SUPERHYDROPHOBIC POLYMERIC HOLLOW FIBER MEMBRANE CONTACTORS FOR CO_2 ABSORPTION

HARITH NOORI MOHAMMED

UNIVERSITI SAINS MALAYSIA

2014

SUPERHYDROPHOBIC POLYMERIC HOLLOW FIBER MEMBRANE CONTACTORS FOR CO_2 ABSORPTION

by

HARITH NOORI MOHAMMED

Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy

August 2014

ACKNOWLEDGMENTS

First, I express my profound thanks and praise to **ALLAH**, the Almighty, the most Gracious, the most Merciful and peace be upon His Prophet Mohammad (Sallahu alihi wa sallam).

I am highly grateful to my supervisor Prof. Dr. Abdul Latif Ahmad for his guidance, encouragement, expert suggestions and generous support throughout this work. I would also like to extend my heartfelt thanks to Dr. Ooi Boon Seng and Dr. Leo Choe Peng for their support throughout the work. I really was honored to have the opportunity to work under the supervision of all of them.

I would also like to express my appreciation to the Dean, Prof. Dr. Azlina Harun @ Kamaruddin, Assoc. Prof. Dr. Mohamad Zailani Abu Bakar, Assoc. Prof. Dr. Mohd Azmier Ahmad and Assoc. Prof. Dr. Ahmad Zuhairi Abdullah, Deputy Deans of the School of Chemical Engineering USM, for their continuous support and help rendered throughout my studies. My sincere thanks go to all the respective lecturers, staffs and technicians in the School of Chemical Engineering, USM, for their cooperation and support without any hesitation.

I would like to thank all graduate students working under the supervision of Prof. Dr. Abdul Latif Ahmad, Dr. Ooi Boon Seng and Dr. Leo Choe Peng for their

help in the past several years during my study. I would also like to extend my sincere and deepest gratitude to all my adored friends, in Malaysia and in Iraq for their unparalleled help, kindness and moral support towards me. Very special thanks goes to my dear friends Ahmad Daham, Abdullah Adnan, Zainab Abbas, Muataz, Ali Sabri, Saad Raheem, Arkan, Thamer Fahad Tadahmun Ahmed for their useful help and companionship. Also I wish to express my deepest appreciation to Universiti Sains Malaysia for providing comfortable environment that make me feel at home.

I am thankful to my beloved parents for supporting me during the period of my study. Special thanks goes to my darling wife for her continual support, constant prayers and encouragement. My profound gratitude also goes to my children, Abrar, Anas and Lyan, who gave me some recreation time to make this thesis possible. My enormous gratitude to dear brother and wonderful sister for their constant support and encourage.

Finally, it should be mentioned that this thesis was made possible through the help of Almighty Allah (God) and the financial support granted by MOSTI Science Fund (No. 305/PJKIMIA/6013386) and the Membrane Science and Technology Cluster of USM, FRGS (No. 203/PJKIMIA/6071234), RU-PRGS (No. 1001/PJKIMIA/8045029).

Harith Noori Mohammed

January 2014

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

		Unit
a	constant for experimental	-
A	Total contact area	m^2
b	constant for experimental	-
c	constant for experimental	-
$C_{g,i}$	Inlet CO_2 concentration in gas phase	mol/m^3
$C_{g,o}$	Outlet CO_2 concentration in gas phase	mol/m^3
D_{CO2}	CO_2 diffusivity coefficient in absorbent liquid	m/s
$D_{eff,g}$	Effective diffusion coefficient of CO_2 filled membrane pores	m/s
$D_{eff,l}$	Effective diffusion coefficient for CO_2 in the pores filled with the liquid solvent	m/s
$D_{g,b}$	Bulk diffusion coefficient	m/s
$D_{g,k}$	Knudsen diffusion coefficient	m/s
d_h	Hydraulic diameter of the shell side	m
D_i	Inner hollow fiber membrane diameter	m
D_{ln}	Logarithmic mean	m
d_o	outer hollow fiber membrane diameter	m
d_p	Pore diameter	m
f_a	Area fraction of air	-
f_s	Area fraction of solid	-
G_z	Greatz number	-
H_e	Henry’s constant	-
J_{CO2}	CO_2 mass transfer flux	mol/m^2 s
k_B	Boltzmann’s constant	-
k_g	Mass transfer coefficient of gas phase	m/s
k_l	Mass transfer coefficient of liquid phase	m/s
k_m	Mass transfer coefficient of membrane phase	m/s
K_{og}	Overall mass transfer coefficient	m/s
L	Hollow fiber length	m
M	Molecular weight of the gas	g/mol
P	Pressure of the gas	Pa

$Q_{g,i}$	Total inlet gas volumetric flow rate	m^3/s
$Q_{g,o}$	Total outlet gas volumetric flow rate	m^3/s
R	Gas constant	
r	roughness factor	-
R^2	Coefficient of determination	-
Re	Reynolds number	-
r_{pm}	Maximum radius of the membrane pores	m
Sc	Schmit number	-
Sh	Sherwood number	-
T	Gas temperature	K
u_l	Average liquid velocity	m/s
W_d	Weight of dry membrane	g
W_w	Weight of wet membrane	g
$Y_{g,in}$	Volumetric rations of CO_2 in the gas phase at the inlet	%
$Y_{g,o}$	Volumetric rations of CO_2 in the gas phase at the outlet	%
ΔP_c	Critical pressure	kPa

Greek letters

μ_g	Gas dynamic viscosity	Pa s
μ_l	Viscosity of the absorbent liquid	Pa s
ℓ	Membrane thickness	m
$\varnothing$	Packing density	%
γ_L	Liquid surface tension	mN/m
γ_{lg}	surface tension of the liquid-gas interface	mN/m
γ_{sg}	surface tension of the solid-gas interface	mN/m
γ_{sl}	surface tension of the solid-liquid interface	mN/m
ε	Membrane porosity	%
η	CO_2 removal efficiency	%
θ	Water contact angle	degree
θ_f	Contact angle of the flat solid surface	degree
θ_h	Contact angle of the porous superhydrophobic surface	degree
θ_w^*	Wenzel contact angle	degree
ρ_i	Density of isopropanol	g/cm^3

