Development of Ionic Liquid Mixed Matrix Membrane (ILMMM) for Carbon Dioxide Removal

by

Muhammad Hariez bin Mohd Yazri

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons.)
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CERTIFICATION OF APPROVAL

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Approved by,

____

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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 by unspecified sources or persons.

(MUHAMMAD HARIEZ BIN MOHD YAZRI)

ABSTRACT

Separation of acid gases such as carbon dioxide from natural gas is now becoming a vast and developed research especially using mixed matrix membrane. In this project, the aim is to synthesis/fabricate/develop ionic liquid mixed matrix membranes (ILMMM) by using solution-casting method. There were six membranes fabricated which are Polymeric Membrane, Mixed Matrix Membrane, Ionic Liquid Mixed Matrix Membrane 1, 2, 3 and 4. The membranes were characterized by using Field Emission Scanning Electron Microscope (FESEM) and Fourier Transform Infrared Spectroscope (FTIR). Only PM, ILMMM 2 and ILMMM 3 were tested for the performance for CO_2 and CH_4 permeability and CO_2/CH_4 selectivity. Based on the three membranes performances that have been conducted, although ILMMM 3 has the highest permeability of CO_2 across the membrane, ILMMM 2 has the highest permeability of CH_4, but the overall indicator still refers to the selectivity of carbon dioxide over methane across the membrane. ILMMM 2 has the optimum composition of DCM, PSU, [(emim)(CF_3SO_3)] and CMS for carbon dioxide removal from natural gas. It has the highest selectivity of carbon dioxide over methane as compared to the other membrane tested.

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ABBREVIATIONS AND NOMENCLATURES

ABBREVIATION	NAME
CO_2	Carbon dioxide
N_2	Nitrogen
H_2S	Hydrogen Sulphide
COS	Carbonyl Sulphide
CS_2	Carbon Disulphide
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentanes
O_2	Oxygen
Ar	Argon
Xe	Xenon
Ne	Neon
He	Helium
PM	Polymeric Membrane
MMM	Mixed Matrix Membrane
ILMMM	Ionic Liquid Mixed Matrix Membrane

DCM	Dichloromethane
PSU	Polysulfone
CMS	Carbon Molecular Sieve
IL	Ionic Liquid
[(emim)(CF_3SO_3)]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared Spectroscopy
CAS ID	Chemical Abstract Service Identification Number
MW	Molecular Weight
St.	Standard
Scf.	Standard Cubic Feet

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1. Background of Study

Natural gas is a combustible mixture that contains not only hydrocarbon but also other components. Natural gas normally consists mainly of hydrocarbon and also a little amount of other compounds such as carbon dioxide (CO_2), nitrogen (N_2), hydrogen sulphide (H_2S), carbonyl suphide (COS), mercaptans and lots more but most of them are in small amount or quantity. The main hydrocarbon is methane (CH_4) and also with other higher hydrocarbon of ethane (C_2H_6), propane (C_3H_8), butanes (C_4H_{10}), pentanes (C_5H_{12}) and heavier fractions usually present in decreasing proportions. Typically there are several components make up natural gas and it can be illustrated as in Table 1.1.

Table 1-1: Typical Composition of Natural Gas

Components	Composition In Percentage (%)
CH_4	70 – 90
C_2H_6	0 – 20
C_3H_8	
C_4H_{10}	
CO_2	0 – 8
Oxygen (O_2)	0 – 0.2
N_2	0 – 5
H_2S	0 – 5
Rare Gases (Ar, He, Ne, Xe)	Trace

The composition of natural gas may vary according to certain locations and will have different range of composition depending on location, depth and type, underground reservoirs and the geology of that area. For example, Russia is proven to be the world largest natural gas reserves and also other area of natural gas sources such as in Netherlands, North Sea Germany, Algeria, Singapore and Argentina (Dock Sud) and the compositions are as in Table 1-2. (Elvers, 2008) On the other hands, Iran, Qatar, Arab Saudi and United Arab Emirates are believed and considered as major countries with top natural gas reserves too. Based on the table it can be observed that USA has the highest CO_2 content in the natural gas.

Table 1-2: Natural Gas Composition from Different Sources

Source	CH_4 (Mole %)	C_2H_6 (Mole %)	C_3H_8 (Mole %)	N_2 (Mole %)	CO_2 (Mole %)
Russia	96.2	1.20	0.30	1.80	0.30
North Sea Germany	85.6	8.79	2.52	0.59	1.67
Algeria	89.0	8.15	1.03	0.48	0
Singapore	90.9	5.11	1.47	0.3	1.34
Argentina (Dock Sud)	95.4	2.28	0.32	1.23	0.65
USA	48.35	2.96	3.77	1.34	37.58

Natural gas is produced from gas and oil wells. Natural gas can be found same as to that crude oil containing structure and there are two classification of natural gas which is associated gas and non-associated gas. Associated gas is where the natural gas is found to exist with crude oil wells meanwhile non-associated gas is when natural gas is found in the gas wells.

There are several uses of natural gas around the world which includes residential uses, commercial uses, industry uses, in transportation sector which used natural gas and electric generation. For residential uses, the most popular usage of natural gas is for natural gas heating and cooking purposes.

However, before the natural gas is distributed to the end-users, there are several treatments, gas processing and conditions it must go through. To name a few, there are gas/liquid separation, gas dehydration and hydrate prevention, water treating and disposal, gas measurement and compression and the one that this project focused on is carbon dioxide removal. Natural gas may contain acid gases such as H_2S and CO_2. CO_2 and H_2S are corrosive and the latter is very poisonous. When natural gas contains CO_2 and H_2S, it is common that the other sulfur compounds are also present in example mercaptans, COS and carbonyl disulphide (CS_2). When natural gas has certain amount of this sulphur, it can be considered as sour gas or sweet gas. Sour gas can be defined as a gas containing undesirable quantities of H_2S, mercaptans and CO_2. Generally, H_2S will contribute 40% of total amount of natural gas to be classified as sour natural gas. (Elf, 2002)

In order to meet the pipeline quality before the natural gas is being transferred for sale, the natural gas either sweet or sour must be treated to meet the desired saleable quantity. Following table shows the typical standard pipeline quality desired. (PETRONAS Technical Standard (PTS), 1993)

Table 1-3: Typical Standard Pipeline Quality

Components	Specification
CO_2	2% mole max.
N_2	1% mole max.
C_1	85% mole min.
C_{4+}	1.8% mole max.
C_{5+}	0.1% mole max
H_2S	5 mg/m^3 (St.) max.
Total Sulphur	30 mg/m^3 (St.) max.

