

**SUPERHYDROPHOBIC POLYMERIC HOLLOW
FIBER MEMBRANE CONTACTORS FOR CO₂
ABSORPTION**

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**SUPERHYDROPHOBIC POLYMERIC HOLLOW
FIBER MEMBRANE CONTACTORS FOR CO₂
ABSORPTION**

by

HARITH NOORI MOHAMMED

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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_{CO_2} | 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_{CO_2} | 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 |
| \emptyset | 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 ₂ O | Water |
| H ₂ S | Hydrogen sulfide |
| HCl | Hydrochloric acid |
| KOH | Potassium hydroxide |
| LDPE | Low density polyethylene |
| LiCl | Lithium chloride |
| LiCl·H ₂ O | 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 | Polytetrafluoroethylene |
| PVDF | Polyvinylidene fluoride |
| PZ | Piperazine |
| SCNR | Selective non-catalytic reduction |
| SCR | Selective catalytic reduction |
| SEM | Scanning Electron Microscopy |
| SO ₂ | Sulfur dioxide |
| TCD | <i>Thermal conductivity detector</i> |
| TEM | Triethanolamine |
| TEPA | Tetraethylenepentamine |
| TSA | Temperature swing adsorption |
| WCA | Water contact angle |

MEMBRAN PENYENTUH GENTIAN BERONGGA POLIMER SUPERHIDROFOBİK BAGI PENYERAPAN CO₂

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 CO₂). Pelbagai usaha telah dijalankan bagi memerangkap CO₂ daripada aliran-aliran proses industri. Sistem penyerapan gas membran (MGAS) telah dicadangkan sebagai satu teknik alternatif untuk mengatasi kelemahan proses-proses penyerapan CO₂ 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 $161 \pm 2.3^\circ$ and $152 \pm 3.2^\circ$. Suatu sistem MGAS berterusan yang dibina secara dalaman telah direka untuk menilai prestasi membran yang telah diubahsuai dari segi penyingkiran CO₂ daripada aliran gas yang mengandungi 20% (v/v) CO₂ seimbang dengan N₂. Parameter operasi (halaju cecair, halaju gas dan ketumpatan pembungkusan modul membran) dan kesan-kesan lain terhadap penyingkiran CO₂ telah dikaji. Prestasi penyerapan CO₂ 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 CO₂ 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 CO₂ 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 CO₂). Many efforts were conducted to capture CO₂ from the industrial process streams. Membrane gas absorption system (MGAS) was proposed as an alternative technique to overcome disadvantages of the conventional CO₂ 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° to 160±1.4°. 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 $161\pm 2.3^\circ$ and $152\pm 3.2^\circ$, respectively. A continuous MGAS inhouse-built was designed to evaluate the performance of modified membranes in term of CO₂ removal from gas stream of 20% (v/v) CO₂ balanced with N₂. The operating parameters (liquid velocity, gas velocity and packing density of the membrane module) and other effects on the CO₂ removal were studied. The CO₂ 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 CO₂ 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 (CO₂) 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 CO₂ is responsible for the increasing of the temperature of the earth's surface. CO₂ 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. CO₂ composes the major part of the blanket in atmosphere which is responsible for the climate change (Arenillas et al., 2005). It was recorded that CO₂ 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 be 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 CO₂ emissions are produced by the burning of fossil fuels in power plants (Desideri, 1999).

It was estimated that future global CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ emissions in Malaysia for energy generation has increased about 1.6 times, whereby the CO₂ 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 CO₂ emissions.

