

**SILICA NANOPARTICLES INFUSED MIXED
MATRIX MEMBRANE FOR CARBON DIOXIDE
REMOVAL VIA MEMBRANE GAS ABSORPTION**

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by

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requirements for the degree of
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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
BET	Brunauer-Emmett-Teller
CCS	Carbon capture and storage
CDM	Clean Development Mechanism
CERs	Certified Emission Reductions
DLS	Dynamic light scattering
EDX	Energy-dispersive x-ray spectroscopy
EIA	Energy Information Administration
EVA	Ethylene vinyl acetate
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GDP	Gross domestic product
IPCC	Intergovernmental Panel on Climate Change
MGA	Membrane gas absorption
MMM	Mixed matrix membrane
NIPS	Non-solvent induced phase separation
R&D	Research and development
TGA	Thermogravimetric analysis
UNFCCC1	United Nations Framework Convention on Climate Changes

LIST OF SYMBOLS

$1/k_G$	Mass transfer resistance of gas phase boundary layer
$1/k_L$	Mass transfer resistance of membrane
$1/k_m$	Mass transfer resistance of liquid phase boundary layer
$1/K$	Overall mass transfer resistance
A	Area of the membrane
ΔC_{lm}	Logarithmic mean concentration difference
$C_{g,in}$	Inlet CO ₂ concentration in gas phase
C_g	Outlet CO ₂ concentration in the gas phase
$C_{g,i}$	Concentration of substrate at the gas outlet
$C_{L,in}$	Inlet CO ₂ concentration in the liquid phase
C_L	Outlet CO ₂ concentrations in the liquid phase
D_{eff}	Effective diffusion coefficient of CO ₂ in the pores of the membrane
D_K	Knudsen diffusion coefficient
D_M	Molecular diffusion coefficient
d_p	Mean pore size of the membrane
f_i	Model data
LEP_w	Liquid entry pressure
H	Henry's law constant
j	Gas mass transfer through the membrane
J	Absorption flux
K	Overall mass transfer coefficient
k_1	Kinetic parameters
k_L	Liquid mass transfer coefficient

m_n	Mass of absorbed 2-butanol
m_p	Mass of dry membrane
M_{CO_2}	CO ₂ concentration absorbed in the liquid absorbent
M_i	Molecular weight of CO ₂
n_t	Length of the actual data
ΔP_c	Critical entry pressure
ρ_n	Density of 2-butanol
ρ_p	Density of PVDF
ppm	Parts per million
Q	Gas flow rate
Q_L	Absorbent flow rate
r_{pm}	Maximum radius of the membrane pores
R_i	Reaction involved between CO ₂ and liquid absorbent
T_g	Glass transition temperature
V_g	Gas phase volume
vol%	Volume percent
wt%	Weight percent
x	Fraction of the membrane pores wetted by liquid absorbent
y_i	Experimental data

Greek letters

α	Alpha
β	Beta
δ	Membrane thickness

ε	overall membrane porosity
γ_L	Surface tension of the absorbent
τ	Tortuosity of the membrane

**ZARAH NANO SILIKA BERSEPADU MEMBRAN MATRIKS
BERCAMPUR BAGI PENYINGKIRAN KARBON DIOKSIDA MELALUI
PENYERAPAN GAS MEMBRAN**

ABSTRAK

Karbon dioksida (CO₂) merupakan gas rumah hijau yang paling banyak dihasilkan dan merupakan salah satu penyumbang utama kepada pemanasan global. Membran penyerapan gas (MGA) merupakan alternatif yang sangat menarik bagi penyingkiran CO₂ kerana prosesnya yang mudah, cekap tenaga, jimat ruang dan mudah untuk diskala besarkan. Walau bagaimanapun, beberapa isu utama bagi proses MGA adalah dan peningkatan kepemilihan tanpa mengurangkan kebolehtelapannya dan pembasahan membran yang boleh meningkatkan rintangan terhadap pemindahan jisim dengan ketara. Pelbagai bahan dengan sifat yang berbeza telah dikaji untuk penghasilan membran MGA bagi menangkap CO₂, namun membran matriks bercampur (MMM) telah terbukti sebagai alternatif yang memberangsangkan kerana penambahan zarah bukan organik ke dalam polimer membuka kemungkinan meningkatkan prestasi membran. Di dalam kerja penyelidikan ini, polivinilidena fluorida (PVDF) telah dipilih sebagai matriks polimer, manakala zarah nano silika telah dimasukkan ke dalam larutan polimer tersebut untuk menghasilkan MMM. Membran asimetri tanpa kecacatan dengan kedua-dua lapisan seperti jejari dan span telah berjaya dihasilkan dengan konsentrasi polimer sebanyak 15 wt% dengan acuan ketebalan sebanyak 400µm di dalam larutan penggumpal dari campuran etanol dan air. Di antara tiga jenis zarah nano silika yang disiasat dalam kajian ini, zarah nano silika TS-530 yang telah dirawat dengan heksametildisilazana memberikan prestasi penyerapan CO₂ di dalam proses MGA yang terbaik dari segi kepemilihan dan

