Development of PES-SAPO Amine Mixed Matrix Membrane for Carbon Dioxide Removal

by

Nur Nabila Syahira Binti Abdullatib

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2013

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Associate Professor Dr. Hilmi Bin Mukhtar)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done unspecified sources or persons.

NUR NABILA SYAHIRA BINTI ABDULLATIB

ABSTRACT

Purification of natural gas by removing carbon dioxide is the most important step before the gas can be on sale. The aim of this study is to develop SAPO Amine based mixed matrix membrane (MMM) for the removal of carbon dioxide from raw natural gas. This was carried by the blending of SAPO with amine in polysulfone. The membrane was developed by varying the percentage of amine from 10wt% to 20wt%. Characterization showed that the SAPO-amine membrane was dense and the SAPO was distributed homogenously. The performance showed that the highest ideal selectivity was achieved by the addition of amine with 10wt%.The expectation from this study is to able to develop Mixed Matrix Membrane (MMM) for carbon dioxide removal from raw natural gas. In this paper, the material selection , membrane fabrication and performance test were also discussed.

ACKNOWLEDGEMENT

“Praise to Allah, the most Gracious and the most Merciful”

I have taken a lot of efforts during these two semesters to complete the Final Year Project. However, it would not been possible without the kind guidance and support of individuals for this project. Thus, I would personally like to express deep gratitude to my supervisor, AP Dr Hilmi bin Mukhtar for his guidance, comments and supports during this project.

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TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

CHAPTER 2

LITERATURE REVIEW

CHAPTER 3

MATERIALS AND METHODS

CHAPTER 4

RESULTS AND DISCUSSION

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

LIST OF FIGURES

LIST OF TABLES

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CHEMICAL ENGINEERING DEPARTMENT

CBB 4612

FINAL YEAR PROJECT 2

DISSERTATION REPORT

NAME : NUR NABILA SYAHIRA ABDULLATIB

ID : 12803

PROJECT TITLE : DEVELOPMENT OF OF PES-SAPO AMINE MIXED MATRIX MEMBRANE FOR CARBON DIOXIDE REMOVAL

SUPERVISOR : AP DR HILMI BIN MUKHTAR

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas is combustible mixture of hydrocarbon found issuing from the ground or obtained from specially driven wells. Natural gas is an odorless, colorless, and shapeless in its pure form. Natural gas is composed primarily of methane but also contain ethane, propane and heavier hydrocarbons and also carbon dioxide, nitrogen and hydrogen sulphide. Figure 1 shows common natural gas composition and their percentage.

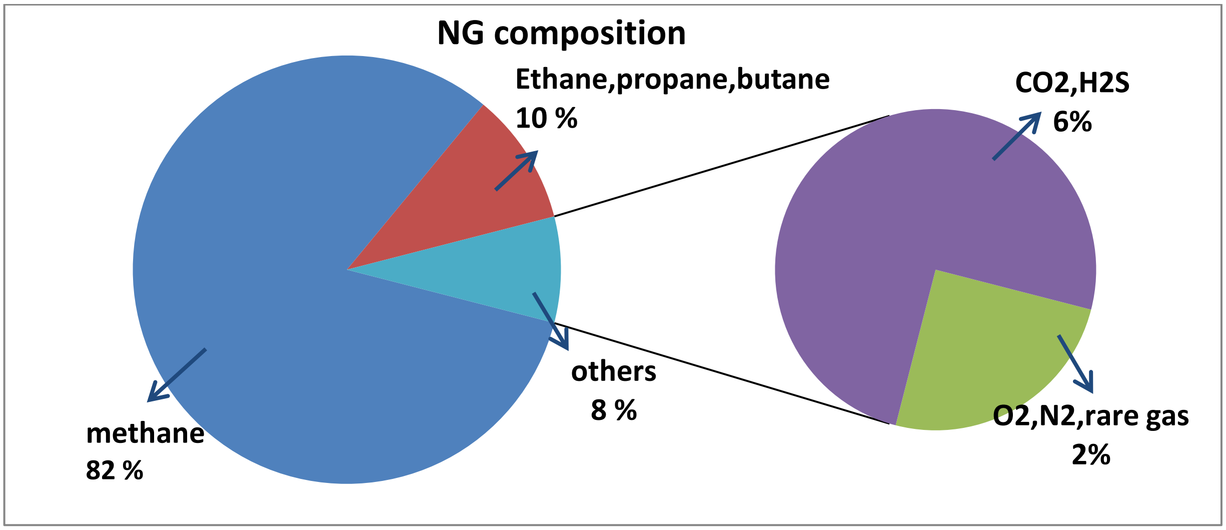


Figure 1.1: Natural gas composition

Natural gas can also be considered as sour gas. Sour gas is defined by natural gas that contain hydrogen sulphide (H_2S) in concentrations more than four part per million (ppm) by volume under standard temperature and pressure.

1.1.1 Natural Gas Specifications

Natural gas specifications have some purposes including preventing corrosion, to avoid liquid drop put in pipelines and burner performance. (Yves Bramoulle, Pascale Morin, & Jean-Yves Capelle, 21-24 March 2004)

Acid gas removal unit treat gas to 50 ppmv CO_2 in order to meet receiving end pipeline specifications. The sulfur specification for Japanese market is 5 mg/Nm^3 maximum and total sulphur content to 30 mg/Nm3 maximum. These specifications also meet the requirement for Europe and US market. But, except for California, the total limit sulfur up to 18 mg/Nm^3. (David Coyle, Felix F.de la Vega, & Charles Durr)

1.1.2 Acid Gas Removal Processes

There are four categories of acid gas removal process which are chemical absorption, physical absorption, physical-chemical absorption, adsorption process and membrane technology. But in this proposal, the author will further explain about chemical absorption process as this process is mainly used in acid gas removal system.

Chemical absorption for acid gas capture is based on exothermic reaction of a sorbent with acid gas present in the gas stream at low temperature. The reaction is then reversed in regeneration at higher temperature. Two groups that have been used in acid gas removal are amines and potassium carbonate. (H & Maarten, 2008)

1.1.2.1 Benfield Process

In the 1950s Benson and Field developed the Benfield Process which used hot potassium carbonate as absorption solvent. Then, in 1970s, alkanolamine is use as rate promoter resulting in substantial lowering of capital and operating costs and higher treated gas purity. (Kohl & Riesenfield, 1985, pp. 211-246)

Benfield process is a thermally regenerated cyclical solvent process that uses an activated hot potassium carbonate solution to remove carbon dioxide (CO_2), hydrogen sulphide (H_2S) other acid gas components. The high temperature operations of the Benfield process will prevents hydrocarbon from condense.

Benfield process is comprises of two columns which are absorber and regenerator. These two columns are operated at close temperature. Removal of acid gas from the feed gas is accomplished by absorption in a counter current flow of hot potassium carbonate solution in the absorber. In Benfield Process, the feed gas which is the raw natural gas is contacted counter currently the hot potassium carbonate in the absorber and the acid gas will be removed. The rich solution loaded with acid gas will passes to the regenerator where it will be stripped by counter current contact with a stream of steam. Figure 1.2 shows the Benfield process in removing acid gas.

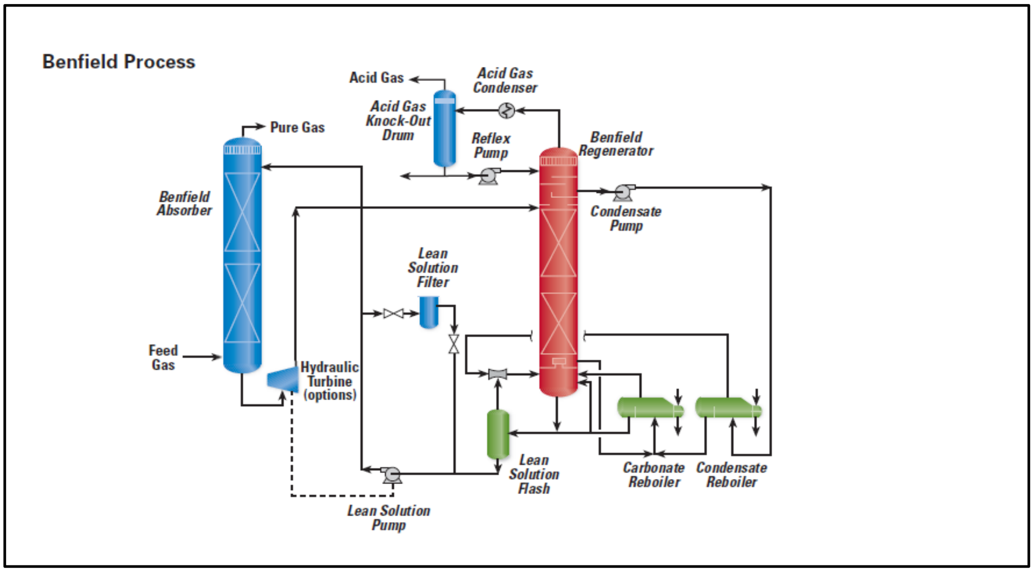


Figure 1.2: Benfield process

1.1.2.2 The Usage Of Amine In Hot Carbonate Process

The most important development in this process is the discovery that small amount of certain organic or inorganic additives or known as promoter can increase the absorption rate. (Riesenfield & Mullowney, 1959, pp. 161-167)

The main alkanolamine products used in acid gas removal are Monoethanolamine (MEA), Diglycolamine (DGA), Diethanolamine (DEA), Diisopropanolamine (DIPA) and Methyldiethanolamine (MDEA). MEA is primary amine, DEA is secondary amine and MDEA is tertiary amine.