ρ_l	Density of the absorbent liquid	Kg/m^3
ρ_p	Density of membrane polymer	g/cm^3
τ	Membrane tortuosity	-
Ω_μ	Collision integral	-
Ω_D	Collision integral	-

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
AMP	2-amino-2-methyl-propanol
CF_2	Difluoromethane
CF_4	Tetrafluoromethane
CO	Carbon monoxide
CO_2	Carbon dioxide
DEA	Diethanolamine
FGD	Flue gas desulphurization
GC	Gas Chromatography
GtC	Giga ton carbon
H_2O	Water
H_2S	Hydrogen sulfide
HCl	Hydrochloric acid
KOH	Potassium hydroxide
LDPE	Low density polyethylene
LiCl	Lithium chloride
$LiCl\cdot H_2O$	Lithium chloride monohydrate
MEA	Monoethanolamine
MEAD	Monodiethanolamine
MEK	Methyl ethyl ketone
MGAS	Membrane gas absorption system
N_2	Nitrogen
NaOH	Sodium hydroxide

NO_2	Nitrogen oxide
O_2	Oxygen
PE	Polyethylene
PEI	Polyetherimide
PG	Potassium glycinate
PP	Polypropylene
ppm	Part per million
PSA	Pressure swing adsorption
PSF	Polysulfone
PTEF	Polytetraflouroethylene
PVDF	Polyvinylidenefloruride
PZ	Piperazine
SCNR	Selective non-catalytic reduction
SCR	Selective catalytic reduction
SEM	Scanning Electron Microscopy
SO_2	Sulfur dioxide
TCD	*Thermal conductivity detector*
TEM	Triethanolamine
TEPA	Tetraethylenepentamine
TSA	Temperature swing adsorption
WCA	Water contact angle

MEMBRAN PENYENTUH GENTIAN BERONGGA POLIMER SUPERHIDROFOBIK BAGI PENYERAPAN CO_2

ABSTRAK

Dalam beberapa tahun ini perubahan cuaca telah menjadi masalah global disebabkan kenaikan suhu permukaan bumi. Fenomena ini menjadi semakin teruk akibat aktiviti-aktiviti industri disebabkan kenaikan pengeluaran gas rumah hijau (terutamanya CO_2). Pelbagai usaha telah dijalankan bagi memerangkap CO_2 daripada aliran-aliran proses industri. Sistem penyerapan gas membran (MGAS) telah dicadangkan sebagai satu teknik alternatif untuk mengatasi kelemahan proses-proses penyerapan CO_2 secara konvensional. Walaubagaimanapun, masih terdapat pelbagai cabaran dalam usaha untuk mengkomersilkan MGAS seperti kestabilan permukaan membran, kecekapan cecair penyerap dan keserasian antara cecair penyerap dan bahan membran. Untuk mengatasi masalah ini, satu lapisan superhidrofobik polietilena berketumpatan rendah (LDPE) berliang telah disalut pada permukaan luar polipropilena (PP) dan polyvinylidene fluorida (PVDF) membran gentian geronggang melalui kaedah pelarut bukan-pelarut. Parameter untuk menyediakan permukaan rata superhidrofobik (jenis bukan-pelarut, kandungan bukan-pelarut dalam larutan salutan dan kepekatan polimer) telah dikaji dan dioptimumkan. Daripada pemerhatian didapati bahawa bukan-pelarut seperti etanol menghasilkan permukaan polimer dengan sudut sentuhan air (WCA) yang tinggi berbanding metil etil keton apabila digunakan sebagai tambahan bukan-pelarut. Peningkatan kandungan etanol dalam larutan salutan sebanyak 50% (v/v) telah membawa kepada kenaikan WCA daripada 110±2.8° kepada 160±1.4°. Sifat hidrofobik lapisan salutan dianalisa dari segi kekasaran permukaan, struktur fizikal dan sudut sentuhan air.

Didapati bahawa WCA bagi permukaan PP dan PVDF membran gentian geronggang bersalut yang disediakan secara salutan celup langsung adalah kurang berbanding permukaan rata. Kaedah secara tidak langsung telah dicadangkan dan WCA maksimum bagi membran PP dan PVDF yang telah diubahsuai adalah 161±2.3° and 152±3.2°. Suatu sistem MGAS berterusan yang dibina secara dalaman telah direka untuk menilai prestasi membran yang telah diubahsuai dari segi penyingkiran CO_2 daripada aliran gas yang mengandungi 20% (v/v) CO_2 seimbang dengan N_2. Parameter operasi (halaju cecair, halaju gas dan ketumpatan pembungkusan modul membran) dan kesan-kesan lain terhadap penyingkiran CO_2 telah dikaji. Prestasi penyerapan CO_2 telah disiasat bagi cecair-cecair penyerap berbeza iaitu piperazin (PZ), monoetanolamina (MEA), dietanolamina (DEA) campurannya. PZ mempamerkan kecekapan penyerapan yang lebih tinggi berbanding penyerap lain. Dari segi keserasian membran dengan PZ, membran PVDF didapati mempunyai kestabilan permukaan yang tinggi berbanding membran PP. Di samping itu, telah diperhatikan bahawa MEA yang telah diaktifkan mempunyai kecekapan penyerapan CO_2 yang tinggi berbanding DEA yang diaktifkan pada kepekatan dan keadaan operasi yang sama. Rintangan pemindahan jisim melalui modul membran telah ditentukan melalui kaedah plot Wilson. Didapati bahawa rintangan pemindahan jisim cecair merupakan langkah kawalan dalam semua larutan amina. Selain itu, pekali pemindahan jisim meningkat dengan peningkatan kepekatan pengaktif dalam campuran amina.