Even though there is a lot of range of compositions of natural gas around the world, the desired composition of delivered gas to the pipeline is very strictly controlled and monitored. One example is at USA and the typical natural gas specification in US is according to the following specification as described in Table 1-4. (Baker R. W., 2004)

Table 1-4: Composition of Natural Gas Required for Delivery to the US National Pipeline Grid

Components	Specification
CO_2	< 2 %
H_2O	< 120 ppm
H_2S	< 4 ppm
C_{3+}	950 - 1050 Btu/scf
Content	Dew point, -20^{0}C
Total Inert (N_2, CO_2, He, etc.)	< 4%

Provided in Table 1-5 are the advantages and disadvantages of technology to treat CO_2 present in the natural gas. The technologies involved are absorption, adsorption, and membrane and cryogenic separation.

Table 1-5: Comparison of Current Technology for Treating Natural Gas

Advantages	Technology	Disadvantages
• Commonly used technology • Can take out 50-100% of CO_2 and H_2S	Absorption	• Not economical • Takes time to purify products
• High purity of product • Mobilized adsorbent	Adsorption	• Low product recovery • Only single pure product can be obtained
• Simple, easy, versatile • Very stable and high recovery • Environmentally friendly	Membrane	• Moderate product purity
• Higher recovery of product other than others • High purity of product	Cryogenic	• Not economical • High energy need for regeneration

1.2. Problem Statement

As of now, the quantity of acid gases in the natural gas around the world is increasing. The highest percentage CO_2 content that can be traced is up to 70% in the natural gas. From Table 1-2, it is obvious that the CO_2 content in the composition of natural gas from USA is the highest among the others which counts about 37.58% mole. This is one example that the project would like to focus and narrow down the scope to such cases. There are several technologies that can remove the carbon dioxide presence to certain low portion, for example, the application of Benfield Process that can only take up 8% of CO_2 from natural gas, is such a limitation to remove bulk proportion of CO_2 in the natural gas. Provided in the table below, is the overall comparison of technologies available to remove the CO_2 from natural gas. (Shimekit & Mukhtar, 2012)

Since current and existing technologies for acid gas removal have their own limitation on performance and operation including their disadvantages, has been described in the previous section, there is a need of new technology to cater the problem involving bulk removal of CO_2 from natural gas. The new technology involves developing a combination of several materials in a membrane known as ionic liquid mixed matrix membrane.

1.3. Objective

a) To synthesis/fabricate/develop ionic liquid mixed matrix membranes (ILMMM)

b) To characterize the ionic liquid mixed matrix membranes (ILMMM)

c) To test the performance of the ionic liquid mixed matrix membranes (ILMMM) on the effect of composition variation of inorganic filler in the ILMMM

1.4. Scope of Study

This project involves in doing experimental lab. The scopes of study are as per below:-

a) The ILMMM is made up dichloromethane (DCM) as a solvent, polysulfone (PSU) which acts a polymer, carbon molecular sieves (CMS) as an inorganic filler, an ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [(emim)(CF_3SO_3)] as a third component. After the solution preparation steps are followed, this solution will be used to be casted on the membrane casting machine and the ILMMM will be formed right after.

b) The ILMMM characterization will be using Field Emission Scanning Electron Microscopy (FESEM) which will be used to evaluate the particles distribution and Fourier Transform Infrared Spectroscopy (FTIR) to give information on molecular interaction.

c) The ILMMM will be tested on its performance through CO_2 and CH_4 permeability and selectivity using Membrane Performance Test Unit. The test will be conducted for using single gas at one time.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

Membrane systems have major advantages over more-traditional methods of carbon dioxide removal:

i. Lower capital cost: Membrane systems are skid mounted and so the scope, cost, and time taken for site preparation are minimal. Installation costs are significantly lower than alternative technologies, especially for remote areas. Furthermore, no additional facilities for solvent storage and water treatment, needed by other processes, are required.
ii. Lower operating costs: The only major operating cost for single-stage membrane systems is membrane replacement. This cost is significantly lower than the solvent replacement and energy costs associated with traditional technologies. The improvements in membrane and pretreatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors are usually comparable to those for traditional technologies.
iii. Operational simplicity and high reliability: Because single-stage membrane systems have no moving parts, they have almost no unscheduled downtime and are extremely simple to operate. They can operate unattended for long periods of time. The addition of a recycle compressor adds some complexity to the system but still much less than with a solvent- or adsorbent-based.
iv. Environmentally friendly: Membrane systems do not involve the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or re-injected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated. (Cnop, Dortmundt, & Schott)

2.1. Membrane

Membrane is to selectively separate some compounds from others and it is a thin permeable barrier. Membrane separation is an energy efficient and economical tool in gas separation applications. (Baker R. W., 2004)Membrane technology is becoming more important for CO_2 separation from natural gas in the new era due to its process simplicity, relative ease of operation and control, compact, and easy to scale up as compared with conventional processes. Polymeric membranes are the current commercial membranes used for CO_2 separation from natural gas. However, polymeric membranes possess drawbacks such as low permeability and selectivity, plasticization at high temperatures, as well as insufficient thermal and chemical stability (Yeo, Chew, Zhu, Mohamed, & Chai, 2012) Membrane separation is a very energy efficient separation technology because it is a continuous process without need for sorbent regeneration or desorption by temperature/pressure variation. (Swenson, Wu, An, Waller, Ku, & Kuznick, 2011) Membrane can be used primarily to remove bulk CO_2 from natural gas. With the application of membrane technology in offshore platform in can help to remove CO_2 to meet pipeline specifications. (Stewart & Arnold, 2011).