The amine promoted hot carbonate process provides an economic and efficient way for acid gas removal process from raw natural gas. However their performance as solvents is limited by a high heat of absorption, and issues of amine loss and degradation and corrosion. One way to improve is to blend a fast reacting amine with a solvent that possesses a low heat of absorption such as potassium carbonate (K_2CO_3). (Hendy Thee, et al., 2012)

Usually primary or secondary amines are used as rate promoters while tertiary amines do not show a significant rate increasing effect in acid gas removal. so, in summary Monoethanolamine (MEA) is the best amine to be added to carbonate solution as it does result in an enhanced absorption rate.

1.2 PROBLEM STATEMENT

To date, the raw natural gas that coming from well are having high carbon dioxide content. But, some of the technology that are used in carbon dioxide removal cannot cope with the high CO_2 content due to their limitation of operation.

Table 1-1 below shows the chemical composition provided by Bergading platform offshore of Terengganu, Malaysia

Table 1.1: Chemical composition of Bergading platform offshore

Chemical name	**Percentage**
Methane	40-50%
Ethane	5-10%
Propane	1-5%
Carbon dioxide	17-20%
Hydrogen sulphide	0-1%

.

It shows the raw natural gas from well are having high carbon dioxide content. The natural gas will then send to onshore plant for acid gas (carbon dioxide and hydrogen sulphide) removal process. So, instead of installing the acid gas removal process at onshore, why the unit are not been installed on offshore platform to reduce the pipeline cost and production cost.

Hence, study and research have been done by researchers in order to develop new technology that is able to remove the acid gas from the raw natural gas at offshore.

1.3 OBJECTIVE

The main objectives of this research are:

1. To fabricate mixed matrix membrane by using SAPO-34 and polysulfone.
2. To characterize the properties of the developed mixed matrix membrane.
3. To test the performance of mixed matrix membrane on carbon dioxide removal based on the permeability and selectivity

1.4 SCOPE OF STUDY

In this study, the main subjects under investigation are:

1. The materials used to synthesis mixed matrix membrane.

The polymer used in this study is polysulphone. SAPO-34 is used as the inorganic filler, and Dichloromethane is used as the solvent. Diethanolamine is added to the membrane as the third component to enhance the carbon dioxide absorption.

2. The membrane will be characterized by using the following equipment :

- Field Emission Scanning Electron Microscope (FESEM) –To inspect the morphology of prepared membranes
- Thermogravimetric analyse (TGA) -To determine the mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture).
- Fourier Transform Infrared Spectroscopy (FTIR) - To give information on the molecular interaction of the molecules and functional group of the membrane.

3. The performance of the prepared membranes will be test using the gas membrane permeation unit. The prepared membranes will be test on the CO_2 and CH_4 permeability and selectivity.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane technology

Membranes are thin semipermeable barriers that selectively separate some compounds from others.

Membrane-based technology has experienced substantial growth during past decades due to its easy to operate and control because the membrane equipment is very simple without moving parts. (Shekhawat, Luebke, & Pennline, 2003). Membrane increasingly being selected for new projects especially for applications that have large flows, and for high carbon dioxide content. (David Dortmundt & Kishore Doshi, 1999)

Membrane technology is also an energy efficient technology as it involves a continuous process without the need for sorbent regeneration or desorption (An, Swenson, Wu, Waller, Ku, & Kuznicki , 2011)

Three major categories of membrane technology for CO_2/CH_4 separation are polymeric membranes, inorganic membranes and mixed matrix membranes. In polymeric membrane the gas molecules are transported through non-porous membrane based on solution-diffusion mechanisms. The selectivity is regulated by the molecular structure that allows certain gas molecules to pass the membrane based on their sizes. While, the permeability is controlled by the gas solubility. Main parameter on gas solubility is the ability of the penetrant gases to condense. (Yuan Zhang, Jaka Sunarso, Shaomin Liu, & Rong Wang, 2013)

Due to shortcomings of polymeric membranes, researchers have developed inorganic membrane to overcome the challenges and limitations of polymeric membranes. Porous inorganic membranes provide better selectivity, thermal and chemical stability as compared with polymeric membranes. But, the main challenges in inorganic membrane is to fabricate the membrane as thin membranes on modules with large surface area at reasonable cost while avoiding formation of cracks that would compromise separation efficiency. (Xomeritakis, Tsai, Jiang , & Brinker, 2009)

While, Mixed Matrix Membrane or also known as MMM comprise of molecular sieve entities embedded in a polymer matrix. But later in this proposal, the author will further explain about MMM.

2.2 Mixed Matrix Membrane (MMM)

Although inorganic membrane had been proven can overcome the limitations of polymeric membranes on the small scale, manufacturing of inorganic membrane incurs large cost. By combining the advantages of polymeric and inorganic components, MMM is able to increase both permeability and selectivity. (Tantekin-Ersolmaz, Atalay-Oral, Tatlier, Erdem-Senatalar, Schoeman, & Sterte, 2000)

Mixed matrix membrane (MMM) is discovered by Kulprathipanja et al at UOP (Kulprathipanja, Neuzil, & Li, 1988) . MMM is heterogeneous membrane composed from inorganic material in the form of micro- or nano- scale particles embedded in continuous polymer matrix. (Yuan Zhang, Jaka Sunarso, Shaomin Liu, & Rong Wang, 2013) . The integration of these two materials with different flux and selectivity provides better design membranes for carbon dioxide separation, allowing the synergistic combinations of polymer's easy processability and superior performance of inorganic materials. (Brunetti, Scura, Barbieri, & Drioli, 2010)

However, the commercialization of this approach has been interrupted by poor adhesion between zeolite and polymer as well as inadequate particle dispersion causing losses in selectivity. (Kim, Pechar, & Marand, 2007)

2.2.1 Limitations and improvements of MMM

One of the big challenges in MMM development is the dispersibility of nano sized inorganic particles in the polymer matrix. The nano particle disperse poorly in the polymer matrix and lead to the formation of numerous stress convergence points under the action of outside forces which will weaken the mechanical stability. (Yang, Zhang, Wang, Zheng, & Li, 2007)

The addition of zeolites into a glassy polymer also leads to the formation of defects at the interface between the zeolite and the polymer attributed to the poor compatibility between zeolites and polymer matrix. (Koros & Mahajan, 2000)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials Selection

The proper material selection for matrix and inorganic phase is very important. This is because the polymer and inorganic phase properties can affect the membrane morphology. (M.A, A.F, T, & M.M, 2010)

3.1.1 Polymer, Polysulfone

Polysulfone is a glassy polymer that has been studied for gas separation and permeation due to its low permeability and comparatively high selectivity, which bring it close to the Robeson's upperbound limit. (Robeson, 2008).

Polysulfone allows easy manufacturing of membranes, with reproducible properties and controllable size of pores down to 40 nanometers.

The main reasons for the choice of polysulfone is due to its tough, rigid, high-strength properties.

3.1.2. Inorganic Filler,SAPO-34

SAPO-34 zeolite is a silicoaluminophosphate molecular sieve with CHA structure formed by introduction of Si atoms into neutral A1PO4 framework. SAPO-34 molecular sieves have pores that are similar in size with CH4. Both have pore diameter of 0.38 nm.