SUPERHYDROPHOBIC POLYMERIC HOLLOW FIBER MEMBRANE CONTACTORS FOR CO_2 ABSORPTION

ABSTRACT

In recent years the climate change became a global concern due to the increasing of the earth's surface temperature. This phenomenon was exacerbated by the expansion of industrial activities due to the increasing emissions of the greenhouse gas (mainly CO_2). Many efforts were conducted to capture CO_2 from the industrial process streams. Membrane gas absorption system (MGAS) was proposed as an alternative technique to overcome disadvantages of the conventional CO_2 absorption processes. However, there are still many challenges in order to commercialize MGAS such as membrane surface stability, absorbent liquid efficiency and compatibility between absorbent liquid and membrane material. In order to solve this problem, a porous superhydrophobic layer of low density polyethylene (LDPE) had been coated on the outer surface of the polypropylene (PP) and polyvinylidene fluoride (PVDF) hollow fiber membrane via solvent non-solvent coating method. Parameters to prepare superhydrophobic flat surface (non-solvent type, non-solvent content in coating solution and polymer concentration) had been studied and optimized. It was observed that non-solvent like ethanol did produce polymeric surface with higher water contact angle (WCA) compared to methyl ethyl ketone used as non-solvent additives. The increasing of ethanol content in the coating solution up to 50% (v/v) led to the increased of WCA from 110 ± 2.8^{o} to 160 ± 1.4^{o}. The hydrophobicity of the coated layers were analysed in terms of surface roughness, physical structure and water contact angle. It was found that the WCA of the coated PP and PVDF hollow fiber membranes surfaces prepared via direct dip coating were less than the flat surface. Indirect method was proposed and the maximum WCA of modified PP and PVDF membranes were 161±2.3° and 152±3.2°, respectively. A continuous MGAS inhouse-built was designed to evaluate the performance of modified membranes in term of CO_2 removal from gas stream of 20% (v/v) CO_2 balanced with N_2. The operating parameters (liquid velocity, gas velocity and packing density of the membrane module) and other effects on the CO_2 removal were studied. The CO_2 absorption performance was investigated for different absorbent liquids namely piperazine (PZ), monoethanolamine (MEA), diethanolamine (DEA) and their blends. PZ exhibited higher absorption efficiency than other absorbents. In terms of the membrane's compatibility with PZ, PVDF membrane was found to have high surface stability compared to the PP membrane. In addition, it was observed that the activated MEA had CO_2 absorption efficiency higher than activated DEA at the same concentrations and operating conditions. The mass transfer resistance through the membrane module was determined via Wilson plot method. It was observed that the liquid mass transfer resistance was the controlling step in all amine solutions. Moreover, the overall mass transfer coefficient was increased with the increasing of the activator concentration in the amine blends.

CHAPTER 1

INTRODUCTION

1.1 Global climate changes

Carbon dioxide (CO_2) is the largest component of greenhouse gases present in the atmosphere than others such as methane, water vapour, nitrous oxide and ozone. It was proven that the CO_2 is responsible for the increasing of the temperature of the earth's surface. CO_2 causes 9-26% of the greenhouse effect whilst water vapour, methane and ozone cause about 36-70%, 4-9% and 3-7% , respectively (Kiehl and Kevin, 1997).

Part of the energy coming from the sun will be absorbed by the earth system while the other will be reflected back into the space. Consequently, the global warming depends on the balance between the energy entering and leaving the planet's system. Greenhouse gases act like a thick blanket which decrease the energy reflecting to the space and trap into atmosphere thus increase the earth's temperature. CO_2 composes the major part of the blanket in atmosphere which is responsible for the climate change (Arenillas et al., 2005). It was recorded that CO_2 emitted into the atmosphere contributes in approximately 55% of the global warming (Kaithwas et al. 2012).

Since the early 20th century, Earth's mean surface temperature has increased by about 0.8 °C, with about two-thirds of the increase occurring since 1980. This increasing in the earth's temperature during this period of time could attributable to the increasing concentrations of greenhouse gases produced by human activities such as the burning of fossil fuels and deforestation. The emission of the flue gas from the thermal power plants is increasing because 30% of the total global fossil fuel is being used for power generation (Bandyopadhyay, 2011). 40% of the total CO_2 emissions are produced by the burning of fossil fuels in power plants (Desideri, 1999).

It was estimated that future global CO_2 emissions will be increased from ~7.4 giga tons of atmospheric carbon (GtC) / year in 1997 to ~26 GtC/year in 2100 (Mercedes et al., 2004). In Malaysia the largest amount (86.7%) of the CO_2 emissions to the atmosphere at 1994 comes from the burning of fuels to produce the energy as presented in Table 1.1. It was expected that the CO_2 emission will be increased due to the development in the Malaysian industries as well as the increasing of power consumption in urban area.

Table 1.1: Summary of CO_2 emission for Malaysia in 1994 (Gurmit, 2000)

CO_2 emission source	**CO_2 quantity (Giga gram)**	**Weight percent (%)**
Fuel combustion for energy generation	84,415	86.7
Cement production	4,973	5.1
Industrial wastewater treatment	318	0.3
Forest and grassland conversion	7,636	7.8
Total	**97,342**	**100**

From 2000 until 2011, the CO_2 emissions in Malaysia for energy generation has increased about 1.6 times, whereby the CO_2 emissions was increased from 117.57 million metric tons in 2000 to 191.44 million metric tons in 2011 (EIA, 2013). Malaysia is one of the signatories of the Kyoto Protocol; it is not bound by any limit of greenhouse emission (Rahman, 2011). However, an alternative energy resource such as biomass, biogas and solar energy was undertaken by Malaysian's government to reduce the CO_2 emissions.

Advanced technology is continuously revolutionised to reduce CO_2 emission and minimize the risks of the global warming. In general, the universal industrial facility for generation of electrical power is the power plant (Thomas et al., 1997). Fossil fuel is mostly used in the power plant combustion chambers. Therefore, reducing CO_2 emissions to the atmosphere could provide a mid-term solution to alleviate environment impacts and allows human to continue to use fossil energy until the development of a reasonable renewable energy technology.

1.2 Separation technology for CO_2

The technologies for CO_2 capture in fossil fuel-fired power stations are commonly classified as pre-combustion, post-combustion and oxyfuel combustion. The choice of suitable technology is depending on the CO_2 removal step through the fuel burning process (before or after fuel burned). According to this classification, various technologies for CO_2 capture were proposed including absorption, adsorption, membrane, cryogenic, and hybrid applications of these technologies. The performance criteria of the technology are CO_2 capture effectiveness, energy consumption, process economy, and other technical and operational issues (Plasynski, and Chen, 2000)). The third technology (oxyfuel combustion) does not require special equipment, but it is not commercialized currently and it is still under development. Many studies have focused on enhancing the current technologies or developing new approaches of CO_2 removal (Yang et al., 2008). The conventional processes applied for CO_2 removal from flue gas are varying from simple to complex multi steps processes. Usually, one of the following processes is considered.