2.2. Mixed Matrix Membrane

Mixed matrix membranes comprise of molecular sieve entities embedded in a polymer matrix. (Yeo, Chew, Zhu, Mohamed, & Chai, 2012) The integration of these two materials with different selectivity and flux provides the possibility of better design membranes for CO_2 separation, allowing the synergistic combinations of polymer's easy process ability and superior performance of inorganic materials. (Brunetti, Scura, Barbieri, & Drioli, 2010) Mixed matrix membranes have the potential to achieve significant improvement in membrane performance in gas separations by combining a continuous polymer bulk phase with a highly selective and/or permeable dispersed inorganic phase. (Marand & Surapathi, 2012) Mixed matrix membranes with zeolite molecular sieve dispersed phase in a polymer matrix have potentials to provide both high gas superior selectivity of the molecular sieves and the desirable mechanical and economical properties of the polymers. (Bastani, Esmaeili, & Asadollahi, 2013) Mixed-matrix membranes (MMMs) are usually characterized by high fluxes and low pressure drops across the membrane wall. (Adams, Dlamini, Nxumalo, Krause, Hoek, & Mamba, 2013)

2.3. Membrane

The materials that make up a membrane for CO_2 removal can be from polymer based in which the properties are modified to enhance performance. The materials can be cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates or polyethermide. (Stewart & Arnold, 2011) The vast majority of mixed matrix membrane configurations are flat sheet configurations; however, hollow fiber MMMs has become a favored configuration for gas separation systems due to its many advantages such as larger membrane area per volume, good flexibility and easy handling in the module fabrication. To enhance gas separation performances, recent works have focused on improving polymeric membranes selectivity and permeability by fabricating mixed matrix membranes (MMMs). Inorganic zeolite materials distributed in the organic polymer matrix enhance the separation performance of the membranes well beyond the intrinsic properties of the polymer matrix. This concept combines the advantages of both components: high selectivity of zeolite molecular sieve, and mechanical integrity as well as economical process ability of the polymeric materials. (Bastani, Esmaeili, & Asadollahi, 2013) Permeability and selectivity are two important parameters of membrane gas separation. (Hulagu, Kramer, Bottger, Kraume, & Lyagin, 2012) It has been shown that the matching of the permeability of the matrix and the filler is an important factor in the design of mixed matrix membranes. (Mahajan & Koros, 2004) One of the challenges of MMM is the performance suffers from defects caused by poor contact at the interface of molecular sieves and polymer which indirectly causes CO_2 gases to flow non-selectively around the solid particles.

CHAPTER 3

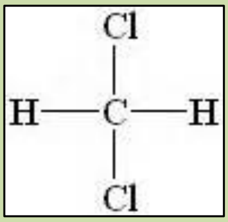
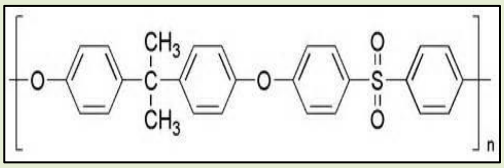
MATERIALS AND METHOD

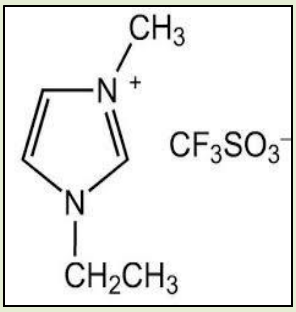
3. MATERIALS AND METHOD

3.1. Membrane Materials

Mixed matrix membrane is made up from several components such as polymer, inorganic filler and solvent. Ionic liquid as the third component is also added up to enhance the performance of the membrane. In order to fabricate an ionic liquid mixed matrix membrane, the polymer needed is polysulfone (PSU), carbon molecular sieves (CMS) as inorganic filler and the ionic liquid,1-ethyl-3-methylimidazolium trifluoromethanesulfonate [(emim)(CF_3SO_3)], besides dichloromethane (DCM) as a solvent. The details and quality of materials being used for the membrane are shown below in Table 3-1.

Table 3-1: Quality of Membrane Materials

	Material Name And Formula	Details & Quality
1.	Dichloromethane (CH_2Cl)  $H-\overset{Cl}{\underset{Cl}{C}}-H$	It is a clear solution in liquid phase and being used as it is. CAS ID : 602-004-00-3 Manufacturer : Merck KGaA, Germany. Purity : ≥ 99.8% MW : 84.93 g mol^{-1}
2.	Polysulfone 	It is a white and very small solid powder and being used as it is. Before using it, dry it at 60°C for one day in drying oven to remove excess moisture. CAS ID : 485-9333 Manufacturer : Solvay Advanced Polymers LLC, USA

3.	Carbon Molecular Sieve (C)	It is a black and large-sized solid powder. Before using it, it was being grinded using Mortar Grinder to obtain small-sized powder form. In addition, dry it at 100°C for 30 minutes to remove excess moisture. CAS ID : 1333-86-4 Manufacturer : R&M Marketing, Essex, UK. MW : 12.01 g mol^{-1}
4.	1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($C_7H_{11}F_3N_2O_3S$) 	It is a clear solution in liquid phase and being used as it is. CAS ID : 145022-44-2 Manufacturer : SIGMA-ALDRICH CHEMIE GmbH, Steinheim, Germany. Purity : ≥ 98% MW : 260.23 g mol^{-1}

3.2. Membrane Casting Solution Preparation According to Composition

In order to study the effect of variation of composition of inorganic filler, provided below in Table 3-2 is the composition required for each membrane.