This membrane also separated CO2/N2, N2/CH4, H2/CH2, H2/CO2, and H/N binary mixtures. (Shiguang Li, John , & Richard, 2004) SAPO-34 is used because of its intermediate acidity, high thermal and chemical stability and small pore size. (Szostak, 1989). X-ray diffraction (XRD) has showed that SAPO-34 crystals are stable up to 1273 K. (Watanabe, Koiwai, Takeuchi, & Hyodo, 1993)

3.1.3. Solvent ,Dichloromethane (DCM)

Solvent that been used is Dichloromethane (DCM). DCM is very dangerous because it’s high volatility rate. DCM is used as solvent in the membrane fabrication due to its rapid evaporation rate.

DCM has low boiling points and also has the closest solubility parameter with polysulfone, PSU. Hence, this makes DCM as the most suitable solvent to be used in the membrane fabrication. By using DCM as the solvent, the author can avoid having problem with the drying rate of the membrane.

3.1.4. Third component, amines

Amine is organic compounds and functional group that contain a basic nitrogen atom with a lone pair. Amine is added in order to enhance the separation of carbon dioxide from methane. In this study, the author used Diethanolamine (DEA).

3.2. Composition

In this work, the composition of SAPO-34 and Polysulfone was kept constant. The amine composition was varied throughout this work to study the effect of amine addition as the third component used in membrane preparation.

Polymer (PSU) = 20 wt %
SAPO-34 = 10 wt %
Amine = 10-20 wt % (10, 15, 20 wt %)

Table 3.1: Composition variation to study the effect of addition of amine in the Mixed Matrix Membrane

Membrane	**Polymer, Polysulfone**	**Inorganic Filler, SAPO-34**	**Amines, Diethanolamine (DEA)**
Pure membrane (M1)	20 wt%	-	-
Pure MMM Polymer + SAPO (M2)	20 wt%	10 wt %	-
Membrane 1(M3)	20 wt%	-	10wt%
MMM1	20 wt %	10 wt %	10 wt %
MMM2	20 wt %	10 wt %	15 wt %
MMM3	20 wt %	10 wt %	20 wt %

The author needs to prepare three samples for each membrane in order to get the best membrane. Equation below shows the calculation for the composition of polymer, SAPO-34, and amines.

$$\boxed{\boldsymbol{polymer}\ (\mathbf{20}\%) = \frac{\text{polymer (g)}}{\text{solvent (g)}} \times 100 = 20\%}$$

$$\boxed{\boldsymbol{SAPO-34}\ (\mathbf{10}\%) = \frac{\text{solvent (g)}}{\text{polymer (g)}} \times 100 = 10\%}$$

$$\boxed{\boldsymbol{amines}\ (\mathbf{10-20}\%) = \frac{\text{amines (g)}}{\text{polymer (g)}} \times 100 = 10-20\%}$$

3.3 Procedures

3.3.1. Membrane casting solution preparation

3.3.1.1 Polymeric membrane

1. Dried polymer, polysulphone was slowly added to solvent, dichloromethane.
2. After all the polymer was added, the solution is left stirred for 24 hours.
3. Then, the solution was allowed to stand for at least 8 hours to remove all air bubbles produce during mixing and stirring.
4. The solution is then will undergo degassing process in order to remove all the air bubbles. This is because the presence of bubbles in the solution will form holes and tiny pores in the membrane films.

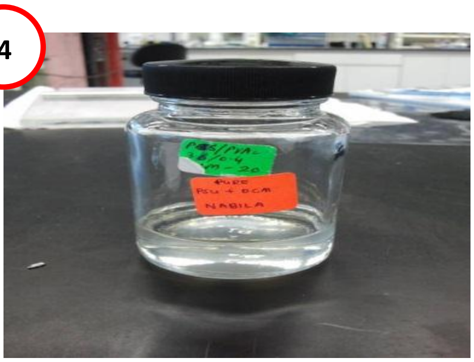
30 grams of Dichloromethane (DCM) is used as solvent

6 grams polysulphone (polymer)

3

1. Polysulphone is added little by little in order to make sure all the polymer is dissolved in the solvent
2. Then, the solution will be left stirred for 24 hours

4



After been stirred for 1 day, the solution will be left for 1 day without stirring

3.3.1.2 Mixed Matrix Membrane with amine

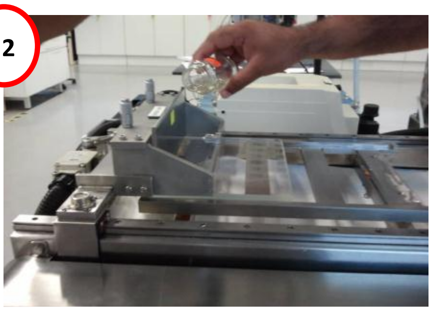
1. Amine was mixed with the solvent and stirred for 24 hours at room temperature.
2. Then,SAPO-34 was added into the solution and the solution was stirred for 24 hours at room temperature.
3. 1/5 from the total polymer was added to the solution and stirred until it dissolved.
4. Then, the remaining polymer was added little by little and stirred until all the polymer dissolved.
5. The solution is then will be stirred for 24 hours until homogenous solution is obtained.
6. Then, to remove the air bubbles form during mixing and stirring ,the solution is left for degassing for 2-4 hours

3.3.2. Casting

1. After degassing the suspensions under vacuum for 2 to 4 hours, they were casted over clean warm glass plates.
2. The prepared solution need to degassing in order to remove the air bubble in the prepared solution.
3. Then, the membrane will be left for drying at room temperature for 24 hours before it was placed in an oven for another 24 hours.
4. The formed films were peeled from the glass surface at high temperature to avoid rupturing during peeling.
5. The membrane was allowed to cool naturally in room temperature

The glass plate needs to wash before membrane casting

②



The prepared solution is poured in the casting machine

③

After membrane casting

④

The membrane then is left at room temperature for 1 day

⑤

Then, put in oven at 60°C for 1 day

3.4. Membrane Characterization

The morphology of prepared membranes was inspected with field emission scanning electron microscopy using the Field Emission Scanning Electron Microscope (FESEM). Thermogravimetric analyse (TGA) is used to determine the mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Differential Scanning Calorimeter (DSC) is use to study the glass transition temperatures T_g of the membrane. Fourier Transform Infrared Spectroscopy (FTIR) is used to give information on the molecular interaction of the molecules and functional group of the membrane. The thickness of membrane was measured using Mitutoyo digital micrometer.

FESEM consist of an electron emission gun which is placed at the top of the microscope. The electron emission gun is used to produce a stream of high energy electron beam. Then, the electron beam travels through series of electromagnetic fields and lenses. Once the beam hits the sample, secondary electrons are emitted from the surface of the sample. Then, detector will collects the secondary electrons and convert to signal.

FTIR is used to study the composition of the membrane and also the presence of certain functional group in the sample. FTIR is equipped with infrared source, interferometer, detector and computer.