1.2.1 Absorption process

The exhaust gas in the post-combustion technology contains CO_2 at low partial pressure and concentration (4 – 14%, v/v) which represents an important limitation for CO_2 capture. Therefore, the absorption process is a promising technology for the CO_2 removal at flue gas streams conditions. The absorption process can be classified into physical and chemical absorption process according to the type of solvent used.

1.2.1.a Physical absorption

In this process, the CO_2 physically absorb into a solvent based on Henry's law. The law states that at constant temperature the solubility of gases in a solvent is directly proportional to the partial pressure of the gas above the solution (Hobler, 1966). As such, the CO_2 absorption takes place at high CO_2 partial pressure and low temperature. As a result, the energy consumption mainly originate from the flue gas pressurization. Physical absorption is therefore acceptable for the flue gas streams of low CO_2 concentration. However, it is not economical for the streams with CO_2 concentration less than 15 vol% (Chakravarti et al., 2001).

The solvent regeneration step occurs by the pressure reduction, heating or both. There are many existing commercial processes using different solvent. The typical solvents are Selexol (dimethylether or propylene), Rectisol (methanol), Purisol (n-Methyl-2-pyrollidone), Morphysorb (morpholine) and Fluor (propylene carbonate) (Olajire, 2010 and Yu et al., 2012). The advantage of Selexol process is the removing possibility of both CO_2 and H_2S gases under low temperature and the solvent regeneration can be achieved mainly by depressurization (Olajire, 2010). However, the operation cost in Morphysorb process is 30% to 40% lower than that for Selexol process (Gielen, 2003).

1.2.1.b Chemical absorption

The chemical absorption referring to the reaction of CO_2 with a chemical solvent to form a weakly bonds intermediate compound. These bonds are broken in the regeneration process by heating to achieve the virgin solvent and CO_2 rich stream. Solvent of high stable compound could increase the energy required in the regeneration stage. In chemical absorption process, relatively high selectivity could be achieved to produce high purity CO_2 stream. By combining the advantages of chemical absorption and flue gas operating conditions (low CO_2 partial pressure, low CO_2 concentration, large flow gases and high temperature) chemical absorption process is well suited for CO_2 removal from industrial flue gases.

Typically, amine solutions are widely used as solvent in chemical absorption process because it is a relatively cheap chemicals, even cheap solvent like monoethanolamine (MEA) (Rao and Rubin, 2002). However, others acidic contaminations such as SO_2 and NO_2 must be removed from flue gas stream before absorption stage. The drawback of these gases is the formation of heat stable salts when reacts with solvent such as (MEA). Usually, SO_2 concentrations in flue gas exhaust of less than 10 ppm are recommended (Davidson., 2007). A flue gas desulphurization (FGD) unit is commonly used to remove SO_2, while selective catalytic reduction (SCR), selective non-catalytic reduction (SCNR) or low NOx burners are employed to remove NOx contaminations. The flue gas must be cooled down to 45-50 ^{o}C before it is being introduced to the absorber (Rao et al., 2004; Ramezan et al., 2007). This operating temperature could enhance CO_2 absorption performance and minimize solvent loss due to evaporation (Wang et al., 2011).

1.2.2 Adsorption process

In principal, the adsorption process occurs when the gas molecules adhere on the surface of the solid adsorbent. The gas-solid contacting can be either physical (physisorption) or chemical (chemisorption). The adsorption quality is determined by the adsorbed particle properties (molecular size, molecular weight and polarity) and the characteristics of the adsorbent surface (polarity and pore size). The CO_2-rich adsorbent can be regenerated by the heat processing (temperature swing adsorption,TSA) or pressure reduction (pressure swing adsorption, PSA). In terms of energy saving, solid sorbents need lower energy in regeneration stage compared to the amine process due to the heating and cooling requirement of the large quantities of water presence in the solvent solution (Figueroa et al., 2008).

The widely applicable adsorbents in CO_2 capture are activated carbon (Himeno, et al., 2005), mesoporous silica (Zelenak et al., 2008), metallic oxides (Lee et al., 2008) and zeolites (Zhao et al., 2007). Numerous adsorbents like zeolites and carbons are commercialized for the removal of CO_2 from flue gases (Belmabkhout, et al., 2011). The main advantage of the adsorption process for the CO_2 capture is the energy saving potential compared to the amine absorption process. However, the most available adsorbents have low adsorption capacity and selectivity. In addition, the treated flue gas stream must have high CO_2 partial pressure, high CO_2 concentrations and low temperature.

1.2.3 Cryogenic process

Cryogenic separation process of gas mixture involves the inducing of phase changes in the gas mixture at low temperature and high pressure conditions. The advantage of this process is the possibility to produce stream of high CO_2 purity (> 90%) in liquid form, which can be transported conveniently for sequestration (Olajire, 2010). In addition, there is no pre-treatment process for the exhaust gases. Despite of the high CO_2 recovery, cryogenic processes are inherently energy intensive (Plasynski & Chen, 2000). The most promising application for cryogenics is expected to be for the separation of CO_2 from stream of high pressure gases and high concentration of CO_2 conditions in the oxyfuel combustion process. In this case, two advantages are achieved namely high CO_2 concentration stream and pure oxygen recycled stream to the combustion chamber.

1.2.4 Membrane process

Membranes are semi-permeable barrier which allow the separation of one or more gases from a feed gas mixture thus producing a specific gas rich permeate stream. The gas separation is taken place by various mechanisms such as solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport. Molecular sieve and solution/diffusion mechanisms are considered the main separation mechanism for nearly all gas separating membranes (Olajire, 2010).

The membranes currently used for the gas separation can be classified according to their material as organic (polymeric) and inorganic (carbon, zeolite, ceramic or metallic). The major characteristics impose on the membrane performance are; permeability, that is the flux of a specific gas through the membrane, and selectivity, the membrane’s preference to pass one gas species over the other (Olajire, 2010). Therefore, high partial pressure and high concentration of a specific gas must be maintained in the feed stream to increase the driving force across the membrane thus increase gas flux in permeate stream. On the other hand, the membrane material dominates the membrane selectivity. The CO_2 separation from light hydrocarbons based on membrane technology has considerably successful in the petroleum, natural gas and chemical industries due to its simplicity resulting from steady state operation, absence of moving parts and modular construction (Kesting and Fritsche, 1993). Currently, gas separation membranes have not been widely applied for CO_2 removal from flue gases because the relatively high mixture flows and the need for flue gas pressurization (Chowdhury, 2011).