Advanced technology is continuously revolutionised to reduce CO₂ 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 CO₂ 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 CO₂

The technologies for CO₂ 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 CO₂ removal step through the fuel burning process (before or after fuel burned). According to this classification, various technologies for CO₂ capture were proposed including absorption, adsorption, membrane, cryogenic, and hybrid applications of these technologies. The performance criteria of the technology are CO₂ 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 CO₂ removal (Yang et al., 2008). The conventional processes applied for CO₂ 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 CO₂ at low partial pressure and concentration (4 - 14%, v/v) which represents an important limitation for CO₂ capture. Therefore, the absorption process is a promising technology for the CO₂ 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 CO₂ 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 CO₂ absorption takes place at high CO₂ 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 CO₂ concentration. However, it is not economical for the streams with CO₂ 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-pyrrolidone), Morphysorb (morpholine) and Fluor (propylene carbonate) (Olajire, 2010 and Yu et al., 2012). The advantage of Selexol process is the removing possibility of both CO₂ and H₂S 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 CO₂ 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 CO₂ 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 CO₂ stream. By combining the advantages of chemical absorption and flue gas operating conditions (low CO₂ partial pressure, low CO₂ concentration, large flow gases and high temperature) chemical absorption process is well suited for CO₂ 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 SO₂ and NO₂ 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, SO₂ 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 SO₂, while selective catalytic reduction (SCR), selective non-catalytic reduction (SCNR) or low NO_x burners are employed to remove NO_x contaminations. The flue gas must be cooled down to 45-50 °C before it is being introduced to the absorber (Rao et al., 2004; Ramezan et al., 2007). This operating temperature could enhance CO₂ 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 CO₂-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 CO₂ 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 CO₂ from flue gases (Belmabkhout, et al., 2011). The main advantage of the adsorption process for the CO₂ 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 CO₂ partial pressure, high CO₂ 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 CO₂ 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 CO₂ recovery, cryogenic processes are inherently energy intensive (Plasynski & Chen, 2000). The most promising application for cryogenics is expected to be for the separation of CO₂ from stream of high pressure gases and high concentration of CO₂ conditions in the oxyfuel combustion process. In this case, two advantages are achieved namely high CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture technology to reduce the CO₂ 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 CO₂ 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 CO₂ 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 CO₂ concentration and high flow rate are not favorable for CO₂ capture in such membrane, adsorption and cryogenic process. In this context, membrane gas absorption is appropriate to remove CO₂ 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 CO₂ 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 CO₂ 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 |
| Polyvinylidene fluoruride (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 CO₂ partial pressure required is relatively lower than the latter as well as the high absorption rate. In MGAS, the expensive absorbents with high CO₂ 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 CO₂ removal efficiency in most open literature. Therefore, it is useful to improve the CO₂ absorption performance for the cheaper absorbent of low CO₂ 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 CO₂ from CO₂/N₂ gas mixture stream.
- c) To evaluate the efficiency and stability of the modified membranes in CO₂ absorption process.
- d) To determine the mass transfer resistances of the MGAS.
- e) To enhance the CO₂ 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 CO₂ from gas mixture (20% CO₂ and 80% N₂). The modified (superhydrophobic) and pristine PP and PVDF membranes were tested in CO₂ absorption system for 10 days. The efficiencies of the tested membranes were evaluated in term of the stability of CO₂ absorption flux under prolong operating time. The performance study of CO₂ 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 CO₂ 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 CO₂ emission was briefly described in chapter 1 (Introduction). The existing CO₂

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 CO₂ 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. CO₂ absorption measurements, liquid absorbents preparation and development of CO₂ 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, CO₂ absorption efficiency, CO₂ 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 CO₂ 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 CO₂ and H₂S (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 CO₂ from combustion process due to its high reactivity with CO₂ 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 CO₂ absorb chemically into the amine solution to form a weakly bonded compound. The resulted CO₂-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 CO₂ stream will be produced. The hot CO₂-lean

amine is cooled down, and then sent back to the absorber. The CO₂ 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 CO₂ removal from flue gas stream by chemical absorption.

