications.

1.3. Objectives of the Study

Based on the above problem statements, the objectives of this research are listed as follow:

- i. To develop porous PVDF and PSF hollow fiber membranes with improved structure for CO₂ absorption.
- ii. To investigate the structure of membranes using various techniques such as field emission scanning electron microscopy (FESEM), gas permeation, critical water entry pressure, overall porosity, water contact angle and mass transfer resistance.
- iii. To evaluate performance of the obtained membranes for CO₂ absorption using the gas-liquid membrane contactor system.

1.4. Research Scopes

In order to achieve the above objectives, the following scope of work was selected;

- i. Selection of membrane materials and non-solvent additives for preparing porous PVDF and PSF hollow fiber membranes.
- ii. Formulation of polymer dopes through ternary phase diagrams of polymer/solvent-additive/water system.
- iii. Wet spinning PVDF and PSF hollow fiber membranes and characterization of the membranes in terms of membrane structure and hydrophobicity.
- iv. Designing and fabricating an experimental gas-liquid membrane contactor system for CO₂ absorption.
- v. Optimization of membrane properties for CO₂ absorption performance.
- vi. Comparing CO₂ absorption performance of the prepared PVDF and PSF hollow fiber membranes with commercial PP and PTFE membranes.
- vii. Studying the effect of operating conditions on the performance of CO₂ absorption through the gas-liquid membrane contactor.

- viii. Evaluation the performance of the PVDF membrane for physical and chemical CO₂ absorption in long-term operation.

1.5. Organization of the Thesis

This thesis describes the development of the PVDF and PSF hollow fiber membranes structure for CO₂ absorption through the gas-liquid membrane contactors, which is divided in eight chapters.

In chapter 1, background of the study, problem statement, objectives and scope of the research were presented. Chapter 2 discusses different aspects of hollow fiber gas-liquid membrane contactors for acid gas capture in details. In addition, current status and future directions of the technology is critically presented. The methodology of the membrane preparation and characterization are described in details in chapter 3.

Preparation of porous polysulfone (PSF) hollow fiber membranes using a wet phase-inversion process is investigated systematically and the results are presented in chapter 4. The effect of different non-solvent additives in the spinning dopes on the structure and performance of the membranes for CO₂ absorption are also discussed. Lithium chloride monohydrate and ortho-phosphoric acid are used as phase-inversion promoter additives in the PVDF spinning dopes and the results are discussed in chapter 5. The prepared porous PVDF hollow fiber membranes are also characterized in terms of gas permeability, wetting resistance and mass transfer resistance. As well, the CO₂ absorption performance of the PVDF membranes is compared with the commercial PP and PTFE hollow fiber membranes.

In chapter 6, the results of the CO₂ absorption performance and structure of porous PVDF and PSF hollow fiber membranes are compared. The membranes are prepared at the same polymers dope composition and spinning conditions.

The effect of the main operating conditions such as absorbent temperature, CO₂ pressure and absorbent flow rate on the physical and chemical CO₂ absorption flux of the PVDF membranes is investigated in chapter 7. The results of long-term operation are presented, as well.

The general conclusions drawn from this research and some recommendations for future research are provided in chapter 8.

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