1.2.5 Membrane gas absorption process

Conventionally, bubble-column, venture-scrubber, packed-tower and sieve-tray columns are used in absorption-based CO_2 capture technology to reduce the CO_2 emissions from flue gas. The gases are randomly dispersed in these equipments to form an interfacial area with a liquid absorbent, which is difficult to estimate. In addition, problems of flooding, loading, foaming, channelling, control of the fluid velocity and the scale-up of these systems are difficult.

In order to solve these problems, an alternative membrane gas absorption system (MGAS) was developed to overcome these disadvantages. The advantages and disadvantages of membrane contactor have been discussed in detail by Gabelman and Hwang (1999). In MGAS, flue gas usually flows inside the hollow fiber membranes (lumen), while the liquid flows at the opposite side (shell) and the solvent contacts the gas at the mouths of membrane pores to form mass transfer film. The first technology for such CO_2 absorption was developed by (Qi and Cussler, 1985a; 1985b), who used sodium hydroxide as a solvent in a hollow fiber membrane contactor. The membrane contactor provides greater gas–liquid contact area, and the overall mass-transfer coefficient is therefore three times greater than that in a packed column using same solvent (Sea et al., 2002). As such, it is suitable for high CO_2 concentration applications (well above 20 vol%) (Favre, 2007). Moreover, Falk-Pederson and Dannstorm, (1997) found that a reduction of greater than 70% in equipment size and 66% in equipment weight can be achieved using a membrane contactor instead of conventional columns.

The major disadvantage of membrane gas absorption is the additional membrane resistance in which is not existent in the conventional gas absorption processes. In addition, the membranes have a finite operational life. Therefore, the periodic membrane replacement cost need to be taken into consideration (Gabelman and Hwang, 1999; Li and Chen, 2005).

1.3 Problems statement

In a typical flue gases system, the conditions of low pressure, low CO_2 concentration and high flow rate are not favorable for CO_2 capture in such membrane, adsorption and cryogenic process. In this context, membrane gas absorption is appropriate to remove CO_2 from mixture gases at the aforementioned conditions.

Despite of the advantages of membrane over conventional absorption equipments, the membrane wetting is the major problem in the gas absorption using membrane contactor which determines the CO_2 separation efficiency. The liquid that penetrates membrane pores increase the membrane mass transfer resistance due to the formation of dead zones inside the pores, thus decrease the CO_2 diffusion through the membrane.

The above problem can be solved by using membranes with high water repellency property. This property is characterized by the high water contact angle of the membrane surface. Hydrophobic materials are satisfying this target due to their low surface energies as shown in Table 1.2.

Table 1.2: Surface energy of membrane polymeric materials (Mulder, 1996)

Membrane material	Surface energy (mN/m)
Polytetraflouroethylene (PTFE)	19.1
Polypropylene (PP)	30.0
Polyvinylidenefloruride (PVDF)	30.3
Polyethylene (PE)	33.2

As presented in Table 1.2, Polytetraflouroethylene (PTFE) has lower surface energy thus probably has high wetting resistance than other membrane materials. Unfortunately, PTFE membranes are very expensive in market due to their fabrication difficulty. Increasing the surface hydrophobicity of the cheaper membrane using simple and inexpensive method could enhance the absorption performance and decrease the cost.

Chemical absorption is more preferable than physical absorption because the CO_2 partial pressure required is relatively lower than the latter as well as the high absorption rate. In MGAS, the expensive absorbents with high CO_2 loading capacity and low generation energy requirement such as methyldiethanolamine (MDEA) and 2-amino-2-methyl-propanol (AMP) were activated with promoter additive to increase the CO_2 removal efficiency in most open literature. Therefore, it is useful to improve the CO_2 absorption performance for the cheaper absorbent of low CO_2 loading capacity via promoter additive.

1.4 Research objectives

Objectives of this study are stated as follows:

a) To modify and characterize PP and PVDF hollow fiber membrane to produce superhydrophobic membrane.

b) To fabricate the continuous hollow fiber membrane gas absorption system to capture CO_2 from CO_2/N_2 gas mixture stream.

c) To evaluate the efficiency and stability of the modified membranes in CO_2 absorption process.

d) To determine the mass transfer resistances of the MGAS.

e) To enhance the CO_2 absorption performance using absorbent coupled with promoter additive.

1.5 Scope of study

In this study, PP and PVDF hollow fiber membrane were modified to produce a superhydrophobic membrane surface via facile "solven- non – solvent coating method". A preliminary study was carried out to form a LDPE superhydrophobic layer on a silicon flat surface under different preparation variables. Two non-solvent additives namely ethanol and methyl ethyl ketone (MEK) were used and their efficiency in term of hydrophobicity was evaluated. The concentration of LDPE in xylene as solvent was varied from 10 to 25 mg/mL to investigate the effect of polymer concentration on the properties of coated surfaces.

The hydrophobicity of surfaces were characterized using water contact angle measurements. The structure and morphology of LDPE surfaces were examined via

Scanning Electron Microscopy (SEM). The examination of topographic map for surfaces was conducted via Atomic Force Microscopy (AFM). The hydrophobicity of the superhydrophobic LDPE surface was tested against the different concentrations of corrosive acidic (HCl), basic (NaOH) and aqueous solutions of MEA, AMP and DEA.

Membrane gas absorption system was developed to capture CO_2 from gas mixture (20% CO_2 and 80% N_2). The modified (superhydrophobic) and pristine PP and PVDF membranes were tested in CO_2 absorption system for 10 days. The efficiencies of the tested membranes were evaluated in term of the stability of CO_2 absorption flux under prolong operating time. The performance study of CO_2 absorption in PP and PVDF membranes was conducted using piperazine (PZ), MEA, DEA, activated MEA and activated DEA aqueous amine solution.

