CORRELATING EFFECT OF POLYMER MOLECULAR CHAIN LENGTH AND PROPERTIES OF POLYVINYLIDENE DIFLUORIDE (PVDF) FOR CARBON DIOXIDE (CO2) REMOVAL IN MEMBRANE GAS ABSORPTION.

by

ISMAT MUHSIN BIN BAHARUDDIN

Project report submitted in partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

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LIST OF SYMBOLS

Symbol	Description	Unit
°C	Degree Celsius	
wt%	weight percent	
µm	Micrometer	
nm	Nanometer	
ε	Porosity	%
m_n	Weight of butanol absorbed	g
p_n	Density of butanol	g/cm^3
m_p	Weight of dry membrane	g
p_p	Density of PVDF	g/cm^3
cm	Centimeter	
J	CO2 flux	$mol/m^2 \cdot s$
$Q_{g,i}$	Initial flowrate	mL/min
$Q_{g,o}$	Final flowrate	mL/min
ρ_g	Density of gas	g/mL
M_g	Molecular weight of the gas	g/mol
A	Area of membrane	m^2
w_w	Wet weight of the membrane	g
w_d	Dry weight of the membrane	g

LIST OF ABBREVIATION

Symbol	Description
PVDF	Polyvinylidene Fluoride
NMP	N-methyl-2-pyrrolidene
MGA	Membrane gas absorption
CO_2	Carbon dioxide gas
MEA	Monoethanolamine
WCA	Water contact angle
WSA	Water sliding angle
SEM	Scanning electron microscope
MDEA	Mono-, die-ethanolamine
R_a	Mean roughness
R_{ms} , R_q	Root mean square roughness
PP	Polypropylene
MEK	Methyl-Ethyl-Ketone
PVDF-HFP	Polyvinylidene fluoride-co-hexafluoropropylene
NaOH	Sodium Hydroxide
TEOS	Tetraethoxysilane
PBI	Polybenzimidazoles
OTS	Octyltrichlorosilane
DTS	Decyltrichlorosilane
DDTS	Dodecyltrichlorosilane
HDTS	Hexadecyltrichlorosilane
TFPA	2,2,3,3-Tetrafluorofluoropropyl
HFBA	2,2,3,3,4,4,4-Hexafluorofluorobutyl acrylate
OFPA	2,2,3,4,4,5,5-Octafluoropentyl acrylate
DFHA	2,2,3,3,4,4,5,5,5,6,6,7,7-Dodecafluoroheptyl acrylate
PFA	Perfluoroalkyl Acrylate
DEA	Diethanolamine
AMP	2-amine-2-methyl-2-propanol
FTIR	Fourier-Transform Infrared Spectroscopy

N_2	Nitrogen gas
SDG	Sustainability Development Goal

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PERKAITAN TENTANG KESAN PANJANG RANTAIAN MOLEKULAR POLIMER DAN CIRI-CIRI POLYVINYLIDENE FLUORIDA (PVDF) UNTUK PEMBUANGAN KARBON DIOKSIDA (CO2) DALAM MEMBRANE PENYERAPAN GAS.

