

SURFACE MODIFIED HOLLOW FIBER MEMBRANE CONTACTOR FOR
CARBON DIOXIDE ABSORPTION AND DESORPTION

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ABSTRACT

Porous asymmetric polysulfone (PSf) and polyvinylidene fluoride (PVDF) hollow fiber membranes were structurally developed using surface modifying macromolecules (SMMs) as additives to improve hydrophobicity, wetting resistance and carbon dioxide (CO₂) absorption/desorption flux in hollow fiber membrane contactor. The membrane structure was examined in terms of gas permeation, critical water entry pressure, overall porosity, contact angle and mass transfer resistance. The morphology of membrane was studied by scanning electron microscopy (SEM) instrument. The CO₂ absorption and desorption performance of both surface modified membranes were investigated in a hollow fiber membrane contactor system and compared against the unmodified membranes. Pore size, overall porosity and contact angle of fabricated membranes increased significantly by surface modification. Surface modified PVDF and PSf membranes showed higher CO₂ absorption and stripping flux compared to plain PVDF and PSf membranes. Results of long-term study demonstrated that after an initial CO₂ flux reduction the surface modified membranes performance maintained constant over 130 h operation. By increasing SMM concentration in spinning dope to 6 wt.%, CO₂ absorption and stripping flux increased. However, by increasing SMM concentration to 8 wt.% both CO₂ absorption and stripping flux decreased, considerably. Thus, it can be concluded that for surface modification of PVDF and PSf hollow fiber membrane contactor 6 wt.% of SMM as additive is an optimum concentration. From CO₂ stripping experiments it was found that liquid absorbent temperature played an important role on CO₂ stripping flux but gas flow rate had no significant effect. Generally, it was found that the porous surface modified membrane can be a promising alternative for CO₂ removal and stripping process.

ABSTRAK

Membran berliang simetri polysulfone (PSf) dan gentian geronggang polyvinyliden flourida (PVDF) telah dibangunkan strukturnya menggunakan makromolekul pengubahsuaian permukaan (SMMs) sebagai bahan tambah untuk meningkatkan kehidrofobikan, rintangan pembasah dan fluks penyerapan / nyah penyerapan karbon dioksida (CO_2) dalam kontaktor membran gentian geronggang. Struktur membran telah diperiksa dari segi penyerapan gas, tekanan kritikal kemasukan air, keseluruhan keliangan, sudut sentuhan, dan rintangan pemindahan jisim. Morfologi membran telah dikaji menggunakan mikroskopi pengimbasan elektron (SEM). Penyerapan CO_2 dan prestasi nyah penyerapan bagi kedua-dua membran permukaan terubahsuaian telah dikaji dengan sistem kontaktor membran gentian geronggang dan dibuat perbandingan. Saiz liang, keliangan keseluruhan dan sudut sentuh membran meningkat dengan ketara dengan pengubahsuaian permukaan. Permukaan membran PVDF dan PSf yang diubahsuaian menunjukkan penyerapan CO_2 dan fluks pelucutan yang lebih tinggi berbanding PVDF dan membran PSf yang tidak diubahsuaian. Keputusan kajian jangka panjang menunjukkan bahawa selepas pengurangan awal fluks CO_2 , prestasi membran permukaan diubahsuaian adalah tidak berubah selama lebih 130 jam operasi. Dengan meningkatkan kepekatan SMM dalam larutan polimer hingga 6% berat, penyerapan CO_2 dan fluks pelucutan meningkat tetapi selepas peningkatan kepekatan SMM kepada 8% berat, kedua-dua fluks penyerapan CO_2 dan pelucutan menurun dengan ketara. Oleh itu, dapat disimpulkan bahawa untuk pengubahsuaian permukaan PVDF dan PSf membran gentian geronggang kontaktor, 6% berat SMM sebagai bahan tambah adalah kepekatan optimum. Daripada eksperimen pelucutan CO_2 , didapati bahawa suhu penyerap cecair memainkan peranan penting kepada fluks pelucutan CO_2 tetapi kadar aliran gas tidak mempunyai kesan yang penting. Secara umumnya, membran permukaan berliang diubahsuaian boleh menjadi alternatif yang baik untuk proses penyingkiran dan pelucutan CO_2 .