kebolehtelapan masing-masing sebanyak 22.5 dan 1.9×10^{-4} mol/m²s pada kepekatan silika sebanyak 1 wt%. Peningkatan kepemilihan MMM TS-530 berbanding dengan membran PVDF tulen yang mempunyai kepemilihan sebanyak 7.18 mungkin disebabkan penyebaran zarah nano yang sekata di dalam matriks polimer PVDF, lalu berkesan untuk mengubah struktur membran bagi meningkatkan kawasan sentuhan, seterusnya menyebabkan peningkatan kepemilihan CO₂ berbanding nitrogen tanpa terlalu menjejaskan kebolehtelapannya. Prestasi MMM ditingkatkan lagi dengan menyalut selapisan polietilena berkepekatan rendah (LDPE) di atas permukaan membran untuk meningkatkan sifat hidrofobik dan ketahanannya terhadap pembasahan membran. MMM yang disalut terbukti lebih baik daripada MMM yang tidak bersalut dari segi kebolehtelapan, kepemilihan dan kemampunan jangka masa panjangnya, dengan fluks penyerapan CO₂ dan kepemilihan masing-masing sebanyak 2.4×10^{-4} mol/m²s and 22.8. Seterusnya, satu model dinamik telah dicadangkan untuk menyimulasi penyerapan CO₂ di dalam proses MGA, bukan sahaja mengambil kira kelarutan gas dalam penyerap cecair tapi juga kelarutan gas dalam membran. Model tersebut didapati sesuai dengan keputusan eksperimen yang dijalankan, dengan nilai R² melebihi 0.92. MMM optima yang mempunyai kepemilihan yang lebih tinggi dan ketahanan yang lebih baik terhadap pembasahan membran dengan tekanan kemasukan cecair sebanyak 13.55 bar dan sudut sentuhan sebanyak 120° telah digunakan bersama parameter operasi terbaik untuk memerhatikan prestasinya di bawah pengaruh gas binari bagi tempoh yang lebih panjang. Menerusi kajian penghasilan membran ini, prestasi membran untuk pemisahan CO₂ disiasat dari beberapa sudut parameter dan sifat fizikalnya bagi membolehkan pemantauan prestasi membran di bawah pengaruh pemboleh ubah yang berbeza.

SILICA NANOPARTICLES INFUSED MIXED MATRIX MEMBRANE FOR CARBON DIOXIDE REMOVAL VIA MEMBRANE GAS ABSORPTION

ABSTRACT

Carbon dioxide (CO₂) is the most produced, heat-trapping greenhouse gas and one of the main contributors to global warming. Membrane gas absorption (MGA) is a very attractive alternative for CO₂ removal as it is simple, energy efficient, less space consuming and easy to scale up. However, major issues in MGA process are improving the membrane selectivity without reducing the permeability and membrane wetting, which can increase membrane mass transfer resistance significantly. Various materials with differing properties have been researched for the synthesis of MGA membranes to capture CO₂, however, mixed matrix membranes (MMM) are proving to be a promising alternative, as the addition of inorganic particles into polymers opens the possibility of augmenting the membrane performance. In this work, polyvinylidene fluoride (PVDF) was chosen as the polymer matrix and fumed silica nanoparticles were incorporated into the polymer dope to produce MMM. A defect-free asymmetric membrane with both finger-like layer and sponge-like layer was successfully synthesised using 15 wt% polymer concentration with a casting thickness of 400µm in a coagulation bath of a mixture of ethanol and water. Among the three different silica nanoparticles investigated in this study, TS-530 silica nanoparticles that had been treated with hexamethyldisilazane gave superior CO₂ absorption performance in MGA process in terms of selectivity and permeability of 22.5 and 1.9 x 10⁻⁴ mol/m²s respectively at 1 wt% silica loading. This improvement of selectivity of TS-530 MMM compared to pristine PVDF membrane, which had a selectivity of 7.18 could be due to the homogenous dispersion of the nanoparticles in the PVDF polymer matrix,

effectively altering the structure of the membrane to increase membrane contact area, resulting in better selectivity of CO₂ over nitrogen while hardly affecting the permeability. The performance of the MMM was further improved by adding a layer of low-density polyethylene (LDPE) coating on the membrane to increase its hydrophobicity and resistance to membrane wetting. The coated MMM proved to be better than the non-coated MMM in both permselectivity and sustainability in an extended run, with CO₂ absorption flux and selectivity of 2.4×10^{-4} mol/m²s and 22.8 respectively. A dynamic model was then proposed to simulate CO₂ absorption in the MGA process, taking not only the gas solubility into the liquid absorbent into account, but also the gas solubility into the membrane. The model was found to be in good fit with experimental results, with R² values exceeding 0.92. The optimum coated MMM with superior selectivity and better resistance to membrane wetting with liquid entry pressure of 13.55 bar and contact angle of 120° was used with the best operating parameters to observe the binary gas performance over an extended period. Throughout the study of the membrane synthesis, the potential membrane CO₂ separation performance was observed in regards to a multitude of parameters and its resulting physical properties, which allowed for the monitoring of membrane performance under various influences.

CHAPTER ONE

INTRODUCTION

1.1 Global Warming

The process described as the greenhouse effect involves thermal radiation from a planetary surface being absorbed by greenhouse gases in the atmosphere, and is then re-radiated in all directions. As part of this re-radiation goes back towards the surface and the lower atmosphere, it increases the average surface temperature above what the temperature would be in the absence of the gases. The natural greenhouse effect makes earth habitable, but human activities have intensified the natural greenhouse effect, leading to global warming (Solomon et al., 2007).

After the beginning of the Industrial Revolution in the 1700s, the burning of fossil fuels, forest cutting and other activities have increased the amount of the greenhouse gases in the atmosphere substantially. Although chemical reactions and emissions sinks eventually remove these gases from the atmosphere, these gases are entering the atmosphere faster than their removal is occurring, and as a result, their concentrations are increasing at an alarming rate. The top ten warmest years around the world have all occurred after 1998 (Climate Central, 2016).

