

SURFACE MODIFIED POLYVINYLIDENE FLUORIDE HOLLOW FIBER  
MEMBRANE CONTACTOR WITH DIFFERENT AIR-GAPS FOR  
CARBON DIOXIDE ABSORPTION

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*To my beloved mother, father and sister for their endless love, support and  
encouragement*

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## ABSTRACT

The main objective in this research was to study the effect of air-gap length, one of the main spinning parameters, on the structure and carbon dioxide (CO<sub>2</sub>) absorption performance of hollow fiber membrane (HFM), while other spinning conditions were kept constant. Firstly, surface modified Polyvinylidene fluoride (PVDF) hollow fiber membranes were spun via dry-wet spinning method under different air-gap lengths (0-20 cm). Then the morphology of prepared membranes was evaluated by scanning electron microscopy (SEM). Also membranes structure was examined in terms of gas permeation, overall porosity, critical water entry pressure (CEPw) and contact angle. To determine the CO<sub>2</sub> flux of HFMs, a system of gas-liquid membrane contactor was used. Experimental results of this study reveal that by increasing the air-gap distance from 0 to 20 cm, wetting resistance and contact angle of fabricated membranes increased due to enhancement of membrane surface hydrophobicity in higher air-gaps. Moreover, a decrease in average pore size of fabricated membranes was observed in higher air-gaps. The highest helium (He) permeation was achieved for the spun fiber at the air-gap of 10 cm. From CO<sub>2</sub> absorption experiment it was found that the prepared membrane at the air-gap of 10 cm had the maximum CO<sub>2</sub> flux of  $1.57 \times 10^{-3}$  mol/m<sup>2</sup>.s at the absorbent flow rate of 300 ml/min, which was significantly higher than CO<sub>2</sub> flux of other PVDF membranes produced by other researchers. This significant increase in the CO<sub>2</sub> flux could be related to its high effective surface porosity. Considering the high CO<sub>2</sub> flux of this membrane, it can be concluded that in this study, the optimum air-gap distance was 10 cm to fabricate surface modified PVDF hollow fiber membranes using dry-wet spinning method. Lastly, it was found that applying an appropriate air-gap length for fabrication of surface modified hollow fiber membranes could be a promising method to improve CO<sub>2</sub> removal in membrane contactor systems.

## ABSTRAK

Objektif utama kajian ini dijalankan adalah untuk mengkaji kesan panjang jarak-udara yang merupakan salah satu parameter utama dalam proses penghasilan membran dalam konfigurasi gentian geronggang, terhadap struktur dan kadar resapan gas karbon dioksida (CO<sub>2</sub>) membran gentian geronggang (HFM). Kondisi-kondisi lain ketika proses fabrikasi membran dijalankan adalah dimalarkan. Langkah pertama, membran gentian geronggang daripada polimer polyvinylidene fluorida (PVDF) yang telah diubahsuai permukaannya dihasilkan melalui kaedah pintalan kering-basah pada jarak-udara (0-20 cm). Kemudian, ciri-ciri fizikal dari segi morfologi permukaan membran dikaji dengan menggunakan alat mikroskopi imbasan elektron (SEM). Struktur membran juga telah dikaji dan dicirikan melalui ujian kebolehtelapan gas, keporosan, tekanan kritikal kemasukan air (CEP<sub>w</sub>) dan sudut sentuh membran. Untuk mengenal pasti kadar resapan CO<sub>2</sub> terhadap HFMs, sistem kontaktor gas-cecair membran telah diaplikasikan. Hasil daripada ujikaji yang telah dijalankan mendapati bahawa semakin tinggi jarak-udara yang digunakan daripada tinggi 0-20 cm, semakin tinggi ketahanan lembapan dan sudut sentuh membran yang disebabkan oleh peningkatan permukaan hidrofobia membran. Nilai kebolehtelapan gas helium (He) yang paling tinggi diperoleh daripada membran yang difabrikasi pada jarak udara 10 cm. Kadar resapan gas CO<sub>2</sub> yang maksimum diperoleh pada jarak-udara 10 cm dengan nilai  $1.57 \times 10^{-3} \text{ mol/m}^2 \cdot \text{s}$  dan kadar aliran bersamaan 300 ml/min yang mana perbezaannya adalah ketara berbanding dengan membran yang telah dihasilkan oleh penyelidik lain sebelumnya. Perbezaan yang ketara dalam kadar resapan gas CO<sub>2</sub> dapat dikaitkan dengan keberkesanan liang terbuka pada permukaan membran. Maka dapat disimpulkan daripada kajian yang telah dijalankan ini, nilai optimum jarak-udara yang diperlukan adalah 10 cm bagi proses fabrikasi membran gentian geronggang yang berasaskan polimer PVDF yang telah diubahsuai permukaannya melalui kaedah/teknik pintalan kering-basah. Yang terakhirnya, dapat dibuktikan dengan mengaplikasikan jarak-udara yang sesuai dalam proses fabrikasi membran gentian geronggang yang telah diubahsuai permukaannya, dapat meningkatkan efisiensi penyisihan gas CO<sub>2</sub> dalam sistem kontaktor membran.