ABSTRAK

Salah satu parameter yang memainkan peranan penting dalam memerhatikan sama ada sebuah membran dapat mengasingkan gas dengan cekap ialah apabila ia memiliki ciri-ciri hidrofobik. Eksperimen untuk menghasilkan membran, mengenal pasti ciri-ciri sesebuah membran, dan juga ujian prestasi sesebuah membran telah dijalankan untuk membandingkan diantara Alfa Aeser dan Solvex Polyvyniliden Fluorida (PVDF). Kedua-dua membran telah dihasilkan dengan mencampurkan PVDF dan juga N-methyl-2-pyrroliden (NMP) dengan menggunakan teknik inversi fasa dan mandian pembekuan yang diperbuat daripada campuran etanol dan air suling dengan nisbah 20:80. Dengan meguji sudut sentuhan air terhadap Alfa Aeser dan Solvex membran telah memberikan hasil 98.01° dan 128.46° masing-masing. Ini menunjukkan membran-membran yang terhasil ini menunjukkan sifat hidrofobik dan superhidrofobik untuk Alfa Aeser dan Solvex membran masing-masing. Untuk ujian membran penyerapan gas, Solvex membran telah berjaya memberikan hasil yang lebih baik dalam mengasingkan gas karbon dioksida (CO_2) dengan menggunakan larutan monoethanolamin (MEA) jika dibandingkan dengan hasil ujian dari Alfa Aeser. Selepas semua hasil dari ujian dan pemerhatian dan perbandingan terhadap kedua-dua membran, Solvex membran dijangka memiliki berat molekul yang lebih ringan berbanding Alfa Aeser kerana ia menunjukkan sifat hidrofobik yang lebih baik dan prestasi yang lebih baik dan efisien berbanding Alfa Aeser.

CORRELATING EFFECT OF POLYMER MOLECULAR CHAIN LENGTH AND PROPERTIES OF POLYVINYLIDENE DIFLUORIDE (PVDF) FOR CARBON DIOXIDE (CO2) REMOVAL IN MEMBRANE GAS ABSORPTION.

ABSTRACT

Hydrophobicity of a membrane is one of the main parameters that need to be observed for a membrane to exhibit high efficiency when diffusing gas. The experiment to synthesizing the membrane, characterizing the membrane and performance test on the membrane has been done to compare the ability of Alpha Aeser Polyvinylidene fluoride (PVDF) and Solvex PVDF. Both of the membranes were synthesis by mixing the PVDFs and N-methyl-2-pyrrolidene (NMP) solutions by using the phase inversion method and the coagulation bath used to immerse the membranes was made up of mixture of ethanol and distilled water in the ratio of 20:80. By testing the result using water contact angle test, Alpha Aeser and Solvex membrane exhibit 98.01° and 128.46° respectively. The result shows that the membranes are hydrophobic and superhydrophobic. For the membrane gas absorption (MGA) test, Solvex membrane give better result in separating CO_2 gas with monoethanolamine (MEA) compare to Alpha Aeser. After obtaining the all the results and after comparing between both membranes, Solvex membrane was expected to be having lower molecular weight compare to Alpha Aeser because it shows better hydrophobicity and better performance compare to Alpha Aeser.

CHAPTER 1

INTRODUCTION

Chapter 1 will introduce the overview for the research conducted together with the importance of the membrane gas absorption (MGA) of carbon dioxide (CO_2). In short, chapter 1 will be summarizing the research background of the CO_2 emission and the membrane gas absorption of CO_2, the problem statement, scope of study, thesis organization. And the objectives of research for the final year project.

1.1 CO_2 emission

Carbon dioxide, CO_2 is one of the gas that is presence in our surrounding. CO_2 are mainly used by plant for them to undergo photosynthesis. By using CO_2 gas, the plant could produce their own food and also oxygen gas to be used by others such as animals and human. Although CO_2 gas is important for life cycle, if there are an abundant amount of CO_2, it will be causing severe problem to earth. Besides being useful to plant, CO_2 gas is also one of the toxic gas. Once accumulated and become concentrated, it can cause breathing difficulty and other health problems to humans. Furthermore, accumulated CO_2 gas in our atmosphere will make our earth to suffer. Increased in earth temperature, forest burning and many more environmental problems will be caused.