Table 3-2: Membrane Types and Its Composition Variation of Inorganic Filler in the Membranes

No	Membrane Type	Membrane Label Name	Composition of PSU	Composition of CMS	Composition of [(emim)(CF_3SO_3)]
1.	Polymeric Membrane	PM	20 wt./wt.%	-	-
2.	Mixed Matrix Membrane	MMMM	20 wt./wt.%	10 wt./wt.%	-
3.	Ionic Liquid Mixed Matrix Membrane 1	ILMMM 1	20 wt./wt.%	-	10 wt./wt.%
4.	Ionic Liquid Mixed Matrix Membrane 2	ILMMM 2	20 wt./wt.%	10 wt./wt.%	10 wt./wt.%
5.	Ionic Liquid Mixed Matrix Membrane 3	ILMMM 3	20 wt./wt.%	20 wt./wt.%	10 wt./wt.%
6.	Ionic Liquid Mixed Matrix Membrane 4	ILMMM 4	20 wt./wt.%	30 wt./wt.%	10 wt./wt.%

Provided below is the summary on how to calculate the mass of each PSU, CMS and IL used in all membranes.

$$Weight\ Percentage\ of\ Polymer(\%) = \frac{Mass\ of\ Polymer\ (g)}{Mass\ of\ Solvent\ (g)} \times 100\% \tag{3.1}$$

$$Weight\ Percentage\ of\ Inorganic\ Filler(\%) = \frac{Mass\ of\ Inorganic\ Filler\ (g)}{Mass\ of\ Polymer\ (g)} \times 100\% \tag{3.2}$$

$$Weight\ Percentage\ of\ Ionic\ Liquid(\%) = \frac{Mass\ of\ Ionic\ Liquid\ (g)}{Mass\ of\ Polymer\ (g)} \times 100\% \tag{3.3}$$

Based on the formula given, the mass of for each component in the materials had been determined and were tabulated in the following table.

Table 3-3: Mass of Components in the Membranes

No.	Membrane Label No.	Mass of DCM	Mass of PSU	Mass of CMS	Mass of [(emim)(CF_3SO_3)]
1.	PM	30 g	6 g	-	-
2.	MMMM	30 g	6 g	0.6 g	-
3.	ILMMM 1	30 g	6 g	-	0.6 g
4.	ILMMM 2	30 g	6 g	0.6 g	0.6 g
5.	ILMMM 3	30 g	6 g	1.2 g	0.6 g
6.	ILMMM 4	30 g	6 g	1.8 g	0.6 g

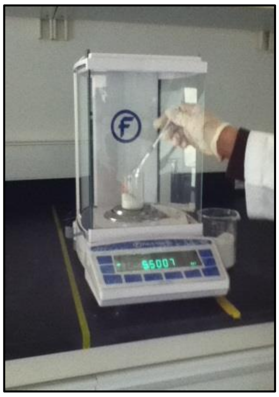
3.3. Membrane Casting Solution Preparation Steps

Different membranes will have different ways of preparing the solution. The followings are the procedural steps for each membrane.

3.3.1. PM Membrane Solution Preparation Steps

Polymeric membrane solution was firstly prepared before casting it on the membrane fabrication unit. The following is the procedure to prepare the membrane solution.

i. 6 g of PSU was weighed in a beaker.



ii. 30 g of DCM was weighed in a glass bottle with cap.

iii. A magnetic bar was put into the glass bottle. The glass bottle was put on a magnetic stirring plate. The stirring speed was set to 1 and switched on.

iv. 1/5 g of PSU was put first into the glass bottle and left for 15 minutes to let the PSU to dissolve in DCM.

v. After 15 minutes, another 1/5 g of PSU was added and let to be dissolved for 15 minutes. This step was repeated until all PSU had finished.

vi. Once all PSU had dissolved, the stirring was continued for another 24 hours as to ensure all PSU has totally dissolved into DCM.

3.3.2. MMM Solution Preparation Steps

Mixed matrix membrane solution was then prepared according to the following procedure.

i. 30 g of DCM was put into a glass bottle with cap.

ii. 0.6 g of CMS was put into the glass bottle with cap containing the DCM. Priming (or sizing) the sieves with a small quantity of polymer also aided in compatibilizing the sieves and the matrix polymer for improved adhesion and also minimized aggregation at high sieve loadings. (Vu, Koros, & Miller, 2003)

iii. A magnetic bar was put into the glass bottle. The glass bottle was put on a magnetic stirring plate. The stirring speed was set to 1 and switched on.

iv. The mixture then stirred for 15 minutes.

v. After 15 minutes, sonication of the mixture was conducted as to ensure all CMS was homogenously dispersed in the DCM. This step provided shearing of the CMS particles breaking up aggregates of particles and enhanced the homogeneity during the agitation. (Vu, Koros, & Miller, 2003)

vi. After that, 0.6 g (10% of total PSU) was put first into the bottle that was under stirring and waited for all PSU has dissolved. Then, the PSU was added 10% by 10% until all PSU had finished.

vii. Once all PSU had dissolved, the stirring was continued for another 24 hours as to ensure all PSU has totally dissolved into DCM.

3.3.3. ILMMM 1 Solution Preparation Steps

Almost similar steps as before were applied to prepare the solution for this membrane.

i. 30 g of DCM was put into a glass bottle with cap.

ii. 0.6 g of [(emim)(CF_3SO_3)] was put into another glass bottle with cap.

iii. The DCM was then transferred into the [(emim)(CF_3SO_3)]-containing bottle.

iv. A magnetic bar was put into the glass bottle. The glass bottle was put on a magnetic stirring plate. The stirring speed was set to 1 and switched on.

v. The mixture was stirred for 1 hour.

vi. After that, 0.6 g (10% of total PSU) was put first into the bottle that was under stirring and waited for all PSU has dissolved. Then, the PSU was added 10% by 10% until all PSU had finished.

vii. Once all PSU had dissolved, the stirring was continued for another 24 hours as to ensure all PSU has totally dissolved into DCM.