Carbon dioxide (CO₂) is the most produced greenhouse gas (Zhang et al., 2014), a heat-trapping gas and one of the major contributors to global warming. Among the greenhouse gases released into the atmosphere, CO₂ amounts to over 60%, demanding for action to be taken to reduce the emission (Zaini and Kamarudin, 2014). A large part of global warming is caused by the CO₂ emissions from the combustion of fossil fuels, which provides over 85% of energy for industrial and domestic needs

(Korminouri et al., 2015). The power and industrial sectors are responsible for about 60% of the global CO₂ emissions and the natural gas are also contained of significant amounts of CO₂ (Simons et al., 2009). The past few years have seen the concentration of CO₂ in the atmosphere to increase from 275 to 387 ppm, and is set to be the cause of global climate change by 2100 (Korminouri et al., 2015).

The anthropogenic emissions of CO₂ has led to increased global temperatures due to its contribution to global warming (Safaai et al., 2011). The Kyoto protocol under the United Nations Framework Convention on Climate Changes (UNFCCC1) drafts the necessary abatement of greenhouse gases worldwide. Reduced emissions goals are set on various levels for different groups of countries (Adewole et al., 2017). With the support from a sufficient number of countries that produce around 50% of the manmade emissions, in February 2005, the protocol was enforced. However, the mission to reduce emissions intensity of greenhouse gases by 5.2% their 1990 emissions level ultimately failed and the protocol was extended until 2017 (Songolzadeh, 2014).

As a rapidly developing country in industrialisation, Malaysia is heavily dependent on conventional energy supplies such as fossil fuels. At the United Nations Climate Summit 2014, the Prime Minister, Datuk Seri Najib Tun Razak had said that Malaysia had taken a clear step for a cleaner future in the past decade. Although almost US\$2.6billion had been spent to adapt to more frequent floods in the last ten years, he had said, “This is money we could have invested in green industries, or used to slow climate change.” This clearly spoke of Malaysia’s commitment to reduce carbon

emissions, as he also stated that Malaysia would continue to act on climate change (Hamid, 2014).

Increasing energy consumption over the years relying on fossil fuels have resulted in a significant increment in greenhouse gas emissions, especially carbon dioxide (Begum and Pereira, 2010). In the year 2009 United Nations Climate Change Conference, also known as the Copenhagen Summit, the Copenhagen Accord was drafted. The Accord established a Copenhagen Green Climate Fund to support projects, programmes, policies and other activities in developing countries related to mitigation (Bird et al., 2011). In addition, a Technology Mechanism was then established to accelerate technology development and transfer. Although the Accord was not legally binding, it was agreed that deep cuts in global emissions are required and that a low-emission development strategy is indispensable to sustainable development. The Malaysian Prime Minister has stated a target of carbon emissions intensity reduction by 40 percent from 2005 levels by year 2020 in efforts to combat global warming (Nor et al., 2016). The Malaysian government had spent approximately RM2.6billion towards funding 200 green technology projects throughout the country (Alagesh, 2016). It is evident that technology to efficiently capture CO₂ is vital and that many countries financially support researches for such a technology.

One of the most attractive strategies to lower CO₂ emission is by implementing carbon capture and storage (CCS) method. Cost effective capture of CO₂ and the following sequestration have to be considered as the energy demand keeps growing (Nor et al., 2016). In CCS, CO₂ released from power plants is captured and sequestered

underground for a long time in geological structures (Merkel et al., 2010). Intergovernmental Panel on Climate Change (IPCC) in 2007 has estimated an increase in average global temperature by 20°C from 1990 to 2100, and since then CCS has been executed in Malaysia. As the global demand for carbon emission intensity reduction with GDP (gross domestic product) is 40% of 2005 levels by 2020, CCS strategy is considered a vital technology in helping Malaysia reach this target (Zaini and Kamarudin, 2014).

1.2 Carbon Dioxide Capture

The control of carbon dioxide emissions stemming from human activities is a daunting challenge that industrialised countries face (Carapellucci and Milazzo, 2003). Attention is being given to developing technologies for carbon dioxide removal from the atmosphere that is mostly generated from the burning of fossil fuels. CCS is a very attractive strategy as it enables the continuation of fossil fuel utilisation while decreasing CO₂ emission into the atmosphere (Oh, 2010). CO₂ storage options such as geo-sequestration can be used after carbon dioxide capture from large point sources (White et al., 2003). Several technologies that can be utilised in CCS are absorption, adsorption, membrane gas separation and cryogenic separation (Nor et al., 2016).

The main approaches to capture CO₂ are post-combustion capture, pre-combustion capture and oxy-combustion. Various techniques are being investigated, including gas separation, liquid absorption, adsorption onto a solid and membrane systems. In post-combustion capture, which is the focus of this work, CO₂ is separated from other flue gas components by the combustion process. As the name suggests, in pre-combustion capture, CO₂ is separated before the combustion process while the fuel

is burned in an excess of oxygen stream in oxy-combustion (Merkel et al., 2010). Post-combustion capture is best applied to coal-fueled power generators, pre-combustion capture for gasification plants and oxy-combustion for new or retrofitted plants (Songolzadeh et al., 2014).

Another conventional process to capture CO₂ is by reversible solvent absorption called amine scrubbing (Ahmad et al., 2017), although it has high energy consumption (Rao and Rubin, 2002). In the devices used to achieve this, the gas phase is dispersed in the liquid phase to achieve gas-liquid contact over large areas and increase the mass transfer rate. Although this method is widely used in the industry, it has several disadvantages such as being difficult to obtain an accurate estimation for the gas-liquid mass transfer area. It also has a limited range of gas and liquid flow rates due to the operational problems such as flooding, foaming, channelling and entrainment. Therefore, it is not possible to independently control the liquid and gas streams. This gives the incentive to find a better and more efficient alternative to capture CO₂ (Scholes et al., 2008). In addition, a mechanism in the Kyoto Protocol, the clean development mechanism (CDM) provides an avenue for reduction of emissions between industrialised and developing countries such as Malaysia, which are not obligated towards the target for emission reduction. CDM facilitates projects between these countries by offering additional financial and technological investments in projects geared towards reducing greenhouse gases emissions. These reductions would be quantified in units called Certified Emission Reductions (CERs), which is a form of carbon credits that can be traded for money with countries that need to meet their targets (Oh, 2010).