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**LIST OF ABBREVIATIONS**

CEPw	-	Critical water entry pressure
DEA	-	Diethanolamine
DMAc	-	Dimethylacetamide
DMF	-	Dimethylformamide
DMSO	-	Dimethylsulfoxide
EDX	-	Energy Dispersive X-ray
HFM	-	Hollow fiber membrane
MEA	-	Monoethanolamine
NMP	-	N-methyl-1-pyrrolidone
PEG	-	Polyethylene glycol
PEI	-	Polyetherimide
PES	-	Polyethersulfone
PG	-	Potassium glycinate
PP	-	Polypropylene
PSf	-	polysulfone
PTFE	-	Polytetrafluorethylene
PVDF	-	Polyvinylidene fluoride
PVF	-	Polyvinyl fluoride
SEM	-	Scanning electron microscopy
SMM	-	Surface modifying macromolecules

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

The main source for energy generation in industrial and domestic usages is fossil fuel, almost without any alternatives. On the other hand, during combustion of fossil fuels carbon dioxide (CO<sub>2</sub>) will be emitted, which is the main greenhouse gas. The emission of CO<sub>2</sub> in the atmosphere is the most significant cause of global warming. It is expected that concentration of CO<sub>2</sub> will be increased without any substantial actions, major policy and technology changes such as improvement of energy efficiency, enhancement use of nuclear and renewable energy (Favre, 2011).

Beside global climate change, existence of CO<sub>2</sub> in natural gas can also cause other difficulties; it leads to decrease the quality of natural gas, and significant damages to process equipment, for instance corrosion of pipelines, decrease of heating value, and enhancement of transport energy (Atchariyawut *et al.*, 2007). Hence the removal and capture of CO<sub>2</sub> from both industrial and domestic flue gas streams, is a substantial concern to study.

Currently, several methods exist for separation of CO<sub>2</sub> by absorption into alkanolamine aqueous solution by using conventional equipment such as packed columns, bubble columns and spray columns. In these equipment, CO<sub>2</sub> contacts the absorbent and forms a weak complex and then the solution is transferred to a separation unit to remove CO<sub>2</sub> by heating. The use of alkanolamines provides regeneration of liquid absorbent.

Hence, CO<sub>2</sub> capture process involves absorption and desorption units. Conventional equipment used commonly for desorption, but they have operational problems such as flooding and entrainment. Also desorption units operate usually at high temperature and pressure. These shortcomings can adversely influence the energy efficiency.

In recent years, several methods have been applied to remove CO<sub>2</sub> from gas stream. Microporous hollow fiber membrane (HFM) contactor system is a promising choice to overcome the disadvantages of conventional gas absorption, which has been investigated by researchers (Mansourizadeh *et al.*, 2010; Naim *et al.*, 2012; Luis *et al.*, 2011; Feron and Jesen, 2002; Scholes *et al.*, 2010).

Absorption of CO<sub>2</sub> occurs at the mouth of membrane pores, where the gas stream contacts the liquid phase (liquid absorbent) flowing on the opposite side of membrane. In comparison with conventional equipment, gas absorption systems based on membrane, possess several advantages that cause to be applied widely nowadays, for instance offering high specific surface area per unit contactor volume, flexibility (easily scale-up and scale-down), modular structure and small size (Mansourizadeh *et al.*, 2010). In addition, membrane contactors provide higher performance compared to conventional devices, since membrane contactors are compact; they cause the reduction of capital cost and less consumption of energy.