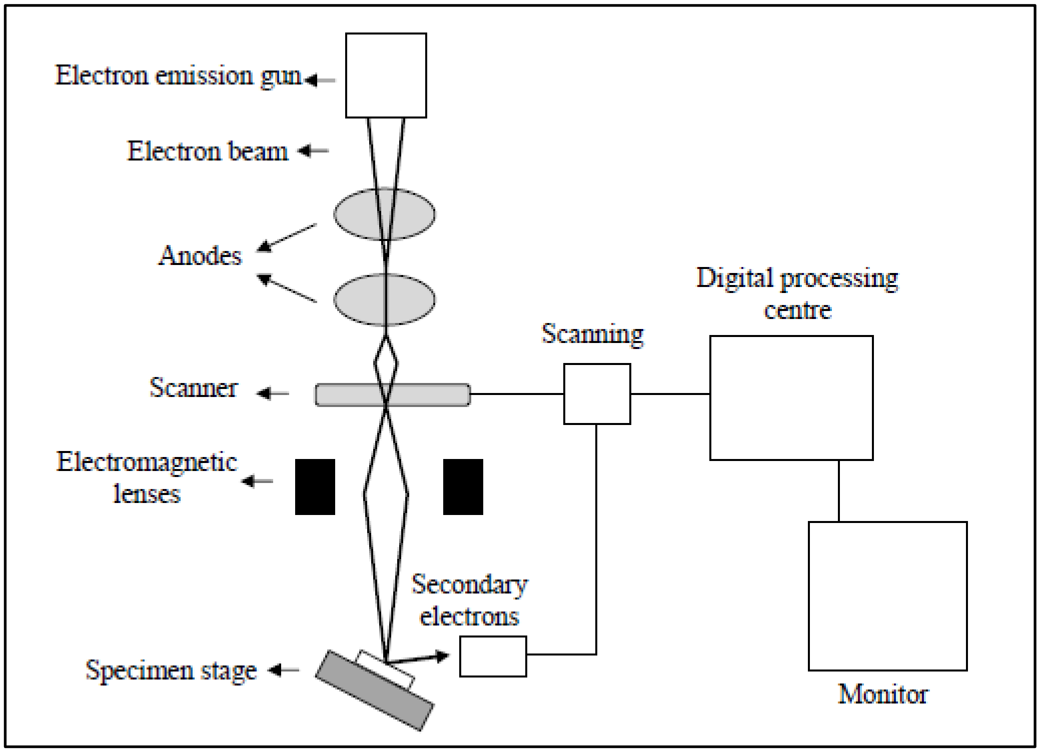


Figure 3.1: Schematic diagram of FESEM

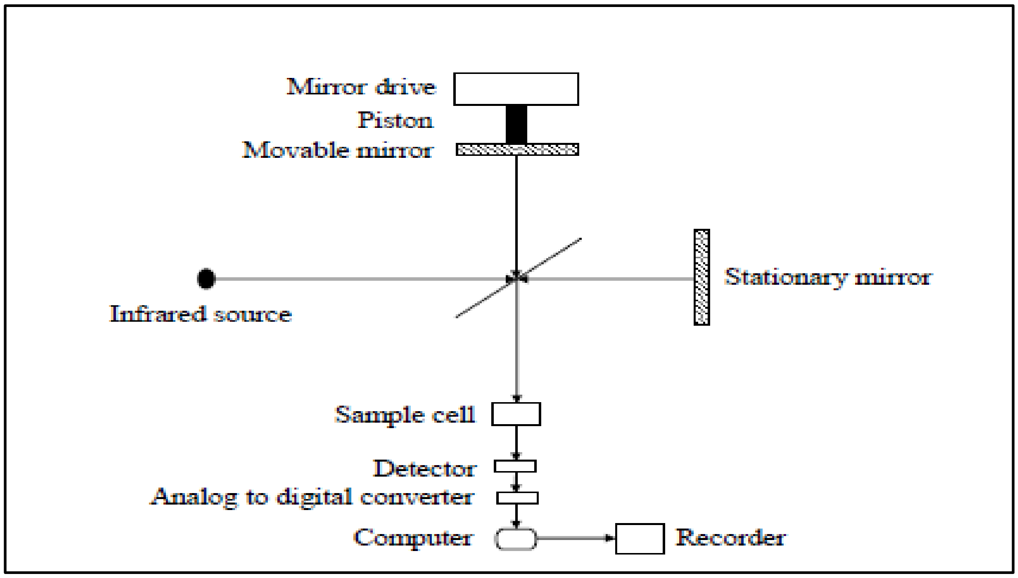


Figure 3.2: The schematic diagram of FTIR

3.5 Test Performance

The membrane performance was determined by the permeability and selectivity of the membrane. The ability of membrane to separate two gases is indicated by the ratio of their permeability or actual selectivity.

Permeability is a quantitative measure of the transport flux of a gas component *i* through a membrane.

$$\boxed{Permeability\ (P_i) = \frac{J_i l}{\Delta P_i}}$$

Where, J_i is the flux, and l is the thickness of the membrane. ΔP_i is the pressure difference across the membrane.

Single gas permeabilities were also measured for CO_2 and CH_4 gas at temperature of 308 K and pressure of 1-10 bar. The membranes are test by using a gas membrane permeation unit. Pure carbon dioxide (CO_2) and methane (CH_4) were employed as the test gases with different pressure.

Selectivity is the efficiency of the membrane in enriching a component over another component in the permeate phase.

$$\boxed{Selectivity\ (\alpha) = \frac{P_{CO_2}}{P_{CH_4}}}$$

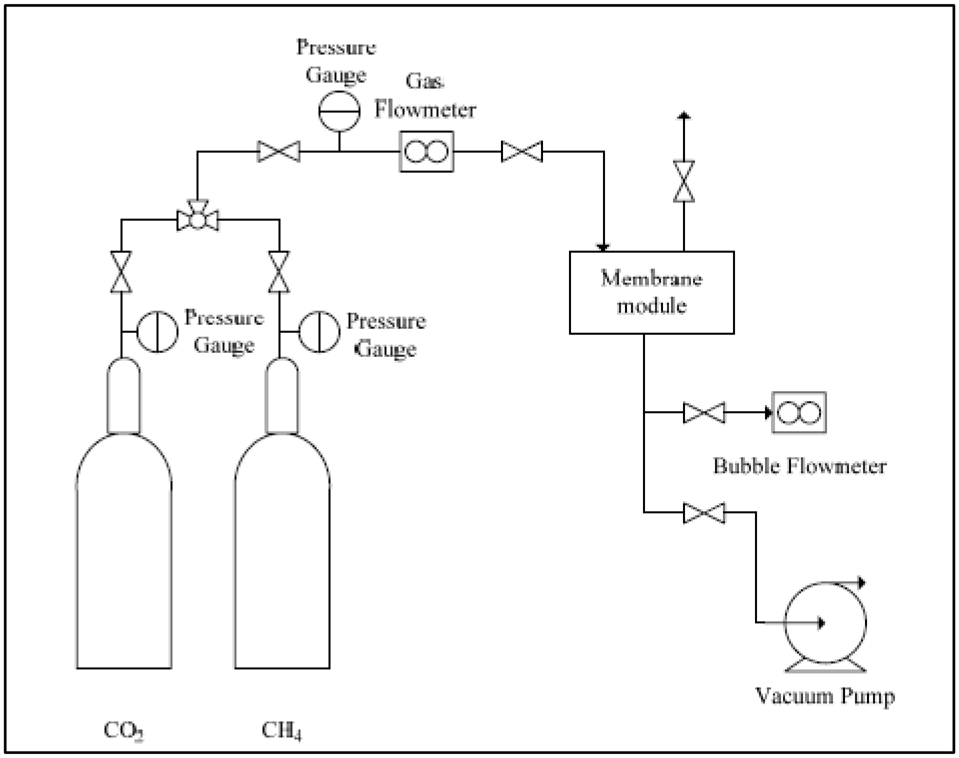


Figure 3.3: The schematic diagram for gas permeation test

Figure 3.3 shows the schematic diagram of the gas permeation unit. The permeation test unit is equipped with feed gas tank (CO_2 and methane gas tank), gas flow meter, pressure gauges, membrane test module, vacuum pump and bubble flow meter.

Before that, the membrane need to be cut into a 5 cm diameter and dried at high temperature in order to remove any left moisture.

GANTT CHART FOR FYP1 AND FYP2

- **FYP 1**

NO	DETAIL WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	🟥	🟥						MID SEMESTER BREAK							
2	Preliminary Research Work and Literature Review		🟥	🟥	🟥	🟥										
3	Submission of Extended Proposal Defence						●									
4	Preparation for Oral Proposal Defence							🟥								
5	Oral Proposal Defence Presentation									🟥						
6	Detailed Literature Review									🟥	🟥	🟥	🟥	🟥		
7	Preparation of Interim Report				🟥	🟥	🟥	🟥		🟥	🟥	🟥	🟥	🟥		
8	Submission of Interim Draft Report														●	
9	Submission of Interim Final Report															●

Figure 3.4: Gantt chart FYP 1

- **FYP2**

NO	DETAIL WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project work continues	🟥	🟥	🟥	🟥	🟥	🟥	🟥	MID SEMESTER BREAK							
2	Submission of progress report									●						
3	Project work continues									🟥	🟥	🟥	🟥	🟥		
4	Pre-SEDEX												●			
5	Submission of Draft Report													●		
6	Submission of Dissertation (soft bound)														●	
7	Submission of Technical Paper														●	
8	Oral presentation															●
9	Submission of Project Dissertation (hard bound)															●

Figure3.5: Gantt chart FYP 2

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Problem Encountered

There are many problems that the author had encountered while doing this study. For the first membrane that the author had cast, the membranes contain a lot of air bubble. The air bubbles are produced in the prepared solution during stirring process. Degassing process can be done in order to remove all the air bubble in the solution. Degassing process can be done for 45 minutes to 4 hours.

Another problem that arise are the solvent that been used are highly volatile and has a very high evaporation rate. After the membrane been casted on the glass plate, the author quickly put the membrane in the oven. The author noticed that the membranes are expand because of the high evaporation rate. Then, the author decided for the next membrane to be dried at the room temperature for 24 hours before being placed in the oven.

Solvent used, Dichloromethane which has high volatility and evaporation rate cause problems during casting process. The casting process cannot be done effectively due to the high evaporation rate. The high evaporation will cause the membrane to be hardened before the casting finish.