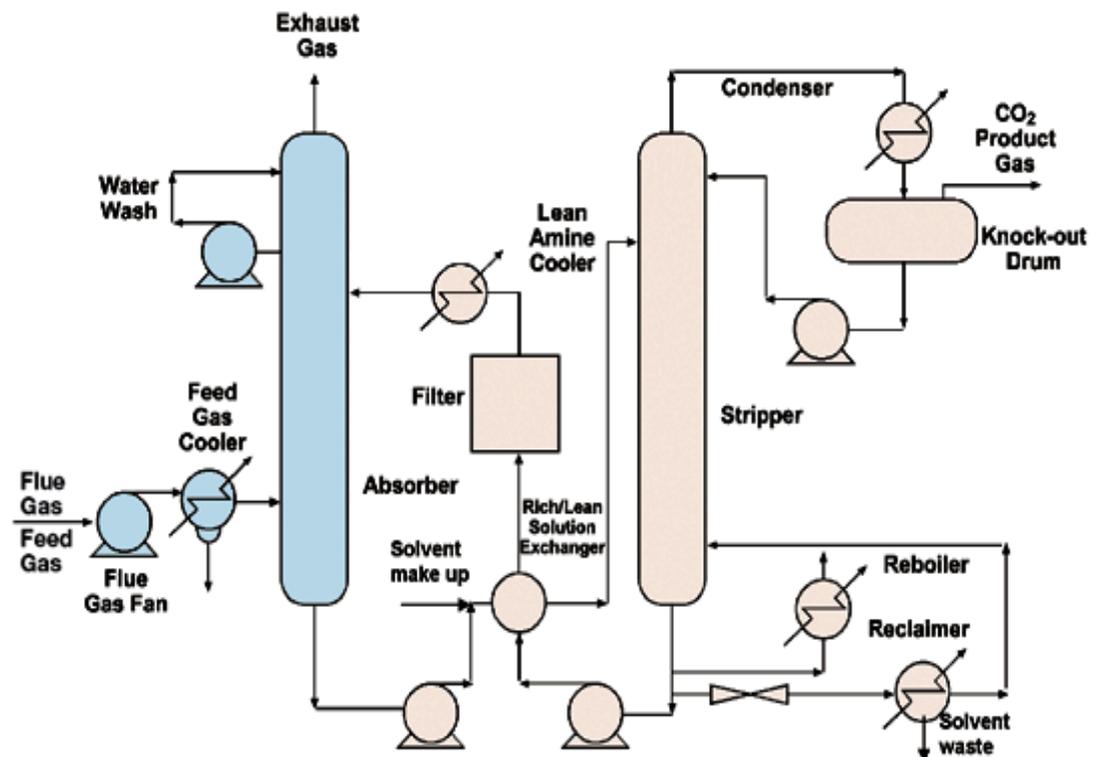


Figure 2.1: Flow diagram for CO₂ capture process by amine (IPCC, 2005)

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 CO₂

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 pyrrolidone | × | × | × | × | × |
| 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 CO₂ 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 m² / m³ 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 CO₂ recovery from gas stream containing 4% CO₂, 17% O₂ and the balance of N₂ 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 CO₂ removal efficiency. However, the CO₂ 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 H₂S or SO₂ from gas streams containing either 17.2 ppm H₂S or 3000 ppb SO₂ in balance of N₂. 10% NaOH solution was used as absorbing liquid for soluble gases H₂S and SO₂. 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 $^\circ\text{C}$.

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 CO₂ 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 CO₂ 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 CO₂ from CH₄ 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 CO₂ flux was improved by the increase of NaOH solution concentration and temperature as well as the CO₂ volume fraction in the feed stream. However, they found that increase of water temperature employed as absorbent resulted in decreasing the CO₂ flux.

PP capillaries membrane as gas-liquid contactors were employed to remove CO₂ from a gas stream containing 15% (v/v) of CO₂ and 85% of N₂ 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 CO₂ 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 CO₂ from gas stream containing 20% (v/v) CO₂ balanced with CH₄ (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 CO₂ removal method from gas mixture of 9.5% CO₂ and 90.5% CH₄ by gas absorption process under elevated pressure (up to 50 bars). Distilled water was used as physical absorbent for CO₂, 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 CO₂ was improved by increasing the gas pressure for both physical and chemical absorbents were applied. However, the increasing in CO₂ flux for physical absorption case was more pronounced than 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.