In addition, the mass transfer resistances in hollow fiber membrane were determined in PP and PVDF membranes modules. The effect of hollow fiber packing density on the flow conditions that brought about impact of absorption rate thus CO_2 absorption rate was experimentally investigated. As such, empirical correlations were developed in term of Sherwood number as a function of Reynolds number, Schmidt number and module dimensions in shell side of membrane module.

1.6 Organization of the thesis

This thesis consists of five chapters. The climate change and its relation to the CO_2 emission was briefly described in chapter 1 (Introduction). The existing CO_2

removal technologies especially MGAS as well as its principles were discussed. These observations lead to the project problem statements, research objectives and scope of the study.

The chronological developments of membrane gas absorption systems were described in chapter 2 (Literature Review). Past researches focused on the developments of CO_2 were reviewed. The determination methods of mass transfer resistances in MGAS were described.

Chapter 3 (Material and Method) involves details of materials and experimental procedures. Materials details including the general properties of the materials used in the experiments were described. While, experimental procedures focused on the developments of LDPE superhydrophobic layer on the flat silicon sheet as well as on PP and PVDF hollow fiber membranes. Characterization techniques on the membrane surfaces were covered in this chapter. CO_2 absorption measurements, liquid absorbents preparation and development of CO_2 absorption system using hollow fiber membranes were described.

Chapter 4 (Results and Discussions) represents the major section in this thesis in which all experimental results achieved from experimental work based on the objectives stated in Chapter 1 were discussed. The findings included the optimum coating conditions of LDPE layer on the silicon flat sheet; PP and PVDF hollow fiber membranes, membrane characterization, CO_2 absorption efficiency, CO_2 flux and overall mass transfer resistance were presented and discussed.

Outcomes of the study presented in Chapter 4 were summarized in Chapter 5 (Conclusions and Recommendations). Concluding remarks were recorded for each of the findings on the aspect of membranes modification, membrane characterization and CO_2 absorption performance. Recommendations for the future work were proposed based on the limitations encountered in the present study.

CHAPTER 2

LITERATURE REVIEW

2.1 Gas separation

Gas separation is one of the applicable separation technologies which used for a long time in the field of chemical engineering. The chemical absorption process based gas separation has existed for more than 60 years. It was developed primarily for acid gas treating such as CO_2 and H_2S (Kohl and Neilsen, 1997). Over the years, a lot of researches were conducted focused on finding the ultimate solvent for chemical absorption. These solvents include the various classes of amines (primary, secondary, tertiary, and hindered). Improvements to the performance of the current chemical absorption process will probably occur with the development of better solvents and contactors.

Currently, monoethanolamine (MEA) based process is commercially available. It was considered as the best near-term strategy to modernize the existing coal power plants for capturing CO_2 from combustion process due to its high reactivity with CO_2 and low cost of raw materials compared to other amines. Using amine based process, the cooled flue gases flow vertically upwards through the absorption tower (absorber) countercurrent to the amine solution. The CO_2 absorb chemically into the amine solution to form a weakly bonded compound. The resulted CO_2-rich solution heated preliminary in a heat exchanger, then further heated in a reboiler. The formed weakly bonded compound is broken down by the application of heat and therefore a concentrated CO_2 stream will be produced. The hot CO_2-lean amine is cooled down, and then sent back to the absorber. The CO_2 product is separated from the amine in a flash separator, and then taken to the drying and compression unit. Figure 2.1 illustrates the process flow diagram for the CO_2 removal from flue gas stream by chemical absorption.

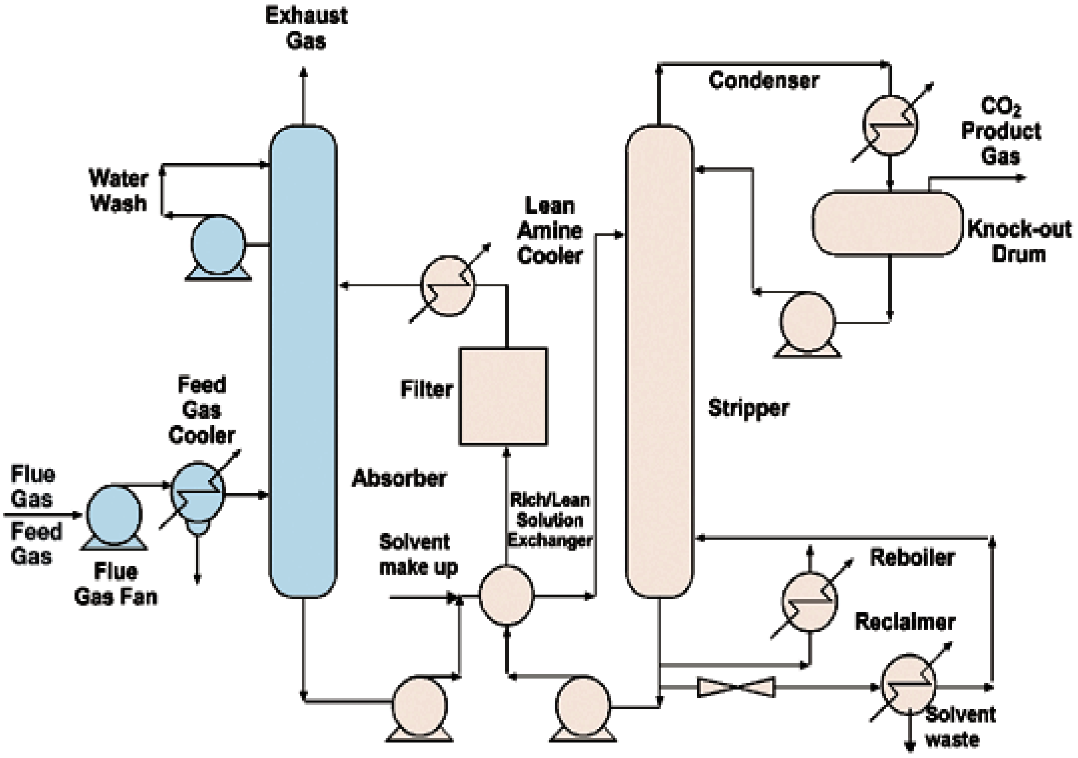

Figure 2.1: Flow diagram for CO_2 capture process by amine (IPCC, 2005)

2.2 Membrane gas-liquid contactors

In recent years, porous membranes have been proposed frequently for fixing gas-liquid interfacial areas. Unlike the conventional gas-liquid contactors used in gas absorption process, membrane gas-liquid contactors are non-dispersive gas-liquid contactors (Dindore, 2003). The membranes used as gas-liquid contactors are inherently non-selective and the solvent used is responsible for the selectivity aspect. Porous polymeric membranes, flat sheet and hollow fiber, are widely used in CO_2

absorption system. The compatibility of absorbent liquid used for gas absorption and membrane materials used as gas-liquid contactor are listed in Table 2.1.