One of the emerging technologies that have shown improvements in terms of efficiency and cost is membrane technology. Various options are possible for membrane technology to be applied in CO₂ capture from flue gas. One such concept is membrane gas absorption (MGA), which involves gas passing across one side of the membrane while a liquid absorbent flows on the other side of the membrane (Mustafa et al., 2016). In this process, CO₂ would pass through the membrane into the liquid absorbent, while the membrane will block impurities from being absorbed into the absorbent, thus decreasing the loss of liquid absorbent. The liquid absorbent will be regenerated and recycled (Gomez-Coma et al., 2016).

1.2.1 Membrane Gas Absorption for Carbon Dioxide Separation

Membrane gas separation is a very attractive alternative for CO₂ capture as it is easy to scale up, simple, energy efficient and is expected to be less space consuming (DashtArzhandi et al., 2015). The overall process is similar to the conventional absorption and desorption cycle, with the energy requirement still dependent on the solvent performance and optimisation of the process. A microporous membrane in MGA becomes a barrier between the gas and liquid phases. Ideally, the membrane selectively allows one component to diffuse through while rejecting others to produce a specific gas rich permeate (Scholes et al. 2008). In this case, it is desirable for CO₂ to diffuse through the membrane and then to be absorbed into the liquid absorbent. The mass transfer resistance posed by the membrane is limited as long as the membrane has not been wetted by the liquid absorbent and the mass transfer resistance is largely on the liquid phase. For this reason, it is vital that the membrane is hydrophobic (Hoff and Svendsen, 2013).

As with any technology, membrane systems have several disadvantages. In an MGA process, the liquid absorbent can be poisoned by chemicals contained in the incoming gas (Meisen and Shuai, 1997). Polymeric membranes used for gas absorption are structurally less stable than ceramic and metal membranes, and its micropores can be clogged by water vapour, decreasing gas permeability (Aaron and Tsouris, 2005). However, the advantages of membranes such as high efficiency, reduced energy requirement, low costs without limitations brought by channeling, entrainment and flooding exceed the disadvantages, making research in this field worthwhile (Zhang et al., 2014).

1.2.2 Mixed Matrix Membranes

Mixed matrix membranes (MMM) encompassing polymer and inorganic nanoparticles is an interesting research topic as they can be used to fabricate membranes with the desirable structure from the interactions between the surface of the nanoparticles and polymer and/or solvents during the preparation of the membrane. The change in the membrane structure can lead to better selectivity and/or permeability of the membranes. Some researchers have also incorporated nanoparticles into the polymer matrix to control membrane fouling (Vatanpour et al., 2012) as well as to improve the mechanical strength and thermal stability of the membrane (Ebert et al., 2004; Li et al., 2009). Polymeric membranes are typically restricted by the trade-off between permeability and selectivity, where any modifications made on the chemical structure of the polymer usually result in an improvement in selectivity at the cost of permeability, and vice versa. Inorganic membranes, on the other hand, rely on differing sizes of molecules in separation but is difficult and expensive to synthesise owing to their fragility (Goh et al., 2011). Thus, the dispersion of inorganic nanoparticles into

the organic or inorganic continuous phase, so as to generate a mixed matrix membrane, is a possible solution to improving the permeability-selectivity trade-off problem.

Many researchers have found that MMM exhibit improved permeability with similar or even better selectivity compared to their pristine polymer membrane counterparts (DashtArzhandi et al., 2015). This is because MMM may combine the strength of each material, such as the flexibility of the polymer with the thermal stability of the inorganic additives. In MMM, the mechanical properties and economical processability of the polymers are the desired properties while inorganic nanoparticles are used for their structure, mechanical strength and surface chemistry. In addition, the performance of MMM can be augmented even further by chemical modification (Ahmad et al., 2017) as it may improve certain attributes such as increased penetrant absorption or better nanoparticles dispersion. Nanoparticles used in MMM can also be chemically modified to improve the hydrophobicity of the resulting MMM to avoid membrane wetting, which is a concerning issue in MGA process (Boributh et al., 2013).

Addition of nanoparticles in the membrane matrix may have three possible effects on membrane performance; the nanoparticles may act as molecular sieves, they may change membrane structure to increase microcavities that increase permeability, or they may create torturous paths to obstruct gas transport, resulting in decreased permeability (Scholes et al., 2008). Even though incorporation of inorganic nanoparticles into the membrane polymer matrix is expected to improve the performance compared to pristine polymeric membranes, not many studies of MMM succeeding in increasing the performance have been reported. This is due to difficulties in the fabrication of MMM that includes poor distribution of the inorganic phase in the

polymer matrix and weak contact between the polymer and inorganic phases. Moreover, characteristics such as particle size, additive load and polymer properties should be taken into account, as they can affect the properties of the resulting MMM (Aroon et al., 2010).

1.3 Problem Statement

Membrane materials that can perform to meet the requirements for membrane gas separation is necessary. Although strides have been made in tailoring the structure of polymer to improve separation performance in the last two decades, further progress to go beyond the trade-off line between selectivity and permeability poses a daunting challenge. The Robeson curve had analysed all permeation data available of polymeric membranes for gas pairs and plotted the permeability of each membranes against the selectivity. The plot revealed the upper bound that demonstrated the limit of permeability-selectivity relationship of the performance of gas polymeric membranes, where an increase in permeability is linear with the decrease in selectivity. Therefore, development of membranes that can surpass the Robeson's upper bound has been a major concern in gas separation (Wahab and Sunarti, 2017). To surpass the Robeson's upper bound, the membrane should exhibit better selectivity than is expected when certain permeability is attained, or vice versa. However, to achieve this goal is not an easy task even when strategies such as alternative membrane materials (Ahmad et al., 2012) and mixing in additives into the membranes are used (Chung et al., 2003). Recently, a lot of research is done on MMM, focusing on incorporating inorganic additives into polymer matrices. MMM consists of additives incorporated into a polymer matrix. This has the potential of a relatively accessible method to alter the properties of existing materials without resorting to the synthesis of an entirely new

chemical species. The purpose for this addition is to engineer a favourable structure for better performance (Vatanpour et al., 2012) and enhance the properties of the resulting MMM (Li et al., 2009). A small amount of inorganic additives is expected to enhance the overall separation efficiency.