3.3.4. ILMMM 2, ILMMM 3 and ILMMM 4 Solution Preparation Steps

As mentioned earlier, an ionic liquid mixed matrix membrane is a blend of inorganic particles in a polymer matrix plus ionic liquid. The first step of ionic liquid mixed matrix membrane fabrication was to prepare a homogeneous solution of polymer, solvent, inorganic filler, and ionic liquid. (Aroon, Ismail, Matsuura, & Montazer-Rahmati,

2010) See Figure 3-1 for the fabrication process. For the fabrication, this procedure has been applied:

i. 30 g of DCM was put into a glass bottle with cap.

ii. 0.6 g of [(emim)(CF_3SO_3)] was put into another glass bottle with cap.

iii. The DCM was transferred into [(emim)(CF_3SO_3)]-containing bottle.

iv. 0.6 g of CMS was poured into the bottle.

v. A magnetic bar was put into the glass bottle. The glass bottle was put on a magnetic stirring plate. The stirring speed was set to 1 and switched on.

vi. It was left under stirring for one day.

vii. Then, 1/5 g of total PSU was added and stirred and waited for 1 hour, then the PSU was added 1/5 g by 1/5 g until all PSU had finished.

viii. Once all PSU had dissolved, the stirring was continued for another 24 hours as to ensure all PSU has totally dissolved into DCM.

ix. Step (i) to (viii) were repeated for preparing the solution for ILMMM 2, ILMMM 3 and ILMMM 4 with different composition as in Table 3-2 and Table 3-3.

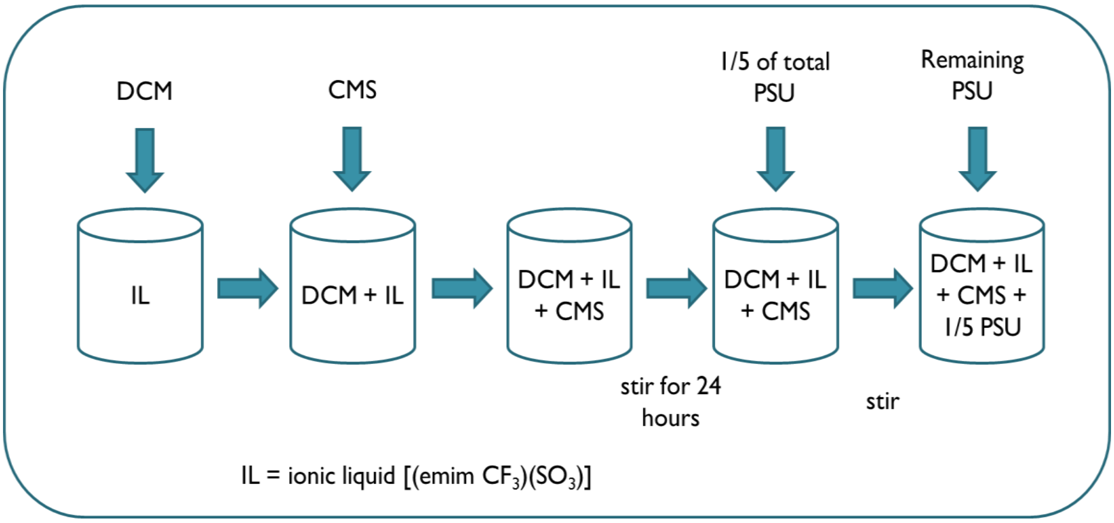


Figure 3-1: ILMMM Solution Preparation Steps

3.4. Membrane Casting Using Membrane Fabrication Unit

Below are the steps in order to cast the membrane.

i. Glass plate was used for the template casting. Acetone was used to remove moisture and compressed air was used to remove dust particles. Casting knife was adjusted to a thickness of 225 micron.

ii. The main switch was switched on. Next, the casting knife was ensured to be in the right position.

iii. Casting solution was poured onto the glass plate. It must be ensured that the membrane casting solution was poured onto all areas on the glass plate.

iv. The motor selector was switched to move forward, and after sometimes, the casting knife automatically moved forwards.

v. Since DCM is a highly evaporated substance, it was left for 24 hours drying with glass cover on top of it before putting it into the drying oven for another 24 hours to let it fully dry.

3.5. Membrane Characterization

There are several instruments and devices required for the membrane characterization once the membranes are already fabricated.

3.5.1. Field Emission Scanning Electron Microscopy (FESEM)

FESEM will be used to observe any fracture of void in membranes and surface images will be employed to evaluate particles distribution and agglomeration in matrix.

FESEM is a widely applied technology to obtain the morphology of a membrane. In this research study, it is used to analyze the surface and cross-section morphology of the flat sheet membrane and the contact between the molecular sieves and the polymeric matrix phases. The morphology was observed by Field Emission Scanning Electron Microscope. The samples for the cross-section characterization were fractured in liquid nitrogen. (Yi, 2006)

3.5.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is basically used to (1) investigate the structural / compositional info of compounds substance through quantitative and qualitative analysis, (2) provide info on analyte of chemical structure like bonding and functional group and (3) as a characterization for sample mixture. The spectrum produced at the end of the characterization of a mixture represents the molecular absorption and transmission, creating molecular fingerprint of the sample. In fact, there are two unique molecular structures produce the same infrared spectrum. Therefore, there is several information that FTIR can provide which are (1) it can identify the unknown materials, (2) it can determine the quality or consistency of a sample and (3) it can determine the amount of components in a mixture.

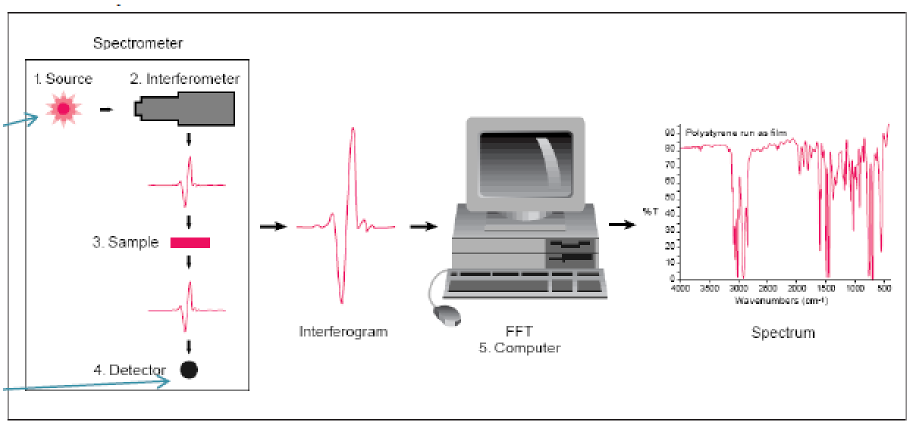


Figure 3-2: FTIR Machine Scheme

Fig. 3-2 above shows the steps in conducting the characterization of membrane using FTIR equipment. The source such as nichrome / rhodium wire was heated at 1100 K. The interferometer then converts the high frequency of infrared spectroscopy (IR) to signal with frequencies which is low enough to be recorded. A waveform was plotted by the magnitude of quantity against time. The frequency composition of a waveform can be determined by Fourier transform. Finally the FTIR spectrum was produced.