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LIST OF ABBRIVATIONS

PVDF	—	Polyvinyliden fluoride
PSf	—	Polysulfone
PTFE	—	Poly(tetrafluorethylene)
PP	—	Polypropylene
PEG	—	Polyethylene glycol
NMP	—	N-methyl-2-pyrrolidone
DMAc	—	Dimethylacetamide
DMF	—	Dimethylformamide
DMSO	—	Dimethylsulfoxide
SEM	—	Scanning electron microscopy
T _g	—	Glass transition temperature
CEP _w	—	Critical water entry pressure
EDX	—	Energy-dispersive X-ray
DCMD	—	Direct contact membrane distillation
MEA	—	Monoethanolamine
DEA	—	Diethanolamine

LIST OF SYMBOLS

A	—	mass transfer area (m^2)
C_{CO_2}	—	CO ₂ concentration in the liquid phase ($kmolm^{-3}$)
d_h	—	hydraulic diameter (m)
d_i	—	inside diameter of membrane (m)
d_{ln}	—	logarithmic mean diameter of membrane (m)
d_o	—	outside diameter of membrane (m)
d_s	—	shell inside diameter (m)
D_i	—	diffusivity of species i ($m^2 s^{-1}$ or $cm^2 s^{-1}$)
E	—	enhancement factor (dimensionless)
G_I	—	inert gas flow rate ($mol s^{-1}$)
G_Z	—	Graetz number (dimensionless)
H	—	Henry's constant (dimensionless)
i.d	—	inner diameter (mm)
o.d	—	outer diameter (mm)
J	—	CO ₂ desorption flux ($molm^{-2} s^{-1}$)
K_o^{-1}	—	overall mass transfer resistance
k_G	—	gas-phase mass transfer coefficient (ms^{-1})
k_L	—	physical liquid-phase mass transfer coefficient (ms^{-1})
k_M	—	membrane mass transfer coefficient (ms^{-1})
K	—	equilibrium constant ($m^3 mol^{-1}$)

K_L	—	overall liquid-phase mass transfer coefficient (ms^{-1})
L	—	effective membrane length (m)
M_i	—	molecular weight of species i ($g\ mol^{-1}$)
n	—	number of hollow fiber membrane
N	—	CO ₂ desorption rate ($mol\ s^{-1}$)
$p_{CO_2,i}$	—	CO ₂ partial pressure at gas–liquid interfacial (kPa)
P	—	Pressure (bar)
Re	—	Reynolds number (dimensionless)
Sc	—	Schmidt number (dimensionless)
Sh	—	Sherwood number (dimensionless)
T	—	temperature (K)
V_i	—	molar volume of species i ($cm^3\ mol^{-1}$)
x_i	—	mole fraction of species i in the liquid phase
y_i	—	mole fraction of species i in the gas phase
Y	—	mole ratio (dimensionless)
Z	—	membrane length (m)

Greek letters

Ω	—	mass percent of amine
Ω_D	—	collision integral for molecular diffusion
φ_i	—	volume fraction of component i
α	—	CO ₂ loading ($mol\ mol^{-1}$)
δ	—	membrane thickness (m)

ε	—	membrane porosity (dimensionless)
λ	—	two-body interaction
μ	—	viscosity ($mPa\ s$)
ν	—	kinematic viscosity ($cm^2\ s^{-1}$)
τ	—	membrane tortuosity (dimensionless)

Subscripts

A	—	component A
B	—	component B
<i>b</i>	—	bulk
<i>f</i>	—	fiber
<i>h</i>	—	hydrolic
<i>i</i>	—	inner
<i>l</i>	—	liquid
<i>g</i>	—	gas
<i>lm</i>	—	log mean

CHAPTER 1

INTRODUCTION

1.1 Research Background

Carbon dioxide (CO₂) is one of the most important greenhouse gases produced by human activities such as industries and domestic usages. Release of this gas in air increases global warming . Therefore, it is essential to remove CO₂ from industrial and domestic flue gas streams in order to manage future climate changes. In addition, with growing concern about gas emissions into atmosphere, improved and economical gas purification equipment will be in great demand in the near future.

Many methods exist to remove CO₂ by absorption into aqueous solution of alkanolamines using conventional equipment including packed columns, bubble columns, and spray columns. The use of aqueous alkanolamines allows regeneration of the liquid absorbents by simple heating. Therefore, a typical process for CO₂ capture consists of two major units, absorption and desorption. Desorption is commonly carried out by using conventional columns that have operational problems such as flooding, channeling, and entrainment. Usually, the stripper unit operates at slightly above normal pressure and high temperature (Khaisri *et al.* 2011).