Other than using porous inorganic additives having similar selectivities as the polymer, a novel MMM design using non-porous nanoparticles has been proposed (Zhang and Wang, 2014). These nanoparticles are added to change the structure of the membrane, which can result in the improvement of separation properties of the polymeric membranes. They have also confirmed that the addition of the nanoparticles increases the average size of free volume. Silica has been attracting interest as its addition to membranes have been shown to improve thermal and mechanical stability in addition to the permeability and/or selectivity of the resulting MMM (Xing and Ho, 2011; Merkel, 2003). However, many researchers found that the increase in permeability still occurred at the cost of selectivity (Goh et al, 2011). In the case of MMM, one of the factors that contributes to this is the poor compatibility between the inorganic filler and the polymer matrix (Zornoza et al., 2011). Thus, the use of inorganic fillers that have good compatibility with the polymer matrix is desired to produce MMM with increased selectivity at little or no cost to permeability.

Gas absorption has been carried out in many processes using various equipments, including packed columns, plate columns and venture scrubbers (Rajabzadeh et al., 2009). Even though good product yields of high purities can be obtained, this method is very energy consuming (Simons et al., 2009). A more efficient separation process that is less expensive and more environmental friendly is needed for CO₂ capture. MGA process to absorb CO₂ combines the advantages of absorption

(high selectivity) and membranes (modularity, large gas-liquid interfacial area and small size) while overcoming the disadvantages of conventional gas absorption apparatuses, providing an appealing alternative, especially for power plant flue gases (Ahmad et al., 2009). However, a major concern in MGA process is membrane wetting by the liquid absorbent, which can greatly affect the CO₂ absorption efficiency. Ideally, the membrane resistance is small compared to the resistance in the liquid boundary layer as the process is operated in the non-wetted mode. Liquid absorbent that penetrates into the membrane pores would increase the membrane resistance to mass transfer as it causes the formation of dead zones within the membrane pores (Mohammed, 2014). The wetting of membrane by the liquid absorbent by even 2% of the membrane pores can increase the membrane mass transfer resistance up to 60% (Zhang and Wang, 2013). Despite the disadvantages of membrane contactors, the benefits that can be reaped from the usage of membranes to separate carbon dioxide from flue gases justify the research needed to optimise systems that incorporate membrane usage so that they can be applied in the industry. Thus, it is important for the membrane used in this process to have high hydrophobicity and resistance to wetting.

Many parameters such as polymer and additives or nanoparticles used in the membrane, conditions in synthesizing the membrane, and liquid absorbent used should be considered, and the effects of the parameters chosen on the performance of the membranes need to be observed. Models investigating the effect of operating parameters and membrane properties on CO₂ absorption have been developed (Boributh et al., 2011; Goyal et al., 2015; Yan et al., 2014). However, most models do not consider the changes in the process with time (Dindore et al., 2005). In addition,

previous research on modelling have only focused on the solubility of CO₂ into the liquid absorbent, represented by Henry's constant, H (Kim and Yang, 2000; Zhang et al., 2006a; Mavroudi et al., 2006; Bishnoi and Rochelle, 2000). However, the solubility of CO₂ in the polymeric membrane has to be considered as well, as it impacts the absorption of CO₂ in the MGA process (Dutta, 2007). Little study has been done on MGA process using membranes with nanoparticles and surface coating, and this is what this research will incorporate.

1.4 Objectives

The research was aimed to separate the greenhouse gas, CO₂ from a gas stream. To achieve this, membrane was synthesised from a dope solution containing polymer with silica nanoparticles to be used in a MGA process. In order to complete this target, a number of objectives were required and they are listed as follows:

- (i) To elucidate the effects of incorporating different types and loading of silica nanoparticles in the dope solution on the characteristics and performance of the resulting MMM.
- (ii) To evaluate and compare the properties and the resulting performance (in terms of permeability and selectivity) of pristine polyvinyl fluoride (PVDF) membranes to the MMM.
- (iii) To study the effect of low density polyethylene (LDPE) membrane coating on the performance of the MMM to further improve the hydrophobicity of the membrane.
- (iv) To propose a model to quantify the CO₂ transport in MGA process using different types of liquid absorbents.

1.5 Scope of Study

The polymer loading from 11 – 19 wt% and the effect of membrane casting temperature between 25°C and 60°C on the morphology, physical properties and absorption performances of the pristine polymeric membranes were studied. The membranes were characterised using thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), porometer, goniometer, atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), as well as tensile, porosity and performance tests to determine the best polymer loading.

In this work, three types of fumed silica nanoparticles, TS-530, TS-610 and TS-720 were incorporated into the polymer matrix respectively to produce MMM. These nanoparticles were characterised using BET test, goniometer, FESEM, zetasizer and FTIR. On the other hand, the resulting MMM were characterised using TGA, FTIR, porometer, goniometer, AFM, FESEM, energy-dispersive x-ray spectroscopy (EDX) as well as tensile, porosity and performance tests to observe the effects of the respective fumed silica when added into the PVDF polymer matrix.