3.6. Membrane Performance Test Using Gas Permeability Unit

There are two important parameters to show how the performance of the membrane is. The CO_2 and CH_4 gas permeability of all fabricated membranes will be calculated using Equation 4.

$$Permeability, P_i = \frac{J_i l}{\Delta P_i} \qquad (4)$$

Where l is membrane thickness, J_i is flux, ΔP_i is change in pressure. At the same time, the selectivity of the membrane will be calculated as follows in Equation 5.

$$Selectivity, \alpha = \frac{P_{CO_2}}{P_{CH_4}} \qquad (5)$$

3.7. Gantt chart

No	Detail/Work	Final Year Project II Week No.													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Membrane Fabrication	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩						
2.	Membrane Casting	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩						
3.	Membrane Characterization	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩				
4.	Membrane Performance Test							🟩	🟩	🟩	🟩				
5.	Performance Result Analysis & Discussion										🟩	🟩	🟩	🟩	
6.	Report Preparation	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

3.8. Key Milestones

No	Detail/Work	Final Year Project II Week No.													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Completion of Membrane Fabrication								●						
2.	Completion of Membrane Casting								●						
3.	Completion of Membrane Characterization										●				
4.	Completion of Membrane Performance Test										●				
5.	Completion of Performance Result Analysis & Discussion													●	
6.	Completion of Report														●

3.9. Tools and Software

There are several tools needed for the project to run. Among them are:

i. Glass Bottle and cap
ii. Beaker
iii. Magnetic Bar
iv. Magnetic Plate
v. Spoon
vi. Glass Plate
vii. Glass Cover
viii. Pipette
ix. Pipette Dropper
x. Mask
xi. Plastic Glove

Also, there are several equipment and machines needed.

i. Membrane Casting Machine
ii. Drying Oven
iii. Mortar Grinder
iv. Weighing Machine
v. Membrane Performance Test Machine
vi. Field Emission Scanning Electron Microscope (FESEM)
vii. Fourier Transform Infrared Spectroscope (FTIR)

The software needed below is basically for report purposes and performance data collection.

i. Microsoft Office Word 2010
ii. Microsoft Office Excel 2010

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

There are 3 phases involved with this project. They are (1) Phase 1 - Membrane Fabrication. (2) Phase 2 – Membrane Characterization and (3) Phase 3 – Membrane Performance.

4.1. Phase 1 – Membrane Fabrication

All membranes have been fabricated according to the compositions provided before. The following figures show the picture taken for each membrane that has been synthesized.

Fig. 4-1 shows the picture of polymeric membrane with 30 g of DCM and 6 g of PSU.

Fig. 4-2 shows the picture of mixed matrix membrane with 30 g of DCM, 6 g of PSU and 0.6 g of CMS.

Fig. 4-3 shows the picture of ionic liquid mixed matrix membrane 1 with 30 g of DCM, 6 g of PSU and 0.6 g of IL.

Fig. 4-4 shows the picture of ionic liquid mixed matrix membrane 2 with 30 g of DCM, 6 g of PSU, 0.6 g of CMS and 0.6 g of IL.

Fig. 4-5 shows the picture of ionic liquid mixed matrix membrane 3 with 30 g of DCM, 6 g of PSU, 1.2 g of CMS and 0.6 g of IL.

Fig. 4-6 shows the picture of ionic liquid mixed matrix membrane 3 with 30 g of DCM, 6 g of PSU, 1.8 g of CMS and 0.6 g of IL.

Figure 4-1: Polymeric Membrane

Figure 4-2: Mixed Matrix Membrane

Figure 4-3: Ionic Liquid Mixed Matrix Membrane 1

Figure 4-4: Ionic Liquid Mixed Matrix Membrane 2

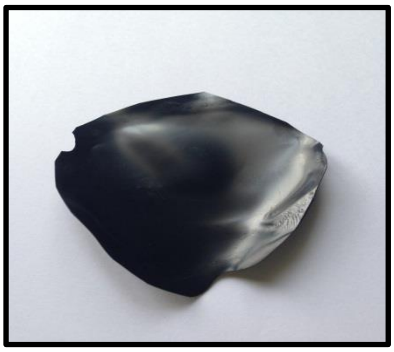


Figure 4-5: Ionic Liquid Mixed Matrix Membrane 3

Figure 4-6: Ionic Liquid Mixed Matrix Membrane 4

4.2. Phase 2 – Membrane Characterization

As for the characterization of the membranes, FESEM and FTIR are used.

4.2.1. Field Emission Scanning Electron Microscopy (FESEM)

The membranes were characterized using FESEM to determine the morphology of the membranes. Figures below show the FESEM images for each membrane.

i. Polymeric Membrane (PM)