Table 2.1: Compatibility of membrane materials and liquid absorbents (Dindore et al., 2004)

Absorbent	PTFE	PP	PVDF	PES	PS
Water	√	√	√	√	√
Propylene carbonate	√	√	×	×	×
selexol	√	×	×	×	×
N-methyl pyrrodilone	×	×	×	×	×
Dimethyl formamide	×	×	×	×	×
Tributyl phosphate	×	×	×	×	×
Glycerol triacetate	√	×	×	×	×
n-Formyl morpholine	√	√	×	×	×

2.3 Development of Membrane gas absorption system (MGAS)

The principles for gas and vapour transportation through porous polymeric membrane was laid by Thomas Graham in 1928 (Pandey and Chauhan, 2001). In 1980’s polypropylene (PP) capillary microporous membrane was used as liquid-liquid contactor to separate water from salt solution.

Polymeric membranes have been used commercially for gas separation since 1980 (Baker, 202; Graham, 1995a; Graham, 1995b). Hydrophobic membranes with low surface energy were frequently performed for gas-liquid processes to reduce the possibility of membrane wetting (Wang, 2009).

An experimental study for CO_2 absorption in absorbent liquids of water, aqueous NaOH and aqueous diethanolamine (DEA) was performed by Rangwala using commercially PP hollow fiber membrane as gas-liquid contactor (Rangwala, 1996). The researcher found that the effective gas-liquid contact areas were 2324 and 870 m^2 / m^3 for the modules of 0.0254 m diameter with 0.2 m length and 0.0510 m with 0.6 m length, respectively. In addition, he observed that membrane mass transfer coefficients (k_m) determined experimentally was much lower than those theoretically calculated for non-wetted mode for aqueous amine and NaOH absorbents.

Li and Teo (1998) investigate the CO_2 recovery from gas stream containing 4% CO_2, 17% O_2 and the balance of N_2 using silicone rubber and polyethersulphone hollow fiber membranes. They observed that the use of water as an absorbing liquid in the permeate side (shell side) of the modules was significantly improved the CO_2 removal efficiency. However, the CO_2 permeation flux was reduced due to presence of the liquid film resistance and therefore the loading capacities of the modules were reduced. In addition, they found that the loading capacities of the modules were improved when alkaline solution was used as absorbing liquid.

The effect of the pore size distribution of the membrane on the membrane mass transfer coefficient was investigated by Li et al., (2000). PVDF hollow fiber membrane module was used for gas removal such as H_2S or SO_2 from gas streams containing either 17.2 ppm H_2S or 3000 ppb SO_2 in balance of N_2. 10% NaOH solution was used as absorbing liquid for soluble gases H_2S and SO_2. They found that the membrane mass transfer coefficient was not affected by the increasing of pores size when its diameter greater than 2 μm and therefore the membrane mass transfer coefficient is governed only by the convective diffusion. On the other hand, they observed that the membrane mass transfer coefficient was decreased when the pores size decreased and thus the membrane mass transfer coefficient is progressively dominated by the Knudsen diffusion.

An experimental study was performed by Kim and Yang (2000) to assess the effect of operating conditions on CO_2 absorption rate using PTFE hollow fiber membrane as gas-liquid contactor. Water and 2-amino-2methyl-1-propanol (AMP) were used as absorbing liquids. The results revealed that the removal rate of CO_2 was increased with increasing of volumetric flow rate of absorbent. As temperature of AMP rose, the absorption rate of CO_2 increased as well. However, vaporized water filled membrane pores when high temperatures were applied and therefore the CO_2 separation efficiency was deteriorated.

New absorbing liquid (CORAL) for CO_2 removal was developed by Feron and Jansen (2002). Polypropylene hollow fiber membrane was used as gas-liquid contactor. They recorded that the mass transfer in the module was dominated by the liquid phase. They achieved loadings of up to 0.4 mol CO_2 per mol of active component. In addition, they found that CO_2 mass flux was increased when liquid solvent temperature was increased up to 40 ^oC.

Mavroudi, et al., (2003) used different concentrations (0.5-2 M) of DEA aqueous solutions and pure water as absorbents for CO_2 removal from stream containing 15% CO_2 balanced with N_2. A commercial Liqui-Cel Extra Flow membrane contactor was used. They achieved CO_2 removal efficiency up to 75% in case of pure water as well as nearly complete (~99) when aqueous solution of 2M DEA was used.

The change of mass transfer resistance with time was examined for membrane-based CO_2 absorption in water by (Mavroudi et al., 2006). Commercial cross-flow membrane module of polypropylene was used. The results show that absorption flux was decreased significantly with time due membrane wetting and therefore the membrane mass transfer resistance was increased. On other hand, the initial flux value was restored after membrane drying.

The separation of CO_2 from CH_4 by using microporous PVDF hollow fiber membrane as gas–liquid contactor was performed by Atchariyawut et al., (2008). Pure water, aqueous NaOH solution and aqueous MEA solution were employed as absorbents. They observed that CO_2 flux was improved by the increase of NaOH solution concentration and temperature as well as the CO_2 volume fraction in the feed stream. However, they found that increase of water temperature employed as absorbent resulted in decreasing the CO_2 flux.

PP capillaries membrane as gas-liquid contactors were employed to remove CO_2 from a gas stream containing 15% (v/v) of CO_2 and 85% of N_2 using an aqueous MEA solution as absorbent (Bottino et al., 2008). The experimental results showed that increase in number of capillaries were resulted in increasing of CO_2 removal efficiency and decreasing the gas flow rate.