Recently, several techniques has been developed for capturing/stripping of CO₂. Microporous hollow fiber membrane contactor system is a favorable choice that has attracted researchers attention (Mansourizadeh and Ismail. (2010a, 2010c), Bakeri *et al.* (2010, 2012b), Naim *et al.* 2012). Fluids are contacted using an appropriate membrane formation. For example in a hollow fiber membrane, the gas-liquid interface is created at the mouth of membrane pores.

Among the numerous advantages of membrane-based gas absorption and desorption over conventional contacting devices one can refer to high surface-area per-unit contactor volume, independent flow rate control of gas and liquid without any flooding, loading, foaming or entrainment, known gas-liquid interfacial area, small size, modular and easy scale- up or scale-down (Mansourizadeh and Ismail, 2009).

Since 1980, much research has been conducted for capturing of the major greenhouse gas (carbon dioxide) from gas streams using a gas-liquid membrane contactor system. To achieve this, researchers have taken into considerations various factors including liquids absorbent, materials for membrane fabrication, and membrane modules to enhance CO₂ removal and stripping.

Recently, Mansourizadeh *et al.* (2010b) used polyvinylidene fluoride (PVDF) hollow-fiber membranes to produce membrane contactors for CO₂ capture. They used ortho-phosphoric acids and lithium chloride monohydrate as additives in spinning dope. Mansourizadeh and Ismail (2010a) also fabricated polysulfone (PSf) hollow fiber membranes by using various additives in the spinning dopes. They used polyethylene glycol (PEG200), ethanol, glycerol and acetic acid as the additives and studied effect of additives on the structure and performance of fabricated membrane for carbon dioxide (CO₂) capture in hollow fiber membrane contactor system. Bakeri *et al.* (2010) fabricated polyetherimide (PEI) hollow fiber membranes with different

concentration of polymer in spinning dope. They used prepared membranes for CO₂ removal in hollow fiber membrane contactor.

Membrane contactors were also applicable for desorption or regeneration of liquid absorbents. Khaisri *et al.* (2011) developed a membrane contactor based regeneration unit to strip CO₂ gas from CO₂ loaded monoethanolamine (MEA) solution. They employed Poly(tetrafluorethylene) (PTFE) hollow fiber membranes to test the desorption performance. The experimental results showed that the CO₂ desorption flux increased with an increase in the liquid velocity, operating temperature, and MEA concentration. They found that excessive increase of MEA concentration resulted in the decrease of the overall mass transfer coefficient due to the effect of viscosity. The maximum MEA concentration that gave the highest CO₂ desorption performance in their work was 5 kmolm⁻³. They also found that the gas phase mass transfer resistance in gas stripping membranes has a minor effect on the CO₂ desorption flux as generally found in a gas absorption membrane. They showed that the desorption rate increased by a factor of two when the available membrane surface was doubled. It indicated that the gas stripping membrane contactor can be linearly scaled-up. Membrane porosity affected the CO₂ desorption flux as well as the membrane wetting. Their experimental results also showed that high membrane porosity resulted in high desorption performance, but the long term performance dropped due to the membrane wetting.

Koonaphapdeelert *et al.* (2009) fabricated ceramic hollow fiber membrane contactors for CO₂ stripping from a monoethanolamine (MEA) solution at high temperature. They found that the membrane contactors could be operated very well even in the region of an ordinary column showing flooding or loading. The maximum capacity factor tested in the experiment was at least 2–10 times higher than the flooding line without any sign of flooding.

A study of CO₂ desorption from CO₂ loaded 2-amino-2-methyl-1-propanol (AMP) solution using the membrane contactor was carried out by Kumazawa (2000). Polytetrafluoroethylene (PTFE) hollow fiber membranes were used in the experiments. It was found that the desorption process was controlled by diffusion and chemical reaction in the liquid film. Their results showed that the overall mass transfer coefficient increased with an increase in AMP solution concentration and CO₂ loading in the solution.