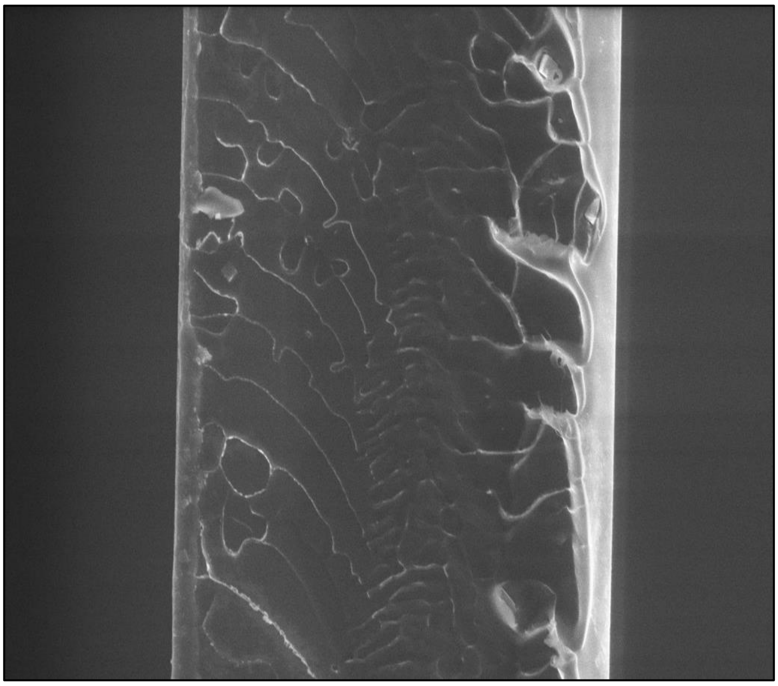


Figure 4-7: FESEM Image of Polymeric Membrane

Figure 4-7 shows the FESEM image of Polymeric Membrane at surface. The PSU and DCM are well mixed and the PSU is distributed homogenously. This is a dense, non-porous membrane. (Zhang, Sunarso, Liu, & Wang, 2013) The polymeric membrane was able to be developed.

ii. Mixed Matrix Membrane (MMM)

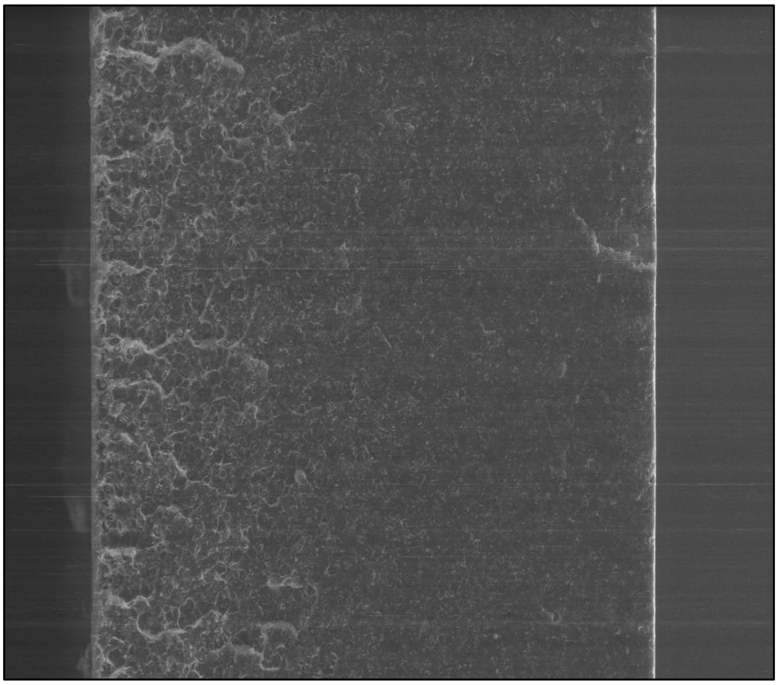


Figure 4-8: FESEM Image of Mixed Matrix Membrane

Figure 4-8 shows the FESEM image of Mixed Matrix Membrane (MMM). CMS was homogeneously distributed within polymer matrix. The CMS does not agglomerate and the mixing of components has ensured the homogeneous distribution of CMS in the membrane. No obvious agglomeration is clearly seen. No observation of pores are detected and seen on this cross section image.

iii. Ionic Liquid Mixed Matrix Membrane 1 (ILMMM 1)

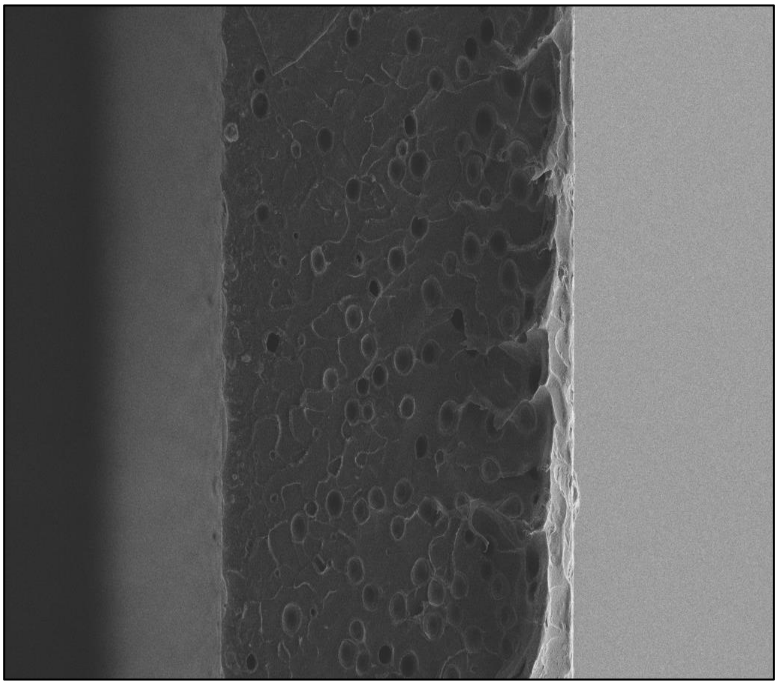


Figure 4-9: FESEM Image of Ionic Liquid Mixed Matrix Membrane 1

Figure 4-9 shows the FESEM image of Ionic Liquid Mixed Matrix Membrane 1 (ILMMM 1). No CMS inserted during the solution preparation step. No very small particles appear on the image. Black circle shows the presence of ionic liquid in the membrane.

iv. Ionic Liquid Mixed Matrix Membrane 3 (ILMMM 3)