As time goes by, the world population keep increasing, thus the supply and demand will also increase. Either the consumable items or facilities to be used. The facilities used such as public transport or private vehicle demand will increased together to keep up with the increased human population. The vehicle which will used a lot of fossil fuel will emit a huge amount of CO_2 over time(Davis & Caldeira, 2010). This is one of the reasons to the increased in the CO_2 level in out surrounding. Besides that, to keep up with the supply and demand, more factory need to be built to increase the production thus industrial has become one of the reason for the increase in the CO_2 emission (Canadell et al., 2007). Most of the CO_2 gas release from the industrial are mixed with other unwanted substances. Thus, there is a need to separate the CO_2 gas from other substances. One of the methods that can be use is the membrane gas absorption method. The method that has been used previously is the conventional method. Conventional method has been implemented by a lot of factories as it is proven to achieve the demand result. But it will have several disadvantages such as the complexity of the process and will cause environmental problems. Thus, to overcome the issues, new method for gas separation was introduced which is the membrane technology. The membrane technology is preferable because will not release pollutant to the surrounding and simpler process. But then, membrane technology by itself will have its problems which is high energy intensive by using dense membrane separation. Thus, to overcome the challenge, a combination of the conventional solvent absorption and membrane separation technology was introduced which is the membrane gas absorption method.

1.2 Membrane Gas Absorption

Gas absorption or known as scrubbing is one of the process to separate a certain component in a mixture of gases. A liquid mixture will be used to scrub off the gas from the mixture, while the required purified gas is the un-scrubbed gas. The latest innovation made to the gas absorption method is by using membrane. The membrane that are produced by using polymer will exhibit hydrophobic properties which only allows the CO_2 to pass through. The mixtures to be separated are CO_2 that come together with a solvent. The selection of the polymer used to produce the membrane will affect the performance later on.

As the selection of polymer will affect the performance of the of the membrane, there also other factors such as the structure of the membrane, the configuration and more (Bernardo et al., 2009). For the membrane to perform at its high efficiency for the gas absorption process, it should possess a super hydrophobic property. Swelling test, finding the water contact angle (WCA) and water sliding angle (WSA) are the method used to find out the hydrophobic properties of the membrane.

Several main factor will affect the membrane hydrophobicity. One of the examples is the alkyl chain length of the polymer used to synthesis the membrane which will contribute an important role in fabricating the membrane hydrophobicity. This is because the properties of either alkyl chain length or the functional group contain together in the alkyl chain length will change the hydrophobicity of the membrane.

In addition, the surface characteristic of the membrane such as roughness of the membrane surface will also affecting the membrane hydrophobicity. The rougher the membrane surface, the attraction between the water droplets with the surface will be lower.

The pore size will also be affecting the efficiency for the gas absorption. As the size of the pore become larger, it will give way for other molecule such as the solvent molecule to enter and probability of buildup resistance.

1.3 Problem Statement

MGA is one of the innovation methods that highly seek nowadays in removing CO_2 efficiently rather than releasing it to the surrounding. Before a membrane is choose for separation, the membrane must possess unique characteristics such as high flux value for the CO_2 diffusion and must be super hydrophobic. One of the basic foundations that will affect the characteristic of the membrane is the polymer chain length for the PVDF used to produce the membrane. Selection between different chain lengths of the PVDF will give an effect to the properties of the membrane. By using different chain length, different properties of the membrane will be obtained, either the desired or undesired properties. Thus, to avoid taking the poor result of the polymer, further study on the physical and the chemical properties of the polymer will be done before proceed with membrane casting.

Besides that, there exist several methods to synthesis the PVDF membrane and the best method must be chosen to get the best result. In this research, two types of PVDF with different chain length will be used to produce PVDF membrane. By using longer chain length of the PVDF, the membrane produce will have high hydrophobic properties compare by using shorter chain length. The experiment conducted will be studying on the interacting properties between polymer chain length, polymer density, and membrane formation mechanism.

After the membranes have been produced, it must be examined under several tests such as the resistance to liquid and the CO_2 permeability. It can ensure that the membrane produced is qualify to be used for MGA process. In this research, two types of PVDF with different chain length will be used to produce PVDF membranes. The membrane will undergo several tests such as the water contact angle (WCA), scanning electron microscope (SEM) and several other methods to get the results on hydrophobicity, permeability, and wettability.