PP hollow fibers membrane and asymmetric poly phenylene oxide (PPO) hollow fibers were applied as membrane contactor to remove CO_2 from gas stream containing 20% (v/v) CO_2 balanced with CH_4 (Simons et al., 2009). Aqueous solution of MEA was used as absorbing liquid. The results showed that PP membrane was outperformed the performance of the PPO membranes in terms of productivity and selectivity. However, PP hollow fiber membranes exhibited high sensitivity to small variations in the feed pressure which resulted in severe performance loss.

Marzouk et al., (2010) fabricated a PTFE hollow fiber membrane module for CO_2 removal method from gas mixture of 9.5% CO_2 and 90.5% CH_4 by gas absorption process under elevated pressure (up to 50 bars). Distilled water was used as physical absorbent for CO_2, while aqueous solution of NaOH and aqueous solutions of amines namely MEA, DEA and triethylenetetramine (TETA) were used as chemical absorbents. The result showed that the flux of CO_2 was improved by increasing the gas pressure for both physical and chemical absorbents were applied. However, the increasing in CO_2 flux for physical absorption case was more pronounced that the flux obtained with chemical absorption when gas pressure increased.

2.4 Membrane wetting property

Membrane wetting is defined as the possibility of the liquid penetrating the membrane pore, which depends on the hydrophobic and hydrophilic properties of the membrane. Therefore, wetting properties can be further classified into three categories:

A- Non-wetted: The membrane pores are filled with gas, which has minimal membrane resistance to mass transfer, as shown in Figure 2.2a.

B- Partially-wetted: The liquid penetrates the pores and partially fills the membrane with liquid, as shown in Figure 2.2b. A prolonged period of stable operation time will affect its performance because the membrane mass-transfer resistance will increase rapidly (deMontigny et al., 2006; Wang et al., 2005). Lv et al. (2010) immersed a polypropylene (PP) fiber in amine solutions for up to 90 days and they observed that the membrane was swollen; this swelling reduced the hydrophobicity of the membrane and increased the degree of membrane wettability.

C- Fully-wetted: In this case, during a prolonged period of operation, the membrane pores completely fill with liquid as presented in Figure 2.2c. The presence of stagnant liquid inside the pore leads to the formation of a dead zone, which reduces the overall mass-transfer rate.

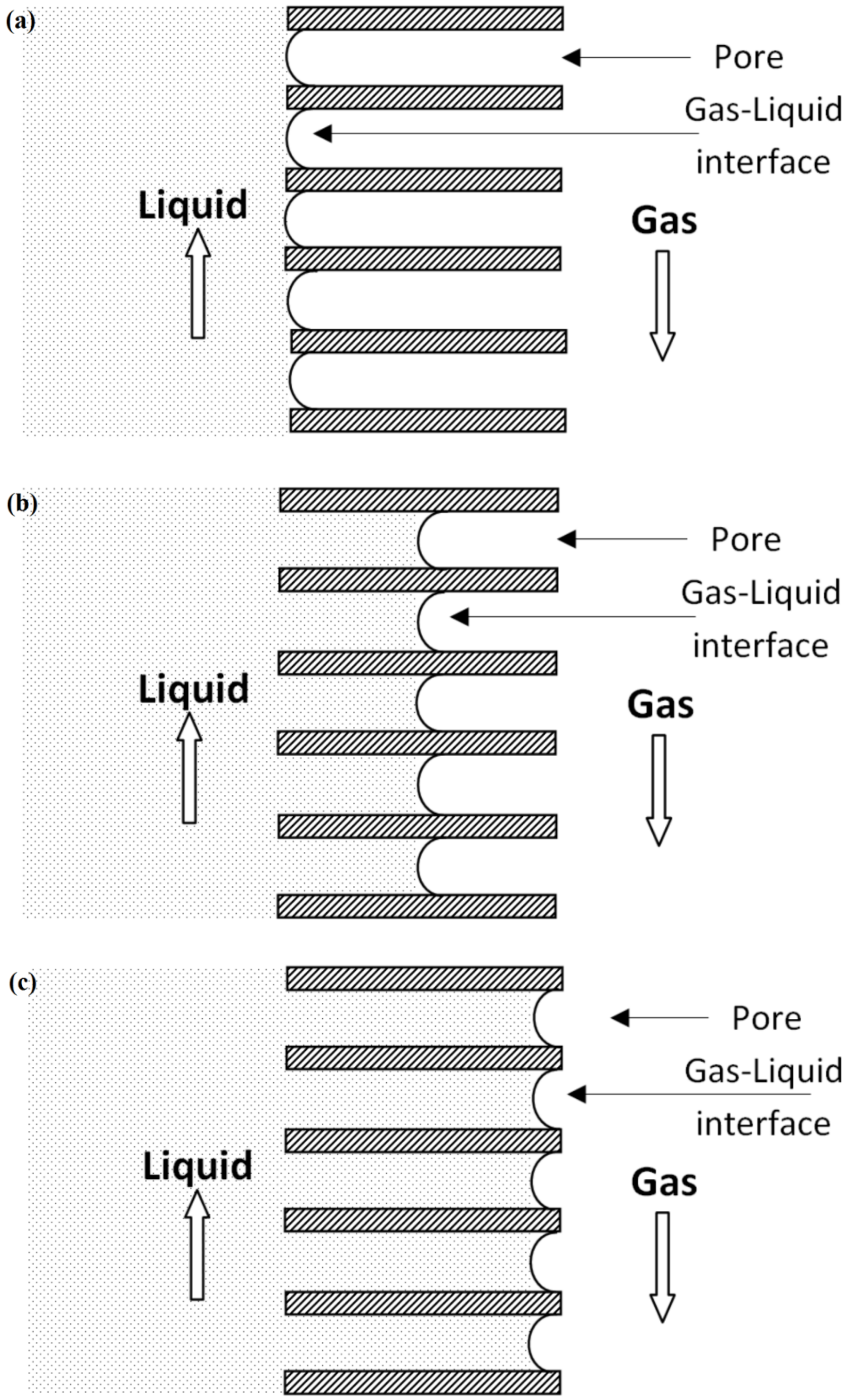

Figure 2.2: Pore wetting pattern in hydrophobic microporous membrane a) non-wetted; b) partially-wetted; c) fully-wetted