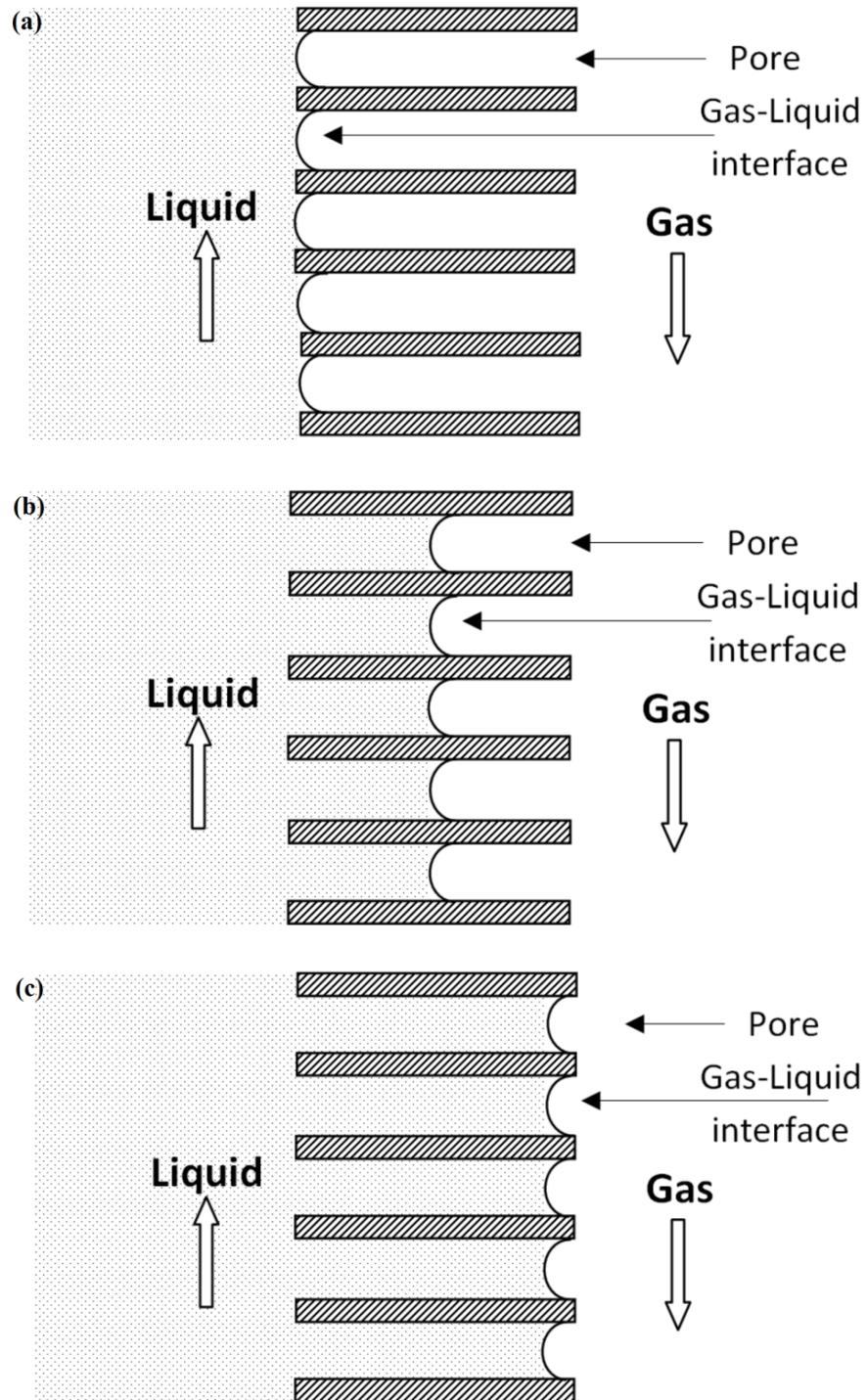


Figure 2.2: Pore wetting pattern in hydrophobic microporous membrane a) non-wetted; b) partially-wetted; c) fully-wetted