The fumed silica nanoparticles that produced the MMM with the best performance in terms of permeability and selectivity was chosen for further evaluations. The effect of different loadings of silica nanoparticles in PVDF polymer matrix was studied in the range of 0.5 – 10wt% of polymer concentration for the silica nanoparticles chosen. The absorption performance of pristine PVDF membrane and the MMM were compared by analysing the permeability and selectivity of the absorption of CO₂ from a mixture of CO₂ and nitrogen (N₂) gases.

In the interest of enhancing the performance of the MMM, the surface of the best MMM was coated with LDPE to increase hydrophobicity. Indirect coating method was used with various non-solvent ratios of acetone:ethanol ranging from 5:1 to 5:6 and the contact angle and performance of the coated membranes were compared to the non-coated ones.

Then a dynamic model was proposed to simulate the CO₂ transport in the MGA process using three different liquid absorbents; distilled water, 2-amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA). One simulation took solubility of CO₂ inside the membrane into account and the other did not. Finally, the optimised synthesised MMM was tested using a CO₂ and N₂ binary gas mixture to observe the ability of the MMM to perform in a mixed gas absorption using MGA process. In this study, 20 vol% CO₂ was used to evaluate the performance.

1.6 Thesis Organisation

Chapter One discussed the consequences of global warming, a serious problem partly caused by CO₂ gas emissions was addressed, followed by CO₂ capture technologies, focusing on MGA, especially by MMM. The following sections covered the problem statements and research objectives. The scope of this research and organisation of this thesis wrapped up the first chapter.

Chapter Two covered various methods used to capture CO₂ and research done using membrane contactors to separate the greenhouse gas from gas mixtures. Investigations done on MMM in gas separation were also presented. Different

inorganic additives used to produce MMM and its challenges were also addressed in this chapter. Several parameters affecting the membrane synthesis and the MGA process were discussed, as well as effects of nanoparticles loading and membrane coating.

Chapter Three described details of the materials and experimental procedures used in this research. Method of synthesising pristine polymeric membranes and MMM were described. Characterisation techniques used to study the properties of the membranes were also covered in this chapter. The method used for preparation of the membrane coating and the procedure to coat the membranes itself were discussed. Operating procedures for CO₂ MGA testing rig to investigate the performance of the synthesised membranes were also presented.

Chapter Four presented the results of the research and discussion on the outcomes based on the objectives. The effects of the fabrication parameters of the pristine PVDF membranes on the properties and performances were discussed. In the next section, the impacts of incorporating different fumed silica nanoparticles into the polymer matrix were explained, as well as the effect of changing the loading of the nanoparticles in the membrane dope solution. The changes in the characteristics and performance of the membranes after they were coated were presented and discussed. In addition, the results of the simulation of the process and its comparison with the laboratory studies were also covered in this chapter.

The last chapter, Chapter Five, summarised the outcomes of the present study based on the objectives of the research. Some recommendations for future work on this topic of research were also proposed, taking the limitations encountered in this present work into account.

CHAPTER TWO

LITERATURE REVIEW

2.1 The Greenhouse Effect

Greenhouse gases can remain in the atmosphere for an amount of years ranging from decades to thousands of years, contributing to global warming. The Intergovernmental Panel on Climate Change (IPCC) have warned about the devastating effects of climate change wracked by global warming if the CO₂ emissions have not decreased by 50 – 80% by the year 2050 (DashtArzhandi et al., 2015). Global warming poses a serious threat to humans, animals and the environment. The increase in Earth's temperature is demonstrated by the rise in temperature of the atmosphere and various sources of water, which leads to other effects such as the rise in humidity and sea level as sea-ice melts (Hartmann et al., 2013).

Plagues and diseases as well as other heat related deaths have spread to northern countries as they became warmer, an environment that encourages the growth and spreading of viruses that brings about diseases such as avian flu, cholera, plague, ebola and tuberculosis ("The Consequences of Global Warming on Health", 2008). The temperature increase of the oceans increases the probability of more frequent and stronger hurricanes, and while some areas will become wetter, other areas will suffer serious droughts and heat waves (Lallanilla, 2013). Not only humans are affected by global warming. Changes in the climate can disrupt the functioning of the ecosystems, which may harm or even cause the extinction of some species. Considering the devastating impacts of global warming, reducing greenhouse gases is becoming increasingly important.

2.2 Carbon Dioxide: Largest Contributor to Global Warming

Studies have shown that in the past few decades, fossil fuel combustion has been responsible for most of the increasing atmospheric burden of CO₂ (Tans, 2009). At the moment, fossil fuels, a non-renewable resource having a high percentage of carbon, provide 85% of the worldwide energy through coal, petroleum and fuel gas as it is cheap, readily available, and the energy production technology that exist are reliable (Mansourizadeh and Ismail, 2011a). CO₂ is the most concerning anthropogenic greenhouse gas, contributing to approximately two-thirds of the greenhouse effects (Zhang and Wang, 2014), even though methane and chloroflorocarbons have a bigger greenhouse impact per mass of gases (He and Hägg, 2011). Between 1990 and 2013, the total warming effect due to greenhouse gases increased by humans to the Earth's atmosphere has increased by 34%. As illustrated in Figure 2.1, greenhouse gas emissions have been steadily increasing year after year with the predicted carbon emissions highlighted in red, showing no signs of abating in the near future. Unfortunately, Energy Information Administration (EIA) 2010 has anticipated an increase in energy demand by 49% between 2007 and 2035 as more countries become industrialised (He and Hägg, 2011). Certain environmental goals have been established to decrease worldwide greenhouse gas emissions to below levels in 1990. Firms are allowed to choose cost effective solutions through a regulatory program known as emission trading to achieve these goals (Show and Lee, 2008).