4.2. Membrane characterization

4.2.1 FESEM images

FESEM images are used to study the morphology of the membrane.

4.2.1.1. Polymeric Membrane

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
Pure membrane	20 %	-	-

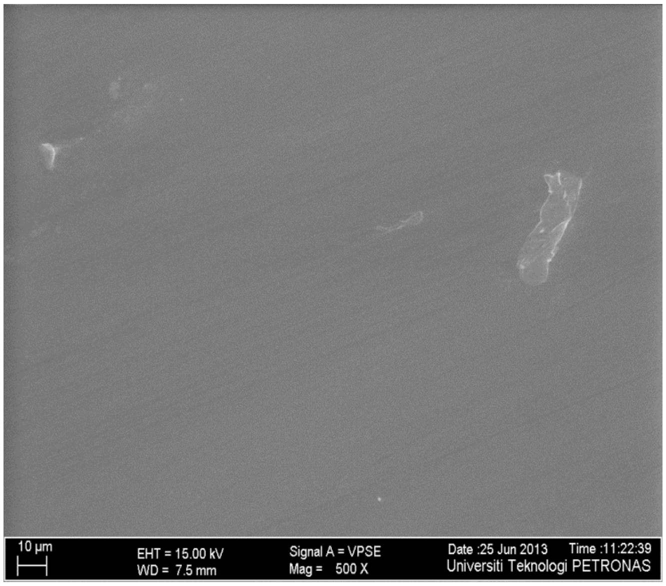


Figure 4.1: Surface of pure membrane

Figure 4.1 shows the FESEM images of the surface of pure polymeric membrane. There is some defect with the membrane surface maybe due to the error happen when the author peels the membrane from the gas plate.

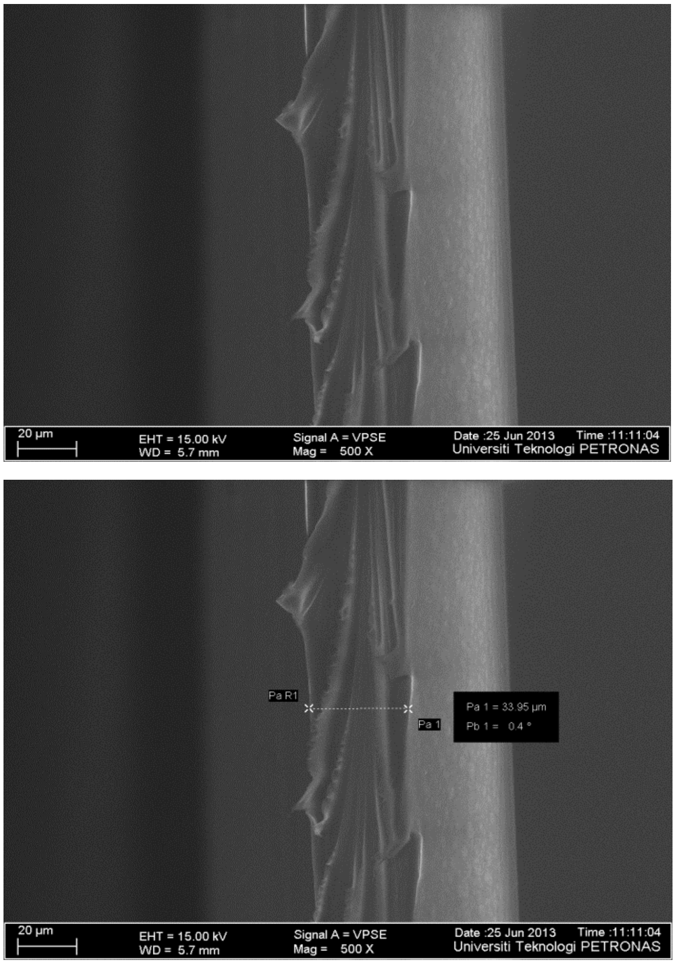


Figure 4.2: The membrane thickness of pure membrane

Figure 4.2 shows the FESEM images for the cross section of the polymeric membrane. The thickness recorded for this membrane is 33.95 µm. From the figure, it is noted that the author are able to prepare a good membrane without having pores.

4.2.1.2. Polymeric membrane with amine

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
Pure MMM	20 %	10%	-

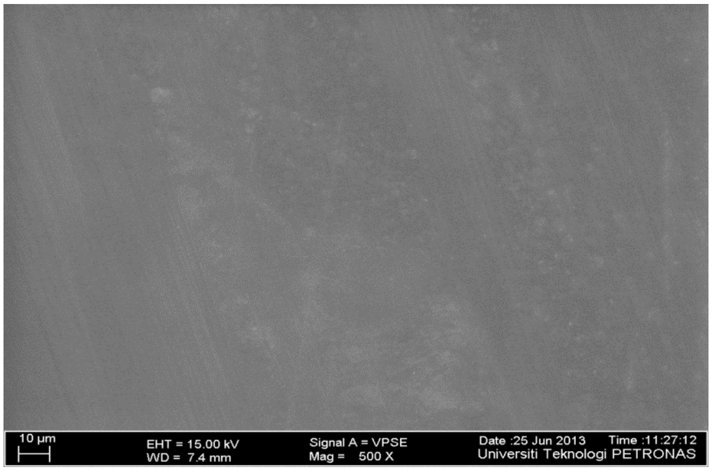


Figure 4.3: The surface of pure MMM

In the Figure 4.3, it shows the surface of the polymeric membrane with the addition of 10 % (by weight percentage) amine. The amine used in this membrane is Diethanolamine, DEA. From the figure, it id noted that the membrane is a dense membrane.

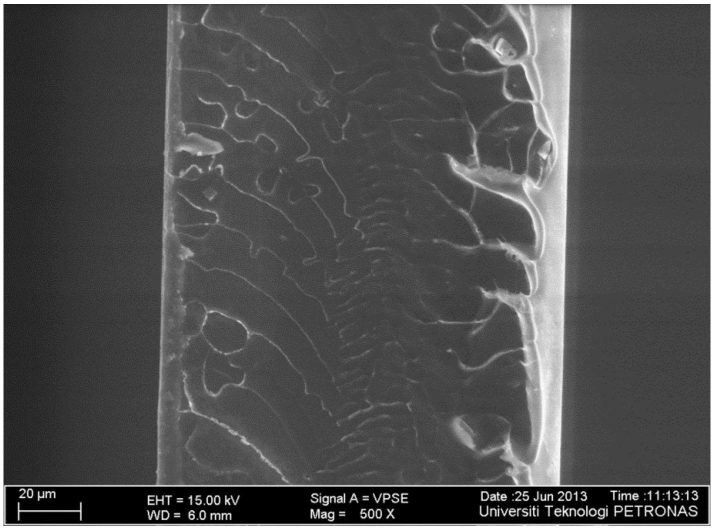


Figure 4.4: The cross section of pure MMM

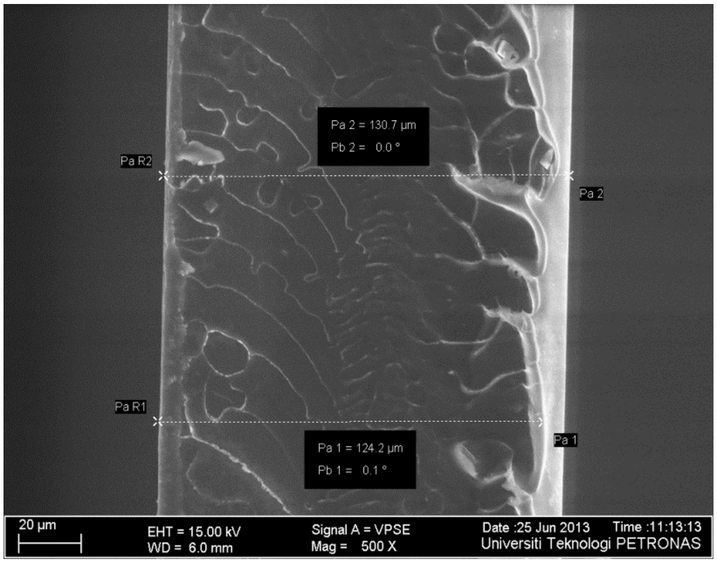


Figure 4.5: The thickness of Pure MMM

In figure 4.4, the picture shows the cutting section of the sample. And in Figure 4.5, the figure shows the thickness of the membrane. The thickness of the membrane is 130.7 µm and 124.2 µm. This shows that the membrane does not have a same thickness. This maybe occurred due to the problem during casting process.