Naim *et al.* (2012) prepared microporous PVDF hollow fiber membranes via wet spinning process for CO₂ stripping from aqueous diethanolamine (DEA) solution. They studied the effects of LiCl concentration in the polymer dope on the membrane properties and the stripping performance of the membranes. Their results demonstrated a linear increase of stripping flux and stripping efficiency as the LiCl concentration increased in the polymer dope. As a result, the stripping flux was found the highest when a combination of finger-like and sponge-like structures was formed at 5 wt% LiCl. The maximum stripping efficiency thus achieved was 62% at 5 wt% LiCl and 0.45 m s⁻¹ of liquid velocity. Finally, they concluded that an enhanced CO₂ stripping flux and efficiency can be achieved by improving the structure of the PVDF hollow fiber membranes.

Thus, the advantages of membrane gas absorption contactors facilitate the use of this technology in acid gas removal from flue gases, natural gas and industrial gas streams, which have prompted investigators to consider various potential.

1.2 Problem Statement

One of the most important factors in gas-liquid membrane contactor which affects absorption and desorption performance is pore wetting. The penetration of

liquid into membrane pores should be prevented as pore wetting reduces the mass transfer in contactor significantly and makes it less competitive compared to the conventional column. One cause of pore wetting is capillary condensation (Mavroudi *et al.* 2006), but more importantly the pressure of the feed liquid should surpass a critical value for the liquid to enter into push the liquid pores. This critical value, called liquid entry pressure of water, depends on some properties of membrane such as pore size, hydrophobicity, surface roughness and chemical resistance to solvent (Dindore *et al.* 2004) and also, on the surface tension of solvent and operating conditions of absorption process. Thus, it is possible to reduce the wettability of membranes by decreasing pore size and using membranes of high hydrophobic surface. In hollow fiber membrane contactor furthermore hydrophobicity, pore size is important as well. Hollow fiber membranes with very small pore size show low mass transfer flux due to lower interfacial surface of gas and liquid. Therefore, in order to decreasing wettability of membrane and increasing mass transfer flux, this is essential to fabricate hollow fiber membrane with high hydrophobic surface and large pore size.

The choice of membrane material affects phenomena such as absorption and chemical stability under condition of actual application. This implies that the requirements for the polymeric material are not primarily determined by the flux and selectivity but also by the chemical and thermal properties of the material. Among various hydrophobic polymers, Polypropylene (PP) and Poly(tetrafluorethylene) PTFE are the most popular materials that are fabricated as symmetric membranes for gas absorption process. However since 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. However, some other hydrophobic polymers like PVDF and PSf can be used to prepare asymmetric membranes via phase-inversion method. It is possible to prepare an asymmetric membrane with high surface porosity and ultra thin skin layer to reduce membrane mass transfer resistance (Ismail and Lai, 2003, Yeow *et al.*, 2004, Mansourizadeh and Ismail, (2010a, 2010c)).

It is possible to decrease membrane wetting by using membranes with high hydrophobic surface. One method to change the hydrophobicity of a membrane surface is to use hydrophobic surface modifying macromolecule (SMM) as an additive to the casting or spinning dope. Hydrophobic SMMs are macromolecules with an amphipathic structure. Their main chain consists of a polyurea or polyurethane polymer (hydrophilic part), which is end-capped with two low polarity fluorine-based polymer (oligomer) chains (hydrophobic part). Since SMM has lower surface energy, after casting or spinning the polymer solution, it tends to migrate to the membrane-air interface to reduce the interfacial energy of the system, making nano-scale agglomerates on the membrane surface and changing the surface properties of the membrane (Pham *et al.* 1999).

One of the important parameter in migration of SMM from the polymer dope to the surface of the membrane is the time between casting or spinning the polymer solution and immersion in the coagulation bath. For the flat sheet membrane, this time can be as long as needed, but in the hollow fiber membrane fabrication process, this time is very limited and depends on the air gap length. In order to study of the air gap effects on the morphology of hollow fiber membranes, several researches have been done. Bakeri *et al.* (2012a) studied the effect of air gap length of surface modified polyetherimide PEI hollow fiber membrane by application of Response Surface Methodology (RSM). Their regression models could provide some statistically meaningful results. For example, their model for membrane pore radius predicted that plot of membrane pore radius versus air gap has a minimum point. Khulbe *et al.* (2007) fabricated PES hollow fiber membrane with blending 1.5 %wt. of SMM in spinning dope. Their results showed the contact angle of the outer surface of the fabricated membranes increased significantly when the air gap had increased from 10 to 30 cm, but the pores diameter were almost constant in that range of air gap.