The Kyoto Protocol marks the first international agreement on greenhouse gases emissions (Songolzadeh et al., 2014), where it states that the emissions should be lessened by 5.2% of those in 1990 within the years 2008-2012, a target that seems to be hard to achieve for many countries (Hägg and Lindbråthen, 2005). In addition,

the Copenhagen Accord requests that the increase in mean global temperature to be limited to $\pm 2^{\circ}\text{C}$ above the pre-industrial level by year 2100 (Yu et al., 2012). Unfortunately, the Kyoto protocol has failed in reducing CO_2 emissions to the target specified, thus in the Durban COP meeting in 2011, it has been extended until 2017. To avoid catastrophic global warming effects, the emissions of greenhouse gases must be reduced by 50 to 80% (Songolzadeh et al., 2014).

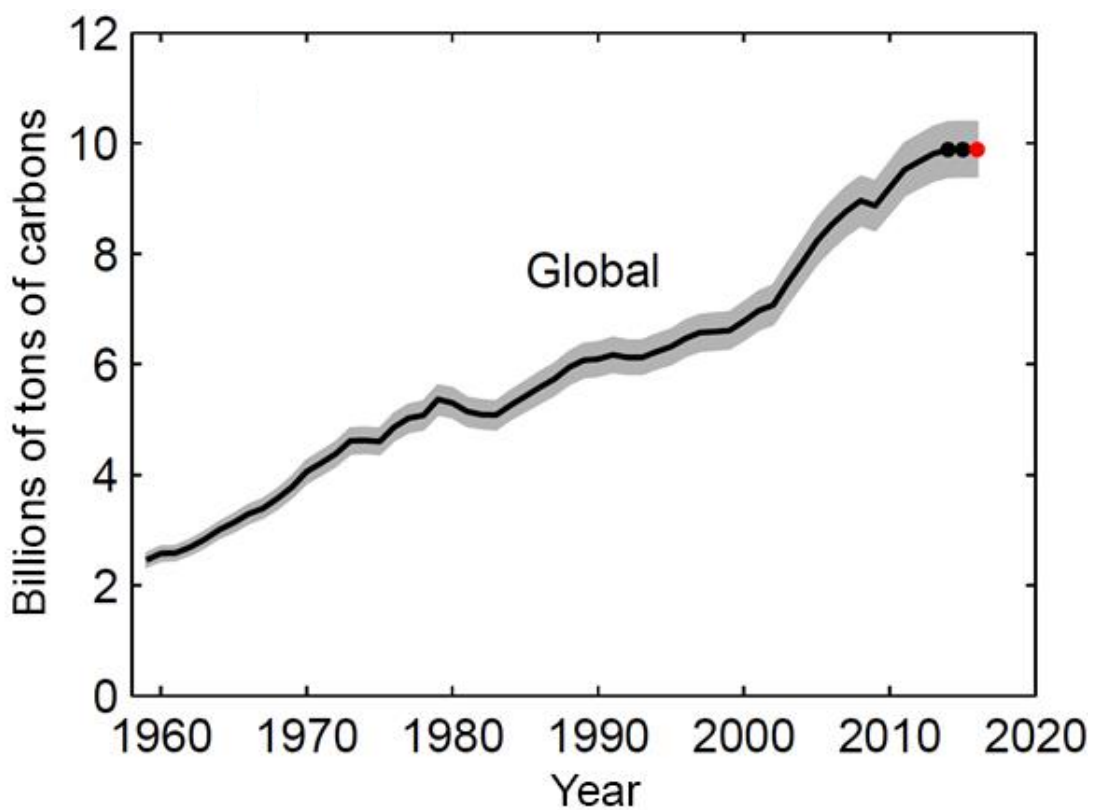


Figure 2.1: Global greenhouse gas emissions in billions of tons of carbons per year (Sueyoshi et al., 2016)

2.3 Removal of CO_2

The greenhouse effect brings serious consequences on both the environment and humans, described in the previous section. There are three ways to decrease the CO_2 emissions; reduce energy consumption, lessen the usage of fossil fuel, and capture and store the CO_2 . Carbon capture and storage (CCS) is the most attractive option to

reduce the CO₂ emissions into the atmosphere as fossil fuels can still be utilised without causing significant release of CO₂ (Songoldazeh et al., 2014). Separation of CO₂ from various gas streams is of significant interest due to the enhanced greenhouse effect (Feron and Jansen, 2002) which contributes to global warming. In addition, there are many uses for pure CO₂ in the food and beverage industry as well as chemical industries such as the fertilizer production and foam blowing (Songolzadeh et al., 2014).

The three basic stages of CCS are CO₂ separation, transportation and storage and of the three, CO₂ separation incurs major costs in the process. Three main approaches to CCS are pre-combustion capture, oxy-fuel process and post-combustion capture (Songolzadeh et al., 2014). Techniques such as chemical and physical absorption, solid adsorption, membrane separation and cryogenic distillation have been used to separate CO₂ and control the release of CO₂ in the atmosphere (Mansourizadeh and Ismail, 2011a). Gas absorption has been carried out in many processes using various equipments, including packed columns, plate columns and ventur scrubbers (Rajabzadeh et al., 2009). Although good product yields with high purities can be obtained, this method consumes a lot of energy, especially during desorption, and high liquid losses occur due to evaporation of solvent in the stripper (Simons et al., 2009). A more efficient separation process that is less expensive and more environmental friendly is needed for carbon dioxide capture.