4.2.1.3. Mixed Matrix Membrane 1 (MMM1)

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
MMM 1	20 %	10%	10%

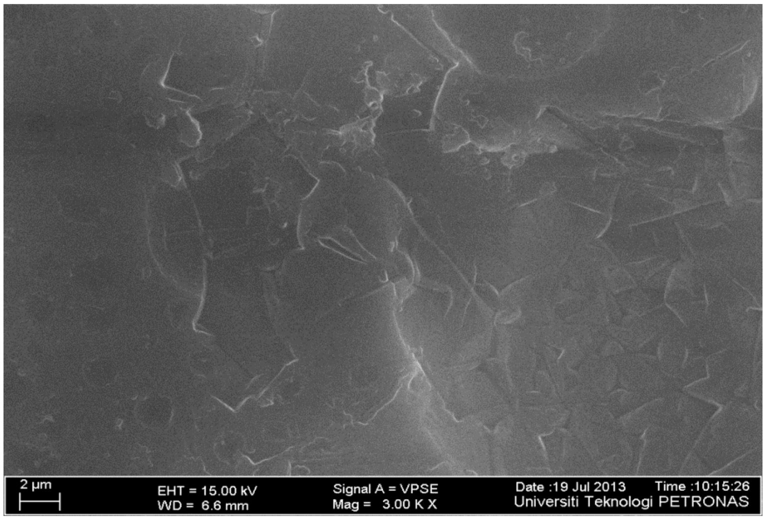


Figure **4.6** : The surface of MMM1

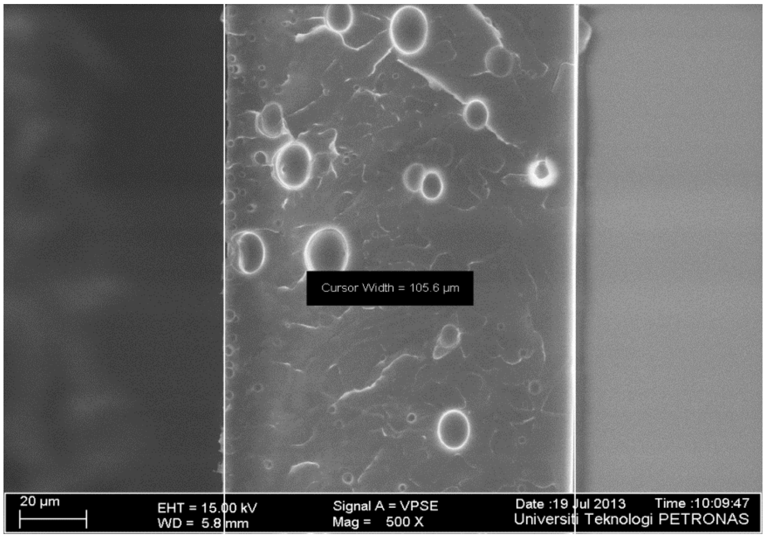


Figure 4.7: The cross section of MMM1

4.2.1.4. Membrane 1

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
Membrane 1	20 %	-	10%

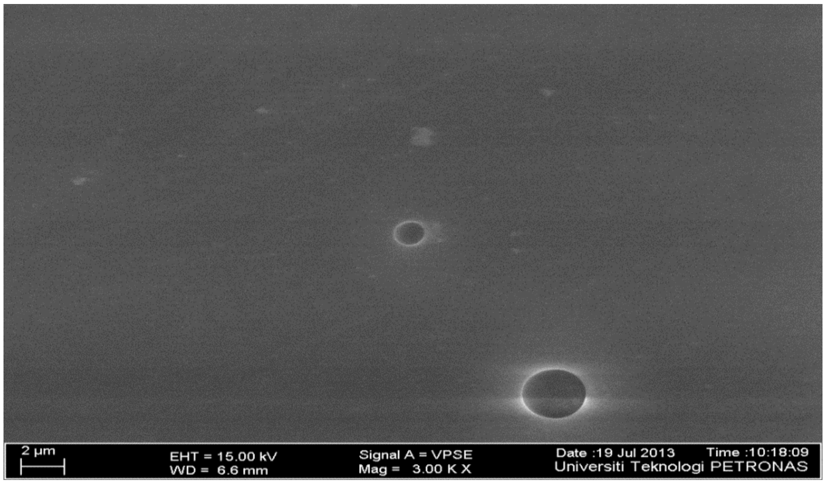


Figure 4.8: The surface of Membrane 1

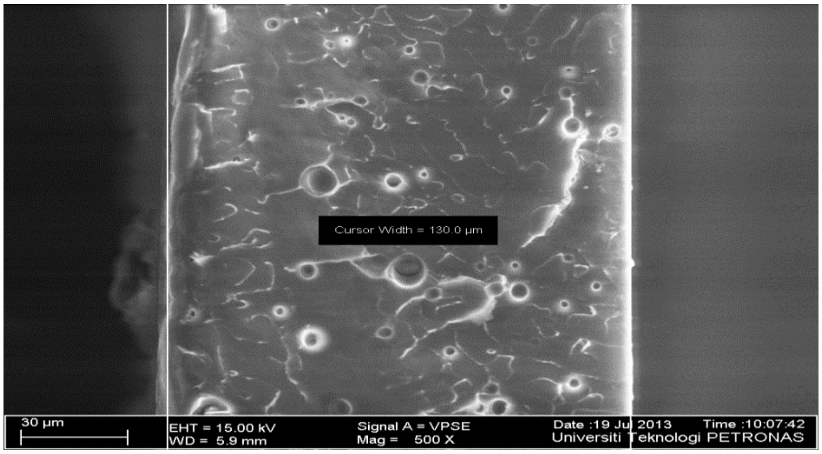


Figure 4.9: The cross section of Membrane 1

Figure 4.8 shows the surface of the Membrane 1 while Figure 4.9 shows the cross section of the membrane 1. From the Figure 4.9, it is noted that the prepared membrane has a defects. This is maybe happen due to the bubble formation during the stirring procedure.