Recently, there is an increasing attention to use gas-liquid membrane contactor system. Many researches have been done to investigate the effect of different parameters such as liquid absorbent and membrane material, on membrane contactor performance. Mansourizadeh *et al.*, (2010) applied polyvinylidene fluoride (PVDF) hollow fiber membranes to fabricate membrane contactor system for CO<sub>2</sub> capturing. PVDF is the most preferable material to produce membrane contactor. They employed additives in spinning dope, which included phosphoric acids and lithium chloride monohydrate. Moreover, Mansourizadeh *et al.*, (2010) produced polysulfone (PSf) hollow fiber membranes through applying various additives in the spinning dopes, these additives are as following: ethanol, glycerol, acetic acid, polyethylene glycol (PEG). In addition, the influence of various additives on the morphology and performance of prepared membrane was investigated by them.

## 1.2 Problem Statement

The membrane pores should be completely gas filled to prevent penetration of liquid phase into the pores. As the liquid feed pressure exceeds the critical water entry pressure (CEP), the lowest needed pressure for permeation of water through membrane pores, the liquid can wet the membrane. CEP<sub>w</sub> is a characteristic parameter that depends on intrinsic membrane characteristics such as its hydrophobicity, pore size and chemical resistance to solvent (Dindore *et al.*, 2004a).

Membrane wetting or pore wetting is one of the most significant parameters in the membrane contactor application, which have an influence on absorption performance. Membrane wetting causes some difficulties that give rise to decreased performance and efficiency of membrane and increase of mass transfer resistance and reduction of CO<sub>2</sub> absorption. The decreased mass transfer in membrane contactor, make the membrane less competitive in comparison with conventional equipment.

Most preferable choices for reduction of the undeniable effect of pore wetting on membrane performance are pore size reduction and increase of membrane surface hydrophobicity. In order to minimize the pore wetting drawback, it is required to fill the pores with gas that will hinder directly the pores filling up with the liquid. Small pore sizes in hollow fiber membrane lead to lower interfacial gas-liquid surface and then reduction of mass transfer flux. So, in order to decrease membrane wettability and mass transfer resistance, it is necessary to fabricate hollow fiber membranes with high hydrophobic surface.

One of the proposed methods to increase the hydrophobicity of the membrane is using hydrophobic surface modified macromolecules (SMM), as an additive in spinning solution. SMM has a lower surface energy, so; it tends to migrate to membrane-air interface to decrease the interfacial energy of the system (greater details about SMM are mentioned in chapter 3). Since, SMM has a hydrophobic part; it increases the hydrophobicity of the membrane surface. On the other hand, one important factor in migration of SMM from polymer dope to the membrane surface is the time between spinning the polymer solution and immersion in coagulation bath. In fabrication of hollow fiber membranes this time is depends on air-gap length.

In this study, interest was centered on the effect of different air-gap lengths on the performance of surfaced modified membranes, while other parameters were kept constant.

### 1.3 Objectives of the Study

Based on the problem statements that mentioned above, the objectives of this study are as follows:

1. To fabricate surface modified PVDF hollow fiber membranes by using hydrophobic surface modifying macromolecules (SMMs) under different air-gap lengths.
2. To study the effect of air-gap lengths on morphology, structure and CO<sub>2</sub> absorption performance of the fabricated membranes.

### 1.4 Scopes of the Study

The following scopes have been considered in order to achieve the above objectives:

1. Preparing polymer dope of PVDF (18 wt.%) using SMM as additive.
2. Dry-wet spinning PVDF hollow fiber membranes under different air-gap lengths from 0 to 20 cm.
3. Characterization of the fabricated membranes, in terms of membrane structure and hydrophobicity, using scanning electron microscopy (SEM), energy dispersive X-ray (EDX), gas permeation, overall porosity, critical water entry pressure and water contact angle measurement.
4. Designing and fabricating an experimental gas-liquid membrane contactor system for CO<sub>2</sub> absorption measurement.
5. Evaluation the performance of the prepared PVDF membranes for CO<sub>2</sub> absorption in a gas-liquid membrane contactor system.

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