2.3.1 Physical Absorption

Physical absorption of CO₂ operates based on Henry's Law, where CO₂ is absorbed at low temperature and high pressure then desorbed at higher temperature and lower pressure. Many industrial processes adopt this technology, such as natural

gas and production of hydrogen containing high levels of CO₂. Some commercial processes that use physical absorption are Selexol Process, Morphysorb Process, Purisol Process, Rectisol Process and Fluor Process. Selexol process uses low vapour pressure, low toxicity and a solvent that is less corrosive, and can be used to remove both CO₂ and hydrogen sulphide at low temperature. Rectisol Process is used to deal with exhausted gas that contains sulfur, and uses a stable and less corrosive absorbent. Purisol Process has the advantage of consuming less energy, while Morphysorb Process, a relatively new one, costs less than the Selexol Process. Fluor Process, on the other hand, is applied for gases consisting of CO₂ at partial pressures exceeding 60 psig (Yu et al., 2012).

2.3.2 Chemical Absorption

Post-combustion CO₂ capture process using absorption has been investigated through many methods, with chemical absorption utilising aqueous alkanolamine solution being one of the most mature technologies for the purpose. The common chemical absorption process involves an absorber and a stripper to regenerate the liquid absorbent. The flue gas containing CO₂ flows into the absorber from the bottom where it contacts the liquid absorbent counter-currently. The CO₂-rich liquid absorbent then flows into the stripper to be regenerated thermally and recycled, while the pure CO₂ produced in the stripper is then compressed for the following transportation and storage (Yu et al., 2012). The alkanolamines used can be classified into primary, secondary and tertiary amines depending on the number of substituents for the amine group.

One of the most common aqueous solution used is the primary amine, monoethanolamine (MEA) owing to its fast rate of reaction and low cost, at the expense of expensive capital costs and energy requirement to regenerate it. Other than MEA, N-methyldiethanolamine (MDEA), DEA, diglycolamine (DGA), triethanolamine (TEA), di-2-propanolamine (DIPA) and AMP have been studied for absorption of CO₂ (Abdeen et al., 2016). Sterically hindered amines such as AMP, despite having lower absorption capacity than MEA, have higher cyclic capacities of CO₂. One of the strategies that have been explored to improve the properties and performance of liquid absorbents include the addition of additives into the liquid absorbent as well as using a combination of two or more amines which can increase the absorption rate and reduce the energy required to regenerate the liquid absorbent (Lin et al., 2008).

A lot of research is being conducted to overcome these disadvantages, such as the one done by Kim et al. (2013) to investigate the absorption characteristics of alkanolamine solutions having differing structures. That being said, the conventional processes for CO₂ absorption has many drawbacks such as entraining, channeling, foaming, flooding and high capital and operating costs. Improving the efficiency of these processes to overcome the problem is a challenge that has been undertaken by many researchers, and MGA is an attractive alternative that has the potential to solve the problems that occur in conventional processes (Marjani et al., 2012).

Since MGA is such an attractive alternative to the conventional process, many researchers have done work to improve various aspects of the MGA process. Mansourizadeh and Ismail (2010b) added non-solvent additives that included LiCl,

acetone, phosphoric acid, glycerine and polyethylene glycol into the dope solution in attempts at producing a porous structure. The non-solvent induced phase separation (NIPS) technique (Ahmad et al., 2012a) and surface modification of the membrane (Rahbari-Sisakht et al., 2012; Ahmad et al., 2013) were also used to increase the hydrophobicity of the membrane.

2.4 Asymmetric Polymeric Membrane for MGA Process

Usually, symmetric membranes are used due to the ease in casting and the intrinsic properties of the polymer that symmetric membranes offer. However, asymmetric and mixed matrix membranes are being widely used in industries due to the excellent mechanical strength and thin separation layer of these membranes. In addition, the asymmetric structure results in a better removal efficiency compared to the symmetric structure (Zhang et al., 2014). An asymmetric membrane has a thin and dense top layer that poses the most resistance to permeation, called the skin layer which rests underneath a porous solid matrix acting as a support. As the characteristics of the top layer determines the performance of the membrane, it is important to control its structure to achieve the desired membrane performance (Chuang et al., 2000).

For MGA applications, the selection of polymer to synthesise the membrane is of vital importance, keeping in mind that prolonged contact with the liquid absorbent may change the properties of the membrane such as the pore structure and performance efficiency (Favre and Svendsen, 2012). Research on mixed matrix membranes using PVDF as polymer matrix has been found to yield great hydrophobicity, mechanical stability and porosity for different applications (Ahmad et al., 2017). Bonyadi and Chung (2007) and Edwie et al. (2012) have added clay particles and fluorinated silica

respectively into PVDF to produce dual-layer hollow fiber membranes. These membranes have been found to have superior hydrophobicity and permeability for use in membrane distillation. DashtArzahandi et al. (2015) reported that incorporating montmorillonite into the PVDF polymer matrix increased the CO₂ flux compared to pristine PVDF membrane and MMM with Cloisite 15A.

2.4.1 Chemical and Physical Properties of PVDF as Polymer Matrix

One of the most important factors in MGA is the choice of membrane. For the case of CO₂ capture, the use of a hydrophobic membrane is desirable. PP, PTFE and PVDF are the three most researched membranes for this application. For this application, it is desirable for the membrane to be hydrophobic, as the hydrophobic behaviour prevents the solvent from entering the membrane pores (membrane wetting). Symmetric membranes made from polypropylene (PP) and polytetrafluoroethylene (PTFE) are commonly used in MGA processes for CO₂ absorption. These membranes are fabricated through stretching and thermal methods, as they are not soluble in common solvents at ambient temperature. Although high in hydrophobicity, these symmetric membranes with big pores cannot avoid wetting in long-term operations (Mansourizadeh, 2012). On the other hand, PVDF is an interesting choice for this application, mainly because it is the only hydrophobic polymer that can dissolve in common organic solvents (Abed et al., 2012). PVDF is a semi-crystalline polymer with piezoelectric properties and a glass transition temperature (T_g) of about -35°C. It can exist in several forms; alpha, beta and gamma phases (Heiji, 1969).