1.4 Objectives

1. To evaluate the polymer chain length and chemical properties of two different molecular weight PVDF.
2. To synthesis and characterize templated PVDF membrane.

3. To evaluate CO_2 permeability and wettability resistance of membrane via membrane gas absorption.

1.5 Scope of study

This study will be split into two which is the polymer and membrane characterization and membrane performances. The first part will be focusing on characterization of two type of polymer which is identifying the alkyl chain length of two different PVDF. Before the membrane will be casted, by classifying the two types of PVDF will help to categorize the membrane later. The polymer will be classified by their alkyl chain length and the molecular weight. For the membrane characterization will be divided into two part which is the membrane gas absorption and the wettability test. The membrane will undergo several tests such as the water contact angle (WCA), scanning electron microscope (SEM) and several other methods to get the results on hydrophobicity, permeability, and wettability.

1.6 Thesis organization

This thesis contains three main chapter which will assemble the thesis. Chapter one will present the overview and background study of the research. It contains brief introduction of the research, problem statement, objectives and scope of study of the research.

Chapter two present the literature review of various research done previously on the CO_2 greenhouse gas impact, membrane gas absorption challenges, membrane hydrophobicity and the method to increase the membrane hydrophobicity.

Chapter three present the material used during the research. The flow and detail of the research is explained in details such as the method to check the membrane performance and polymer characterization and also the membrane gas absorption test.

CHAPTER 2

LITERATURE REVIEW

In previous chapter discussing on the increasing of the CO_2 emission from different sources, and the used of membrane gas absorption to efficiently separate the CO_2 gas. Chapter 2 will show several of the previous finding and research from different scientific records which is related with the final year project. This chapter will cover about the membrane hydrophobicity, the challenges for the membrane gas absorption and the effect of the CO_2 greenhouse effect. Besides that, this chapter will also show the several methods used to increase the hydrophobicity of the membrane in term of membrane module, type of polymer used, the surface roughness and pore size, and the effect of alkyl chain length of the polymer used.

2.1 CO_2 Greenhouse Gas

CO_2 gases are one of the main gases that can be found inside the greenhouses gases (Tsugawa & Kato, 2010). Greenhouse gases also is the biggest contributor that causing global warming to Earth.

2.1.1 Greenhouse Impact

Greenhouse gas had caused several calamities to Earth. The gases will be accumulated between Earth and the atmospheric layer, causing heat to be trapped inside and causing the Earth temperature to rise slowly. Thus, as an effect it has caused global warming to our earth. As an after-effect of global warming, it has caused several disasters issues such as melting of glaciers, the increase of Earth temperature, and increase in the sea level (Jacobson, 2009). As time goes by, the amount of CO_2 gases releases to our surrounding keeps increasing causing the global warming of earth to be unsettled, rather, keep becoming worse. In addition, people awareness of the environmental effect of excessive CO_2 gas is still in negligence.

The release of CO_2 gas either by burning of fossil fuel through vehicle or increased of industrial activities to keep up with the economics growth are the main root that contributed to the global warming, as discussed by Davis and Caldeira, (2010). In fact, reducing the release of CO_2 to atmosphere from there two aspects can serve as a good starting point to save the Earth. It is encouraging to use the public transportation than using private vehicle as the mode of transportation, used the public transport. As for the industrial, use effective measure to prevent the released of CO_2 into the surrounding. Gas separation can be done by several separation method but the common methods are using conventional and membrane separation method.

2.1.2 Conventional Method and Membrane Gas Absorption

For separation of CO_2 gas, there exist several different methods and can be made into two groups which is the conventional and membrane method. The conventional method is one of the oldest methods and has been established for sometimes. the conventional method can be classify into 3 general groups which is the physical absorption, chemical absorption and also physical-chemical absorption (Yeo et al., 2012). Table 2.1 shows the three types of conventional method for CO_2 separation method with the process included.