4.2.2 FTIR Spectroscopy Test Properties

4.2.2.1. Polymeric Membrane

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
Pure membrane	20 %	-	-

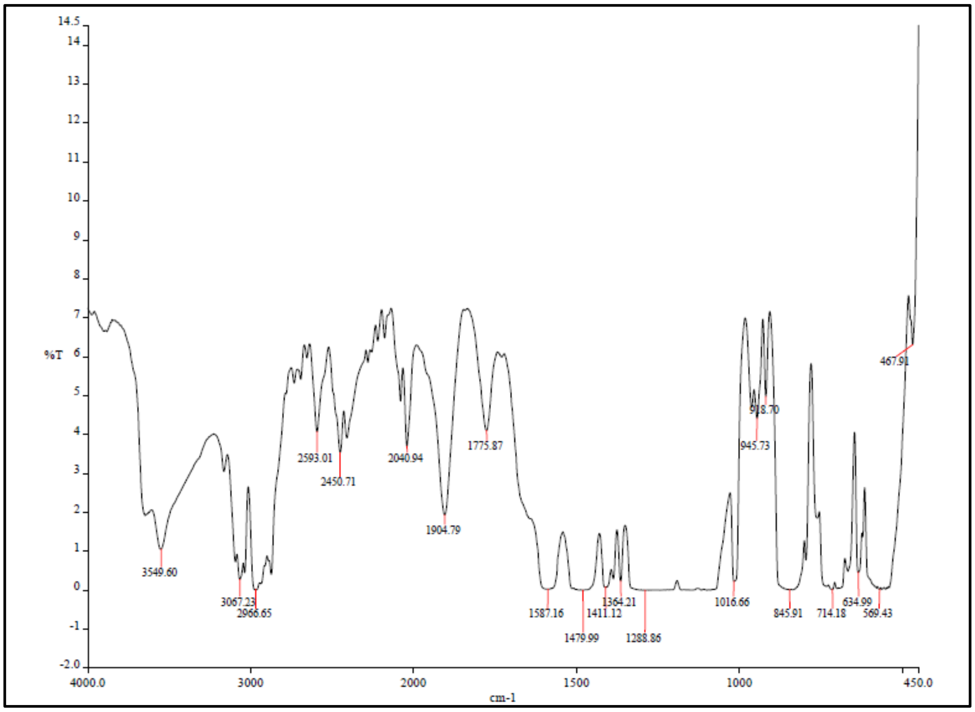


Figure 4.10: FTIR Pure Membrane

4.2.2.2. Polymeric membrane with amine

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
Membrane 1	20 %	-	10%

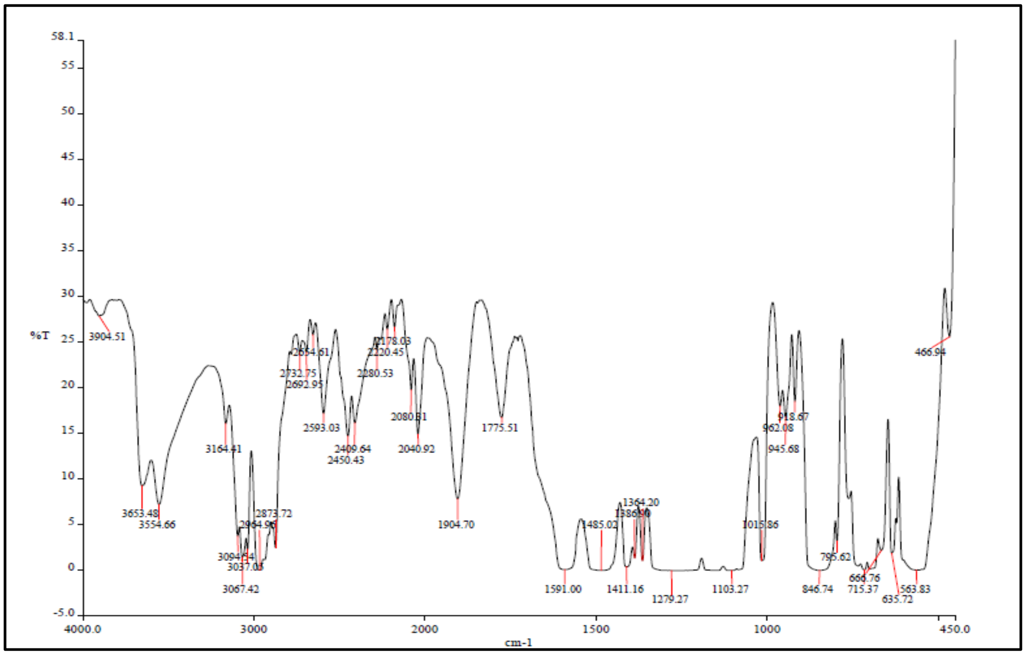


Figure 4.11:FTIR of Membrane 1

4.2.2.3. Mixed Matrix Membrane 1

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
Pure MMM	20 %	10 %	-

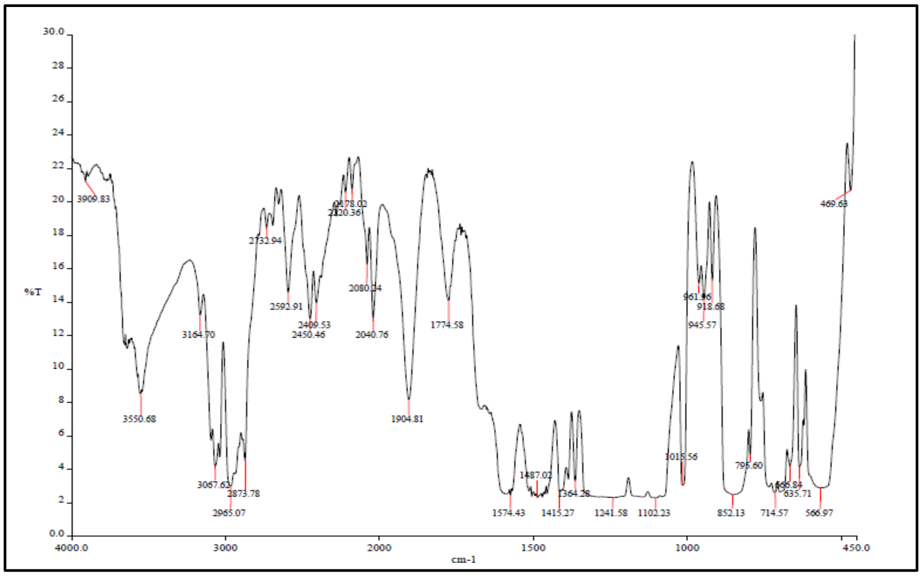


Figure 4.12: FTIR of Pure MMM

4.2.2.4. Mixed Matrix Membrane II (with amine)

Membrane/ wt %	polymer (Polysulfone)	Inorganic membrane (SAPO-34)	Amine (DEA)
MMM1	20 %	10 %	10%

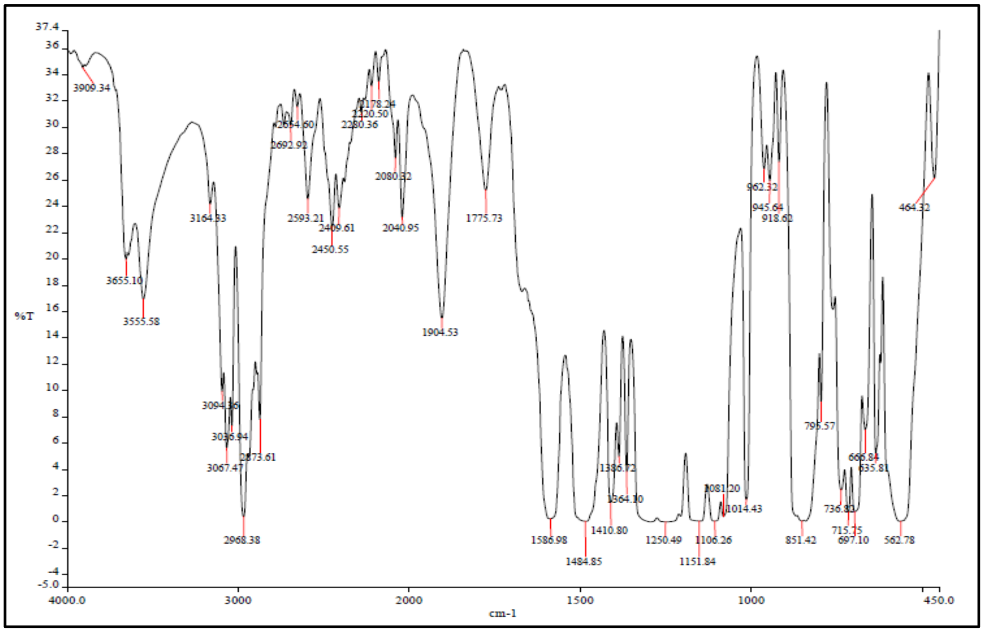


Figure 4.13: FTIR of MMM1

4.3 Permeability Studies

Gas permeability studies of the MMM was evaluated by using pure gas of CO_2 and CH_4. The tests were done using four different pressures of 2, 4, 6 and 8 bars. The permeability of CO_2 and CH_4 versus operating pressure across the membranes is shown in the figure below.