Most of the studies conducted on membrane surface modification using SMM, have been focused on flat sheet membranes and investigations on SMM application for the surface modification of hollow fiber membranes are rare (Bakeri

et al. 2012a, 2012b, Khulbe *et al.* 2007, Bolong *et al.* 2009). For example, the hydrophobic SMM was used to improve the surface hydrophobicity of polyetherimide (PEI) flat sheet membranes for membrane distillation (Khayet *et al.* 2009). The hydrophobic SMM was used to change the hydrophobicity of polyethersulfone (PES) ultrafiltration flat sheet membranes for the separation of humic acid from water. Their results showed that the mean pore size of the surface modified membrane was lower than the unmodified membrane, which leads to higher fouling resistance (Zhang *et al.* 2003). The hydrophobic SMM was added into a PVDF casting solution and the effects of the solvent evaporation time and the SMM concentration in the casting dope were investigated. The surface modified membranes were also used in pervaporation experiments to separate water/chloroform mixtures (Khayet *et al.* 2002b). The authors also studied the blending of hydrophobic SMM into the casting solution to make a composite hydrophilic/hydrophobic membrane for the DCMD process. The composite membrane has a thin hydrophobic top layer which facilitates the transfer of vapor through the membrane, and a thick hydrophilic sublayer which reduces the heat loss across the membrane (Khayet *et al.* 2006). Bakeri *et al.* (2012b) fabricated surface modified PEI hollow fiber membranes where they used SMM as additive in the spinning dope. They evaluated the performance of the surface modified membranes in a contactor application for CO₂ absorption. Their results showed that surface modified membranes have superior performance compared to commercial and in-house made hydrophobic membranes.

Therefore, it is very important to develop porous asymmetric membrane structure with high hydrophobic surface and low mass transfer resistance, which are favorable for gas absorption and desorption in gas-liquid membrane contactor system.

1.3 Objectives of Study

Based on the above-mentioned problem statements, therefore the objectives of the present study are as follows:

- i. To fabricate PSf and PVDF hollow fiber membranes, the surface of which is modified by blending hydrophobic surface modifying macromolecules.
- ii. To investigate the morphology and as well as structure of membranes in terms of gas permeation, overall porosity, critical water entry pressure, water contact angle and mass transfer resistance.
- iii. To evaluate the performance of fabricated PVDF and PSf membranes for CO₂ absorption and desorption and compare their performance.

1.4 Scope of the Study

To achieve the objectives, the following scopes have been considered:

- i. Preparation polymer dope of PVDF (18wt.%) and PSf (15 and 18 wt.%) using SMM (1, 2, 4, 6 and 8 wt.%) as additive.
- ii. Dry-wet spinning PVDF and PSf hollow fiber membranes and characterization of the membrane in terms membrane structure and hydrophobicity.
- iii. Designing and fabricating an experimental gas-liquid membrane contactor system for CO₂ absorption and stripping.
- iv. Comparing absorption and desorption performance of surface modified PVDF and PSf membranes with plain PVDF and PSf membranes.

- v. Studying the effects of SMM concentration on the structure and performance of the surface modified PVDF and PSf hollow fiber membranes for CO₂ absorption and desorption process.
- vi. Investigating the effects of operating parameters on the performance of CO₂ stripping flux.
- vii. Assessing the performance of surface modified PVDF and PSf hollow fiber membranes for CO₂ removal in long-term applications.

1.5 Organization of the Thesis

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

In chapter one, background of the study, problem statement, objective and scope of the research were presented. Chapter two discusses different aspects of hollow fiber gas-liquid membrane contactors for carbon dioxide removal and stripping in details. In addition, the structure and properties of surface modifying macromolecules (SMM) and their application in membrane technology is presented. The methodology of the membrane fabrication and characterization are described in details in chapter three.

Fabrication of porous surface modified PVDF and PSf hollow fiber membrane using a dry-wet phase inversion process, characterization of fabricated membranes and application of membranes for CO₂ absorption and desorption are investigated and the results are presented in chapter four. The effect of SMM concentration on the morphology and performance of surface modified PVDF and

PSf hollow fiber membrane contactor for CO₂ absorption and stripping are presented in chapter four as well.

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

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