Table 2.1: Type of conventional absorption process for CO_2 separation

	Process	Solvent	Description	References
Physical absorption	Rectisol	Cold methanol	Operating condition is at certain range of temperature (-30°C to -60°C) and by using the Lurgi moving-bed	(Higman & van der Burgt, 2008)

			gasifier. It is one of the oldest conventional method	
	Selexol	Dimethyl ether of polyethylene glycol	It operates at low pressure and temperature range from 0°C to 40°C and it consist of a flash, a steam-heated stripping column and an absorber	(Kohl & Nielsen, 1997)
Chemical absorption	Alkanolamine sweetening	Amine group (mono- and diethanolamine, methyldiethanolamine, and etc.). But widely used is MDEA	MDEA is more selective compare to other amines group. Process done by feed the natural gas from bottom of absorber and solvent from top of absorber	(Speight, 2007)
	Carbonate and water washing	Potassium carbonate	The operating temperature for the process around 110°C. The potassium carbonate will absorb the CO_2 and process is highly efficient when the temperature approaches the temperature for the reaction reversibility	(Speight, 2007)

Physical-chemical absorption	Sulfinol	Combination of physical solvent (sulfalone) and amines (diisopropanolamine and methyl diethanolamine) (DIPA and MDEA)	Sulfalone will be used to remove the CO_2 while the MDEA or DIPA will be used to further purify the process gas in the Sulfinol-M and Sulfinol-D process respectively	(Speight, 2007)

Conventional method has been established for a long time, but because it has several disadvantages such as using many equipment which is costly, has a complex process and will caused negative impact to the surrounding area because of various volatile solvent used (Yeo et al., 2012). Thus, new method was found which is by substituting the conventional method with using membrane to separate the CO_2 gas.

Using membrane for CO_2 separation is quite new process where the process was found less than three decades ago (Yeo et al., 2012). In contrary with the conventional method, the membrane separation does not require a complex process such as several absorption columns or stripping column, thus, reducing the energy required to operate. It also will be more environmentally friendly because it does not require a volatile solvent to undergo the process. Furthermore, because of its simplicity of the process, the capital cost and the operating cost will also be lower compare to the conventional method.

2.2 Challenges using the membrane gas absorption techniques

Even though membrane is highly preferable over the conventional method for separation of CO_2, there also several challenges due to the used of membrane. One of the challenges in using the membrane gas absorption techniques is it is considered a new method and does not highly used compare to the conventional method (Yeo et al., 2012). The conventional method which are already widely used such as the amines process or physical absorption techniques are already being used in most of the industry. Thus, to change into new method, will cost the developer a huge amount of money and also will not guaranteed to give profits to the developer.

Furthermore, the membrane selectivity is quite low, and sensitive to the extreme operating condition (Yeo et al., 2012). The membrane will be facing difficulties to operate under high temperature and also in a corrosive environment. Besides that, to get an efficient membrane for the absorption process, it needs to have several unique characteristics to be able to perform at its highest capability. Few examples of its characteristics are, its need to have high CO_2 flux so that the CO_2 gas can enter through the membrane without any hustle, it needs to be water resistance either to water or solvent used. This is to avoid from the membrane to become swelling thus, reducing the its capabilities to separate the CO_2 gas.

Other than that, the membrane will also have to have the physical characteristic that will help to enhance the absorption process in term of the surface roughness and also the pore size. The surface roughness will affect the membrane wettability while the pore size of the membrane will affect the transfer rate of CO_2.

2.3 Membrane hydrophobicity

To indicate either the membrane can operate at its highest efficiency, one of it must have characteristic is its hydrophobicity. Membrane hydrophobicity can be divided into three level which is hydrophilic, hydrophobic and super hydrophobic. The membrane hydrophobicity can be measured by using several methods such as the water contact angle (WCA), water sliding angle (WSA) and using swelling test.

Hydrophilic means it tends to absorb water. The definition comes from its names. Hydro is ‘water’ and Philic is ‘affinity to’. If a membrane exhibits hydrophilic characteristic,