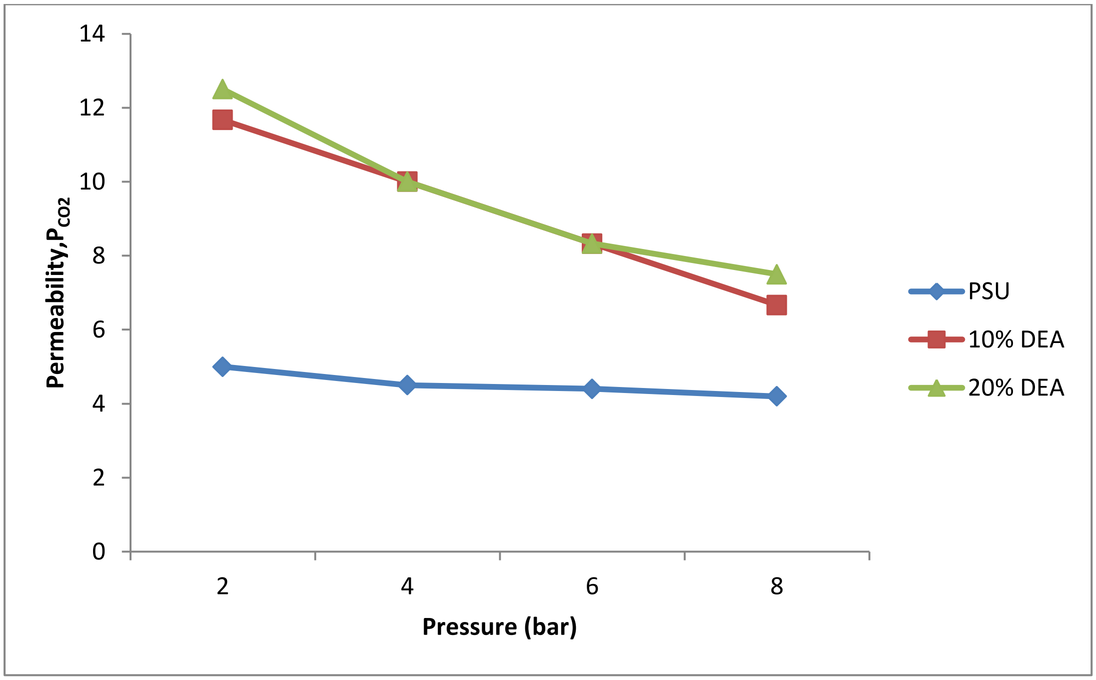


Figure 4.14: The CO2 Permeability

The Figure 4.14 shows the permeability of carbon dioxide versus the operating pressure. It is noted that the permeability of carbon dioxide across the membrane are decreasing as the operating pressure increasing from 2 bar to 8 bar. From the figure shows that the permeability of carbon dioxide across the PSU membrane is slightly decreased as the operating pressure increased. However as the amine was added, it is noted that the permeability of carbon dioxide across the membrane has improved significantly. It is due to since that carbon dioxide is very soluble in amine, so the presence of amine has enhanced the carbon dioxide solubility across the membrane. All membrane showed decreasing trend of permeability with increasing the feed pressure. The nonlinear correlation between pressure and permeability indicates the characteristic of dual sorption modes of gas in glassy polymer. When the diffusion coefficient in Henry and Langmuir environments are constant, the permeability is declined by feed pressure.

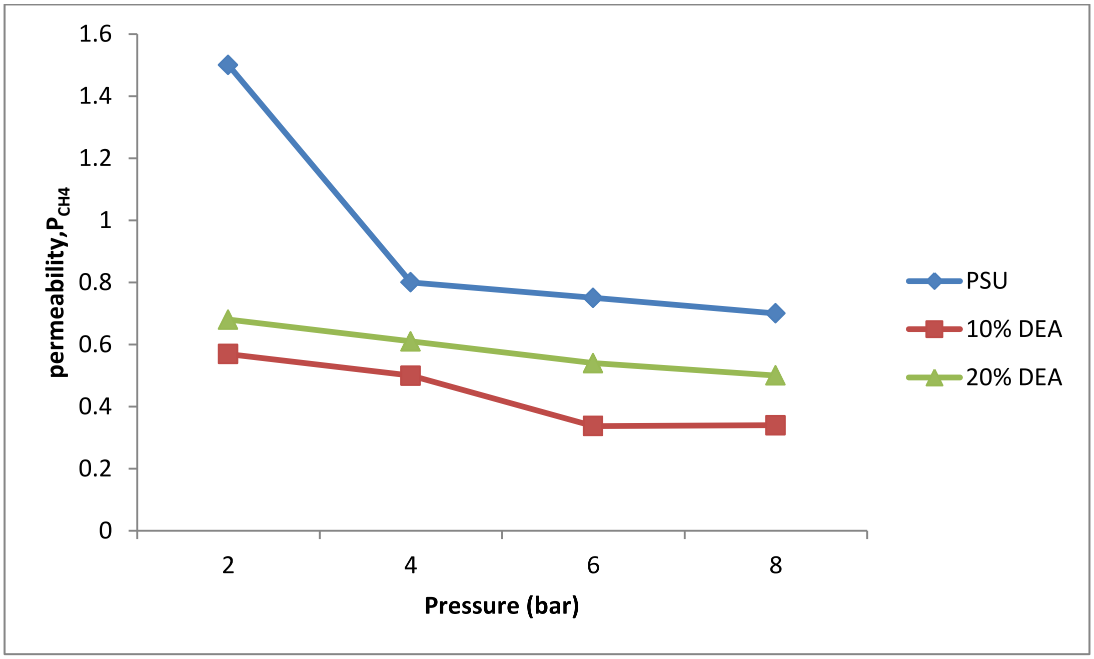


Figure 4.15: The CH_4 permeability

Figure 4.15 shows that the permeability of CH_4 across the membrane versus the operating pressure. As earlier mentioned for carbon dioxide, the permeability of CH_4 is also decreases with the increasing of pressure. However, the presence of amine has further suppressed the permeability of CH_4

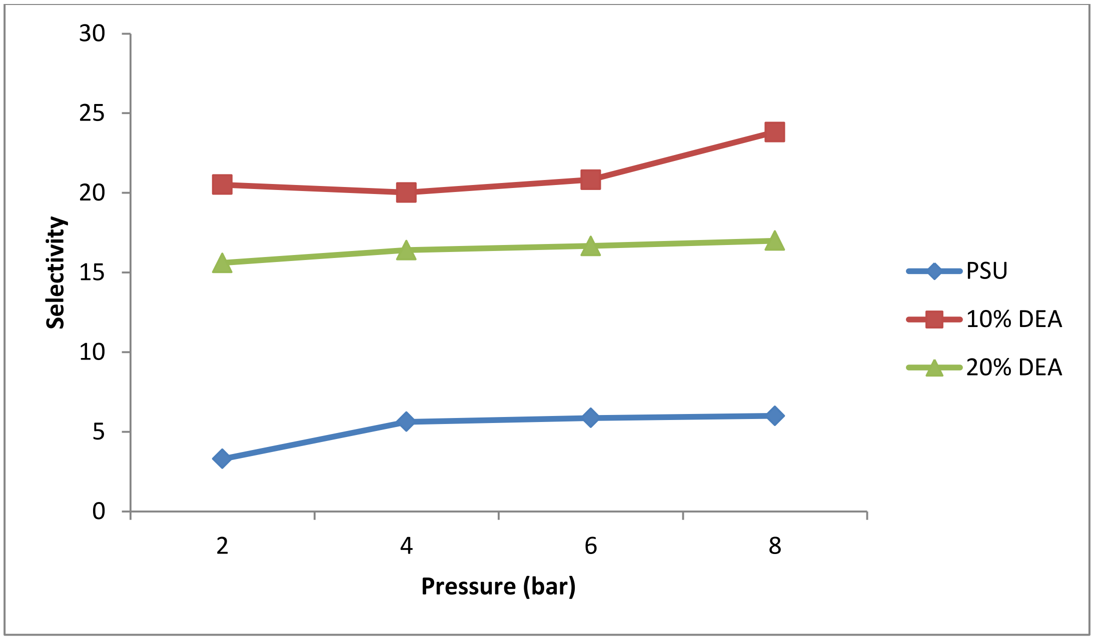


Figure 4.16: Membrane selectivity

Figure 4.16 shows the membrane selectivity versus the operating pressure. From the figure, it is noted that the membrane selectivity across the prepared membrane are slightly increasing with the increasing of operating pressure from 2 to 8 bar. From the figure, it is also noted that the PSU membrane has the lowest selectivity compare to the membrane with 10% DEA and membrane with 20% DEA. The highest ideal selectivity was achieved by the addition of 10% DEA.

CHAPTER 5

COCNLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In conclusion, the objectives of this study are achieved. The author are able to finish develop 6 types of membranes and characterized the prepared membranes by using the analytical equipment such as Field Emission Scanning Electron Microscope (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR). FESEM is used to study the morphology of prepared membranes, while FTIR is used to study the functional group in the membranes. From the FESEM images, it can be said that the author are able to develop good and dense membranes without pores. The author is also able to finish the test performance on 3 types of the membranes based on their permeability and selectivity. From the result, it is noted that the highest ideal selectivity was achieved from the membrane with the addition of 10% DEA. It is also noted that the permeability of carbon dioxide and methane are decreasing as the operating pressure increased.

So, in conclusion the mixed matrix membrane fabrication in the study has shown a very promising potential to be used in the separation of $C0_2$ and CH_4 .However, further study and research is needed in the future.

5.2 RECOMMENDATIONS

Further studies are needed to understand the characteristics of MMM. Based on this project, some recommendations have been suggested to improve the study. The Polysulfone polymer can be blended together with other type of polymer so that the morphology, the separation behavior can be improved.

The gas separation behavior of the membrane should be test by using the mixture of gases in order to stimulate the real situation in natural gas separation process. In this study, the gas separation test is done only with one type of gas passing the membrane. This is happen due to the limitation and restriction of equipment used.

Schedule for FYP 2

NO	Week/ Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Membrane fabrication	■	■	■	■	■	■	■	■	■	■				
2	Membrane characterization	■	■	■	■	■	■	■	■	■	■				
3	Membrane performance test						■	■	■	■	■	■			
4	Performance result analysis and discussion									■	■	■	■		
5	Report preparation											■	■	■	■

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