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

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ABSTRACT

Porous polyvinylidene fluoride (PVDF) and polyetherimide (PEI) hollow fiber membranes were developed for CO_2 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_2 stripping performance of PVDF membrane were investigated. Different polymer concentrations of PEI membranes were studied and their effects on membrane structure and CO_2 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_2 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 4.0×10^{-2} mol/m^{2}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_2 stripping application.

ABSTRAK

Membran gentian geronggang polivinilidin florida berliang (PVDF) dan polieterimida (PEI) dibangunkan untuk penyingkiran karbon dioksida (CO_2) 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_2 pada membran PVDF telah dikaji. Pelbagai kepekatan polimer untuk membran PEI telah dikaji dan kesan terhadap struktur membran dan prestasi penyingkiran CO_2 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 cesair 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_2 oleh membran PVDF dengan bahan tambah polieterlina glikol (PEG) menunjukkan fluks penyingkiran CO_2 dan keberkesanan penyingkiran yang tertinggi berbanding dengan sampel-sampel membrane lain. Peningkatan kepekatan LiCl pada membran PVDF, meningkatkan prestasi fluks penyingkiran dan ini berkaitan 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_2 yang tertinggi 4.0×10^{-2} molm^{-2}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_2.

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LIST OF ABBREVIATIONS

AFM	-	Atomic force microscopy
CO_2	-	Carbon dioxide
DEA	-	Diethanolamine
DMAc	-	Dimethylacetamide
FESEM	-	Field emission scanning electron microscopy
HCl	-	Hydrochloric acid
H_2S	-	Hydrogen sulfide
LEPw	-	Liquid entry pressure of water
LiCl	-	Lithium chloride
MEA	-	Monoethanolamine
M	-	Molarity
MPa	-	Megapascal
N_2	-	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_2	-	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_{ln}	-	log mean diameter of the fiber (m)
D_i	-	diffusivity of species (m^2/s)
δ	-	membrane thickness (m)
ε	-	membrane porosity (dimensionless)
ε_e	-	effective membrane porosity (dimensionless)
τ	-	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)
ρ	-	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)
μ_i	-	viscosity of species (mPa s)
Ω	-	percent mass (%) of solution
α	-	CO_2 loading (mol CO_2/ mol amine)
Re	-	Reynolds number (dimensionless)

Sc	-	Schmidt number (dimensionless)
Sh	-	Sherwood number (dimensionless)

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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_2 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_2 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_2 emissions.

In industrial and natural gas processing, removal of acid gases (mainly CO_2 and H_2S) 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_2 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_2. For stripping process, Weiland *et al.* (1982) designed and analysed packed column for CO_2 stripping from monoethanolamine in gas purification process. Xu *et al.* (1995) used packed column for CO_2 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_2 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 Mojonnier, 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_2 absorption. These include the enhancement of gas permeability (Yeow *et al.*, 2004), high CO_2 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_2 absorption performance (Atchariyawut *et al.*, 2006). Up to present, experimental results on the applications of polymeric membrane in CO_2 stripping have been scarcely reported (Khaisri *et al.*, 2011; Simioni *et al.*, 2011a). Khaisri *et al.* (2011a) performed CO_2 stripping from loaded aqueous monoethanolamine (MEA) solution by using PTFE hollow fiber membrane. A study on plasma sputtering nylon membrane for CO_2 stripping has was 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_2 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 ($fSiO_2$) inorganic layer was studied by Zhang and Wang (2013) for CO_2 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_2 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.

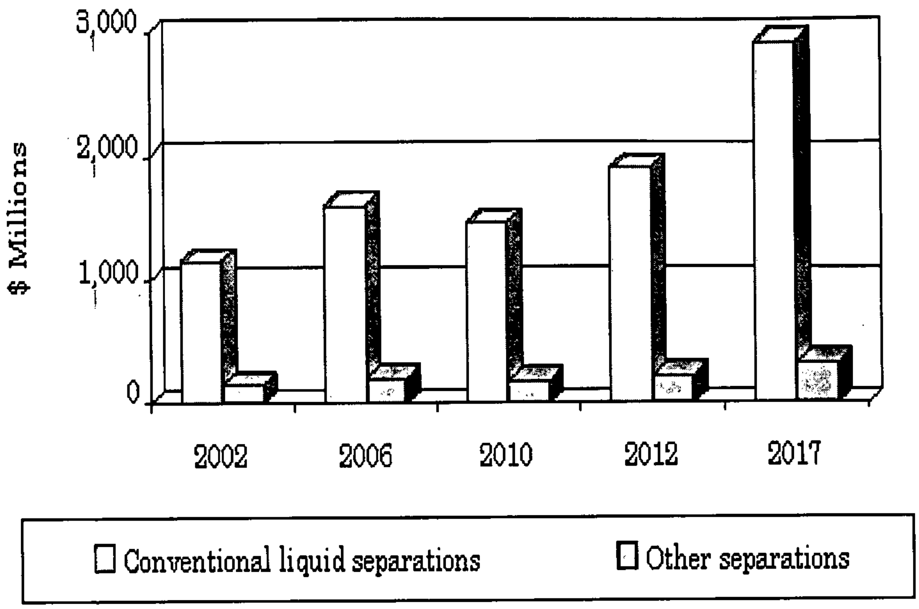

Figure 1.1: Membrane market potential (BCC Research LLC., 2012)

1.2 Problem Statement

In order to be feasible for CO_2 stripping, the membrane contactor should be equipped with a novel membrane that exhibits high CO_2 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_2 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_2 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_2 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_2 stripping performance in membrane contactor system.
ii. To evaluate the effects of additive concentrations on the PVDF hollow fiber membrane surface characteristics and CO_2 stripping performance in membrane contactor system.
iii. To evaluate the potential of polyetherimide (PEI) hollow fiber membrane in CO_2 stripping via membrane contactor application.
iv. To evaluate the long term performance of PVDF and PEI hollow fiber membrane in CO_2 stripping via membrane contactor system.