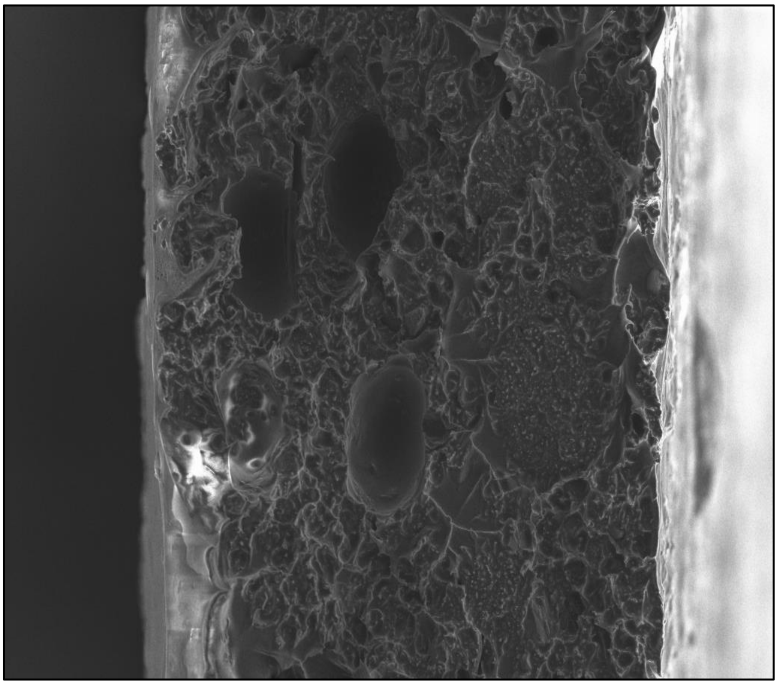


Figure 4-10: FESEM Image of Ionic Liquid Mixed Matrix Membrane 3

Figure 4-10 shows the FESEM image of Ionic Liquid Mixed Matrix Membrane 3 (ILMMM 3). There is no agglomeration of particles found in this membrane. These micrographs demonstrate CMS particles and a better distribution of these particles, as well as very good polymer–sieve contact. (Vu, Koros, & Miller, 2003)

v. Ionic Liquid Mixed Matrix Membrane 4 (ILMMM 4)

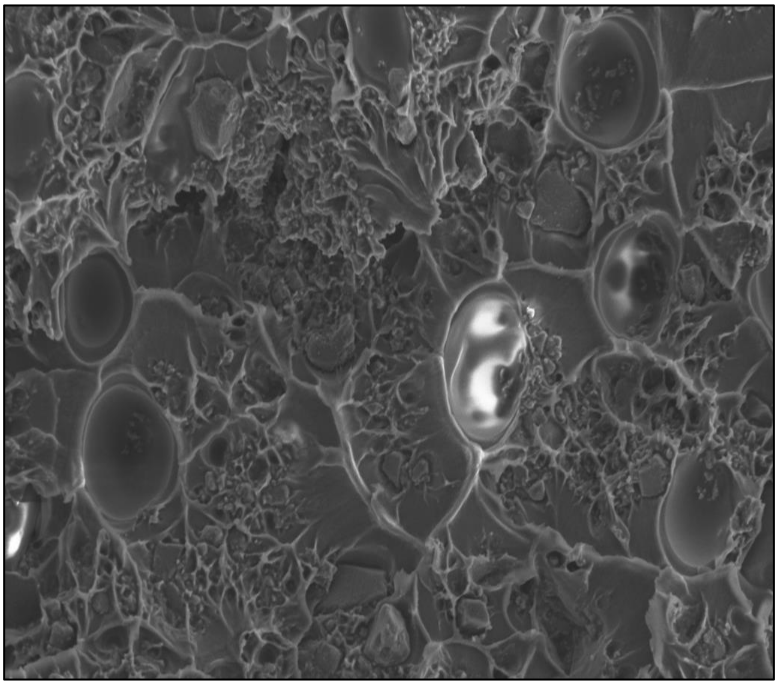


Figure 4-11: FESEM Image of Ionic Liquid Mixed Matrix Membrane 4

Figure 4-11 shows the FESEM image of Ionic Liquid Mixed Matrix Membrane 4 (ILMMM 4). Good adhesion between the polymer matrix and the inorganic interface. (Hudiono, Carlisle, Bara, Zhang, Gin, & Noble, 2010) There is an even distribution of CMS in the membrane.

4.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

In order to study the nature of fabricated membranes, Fourier Transform Infrared Spectroscopy is used. FTIR uses the infrared (IR) portion of the electromagnetic spectrum to characterize materials as molecules absorb specific IR transitions that match the vibrational frequency of chemical bonds present in the molecular structures. A data processing technique called Fourier Transform turns the raw data into the FTIR spectrum. The functions of FTIR are to determine the molecular structure of the membrane, functional group identification and type of chemical bonds.

Fig. 4-12 shows the FTIR spectrum of polymeric membrane which is basically a graph of percentage of transmittance against wavenumber. The polymeric membrane only contains PSU and DCM. The characteristic peaks of this membrane are at wavenumber of 2967.03 cm^{-1} which shows the C-H bond of alkanes, 1410.17 cm^{-1} depicts the present of S=O, sulfone functional group and 1102.92 cm^{-1} shows the C-F stretch. Also present is the benzene functional group at 3065.93 cm^{-1}.

Fig. 4-13 shows the mixed matrix membrane FTIR spectrum. During solution preparations, only DCM, PSU and CMS were mixed. Based on the spectrum, it can be observed that the characteristic peaks of shows the same peak as polymeric membrane. All of the characteristics do not change or shift significantly. There are still C-H bond of alkanes at wavenumber of 2967.03 cm^{-1}, S=O, sulfone functional group at 1410.17 cm^{-1} and 1102.92 cm^{-1} of C-F stretch. It can be said that the addition of CMS into the membrane during solution preparation steps does not change the functional groups present.

Fig. 4-14 shows the FTIR spectrum for ionic liquid mixed matrix membrane 2. There are DCM, PSU, CMS and [(emim)(CF_3SO_3)] in the membrane. The characteristic peak for this membrane is the sulfonate functional group at wavenumber 1363.53 cm^{-1}. When compared to FTIR spectrum of MMM, the functional group of C-H of alkane, has shifted to the left a little bit meanwhile the functional group of S=O of sulfone, has shifted to the right a bit. In addition, the functional group of C-F which presents at MMM FTIR spectrum, has lost in this FTIR spectrum of ILMMM 2.

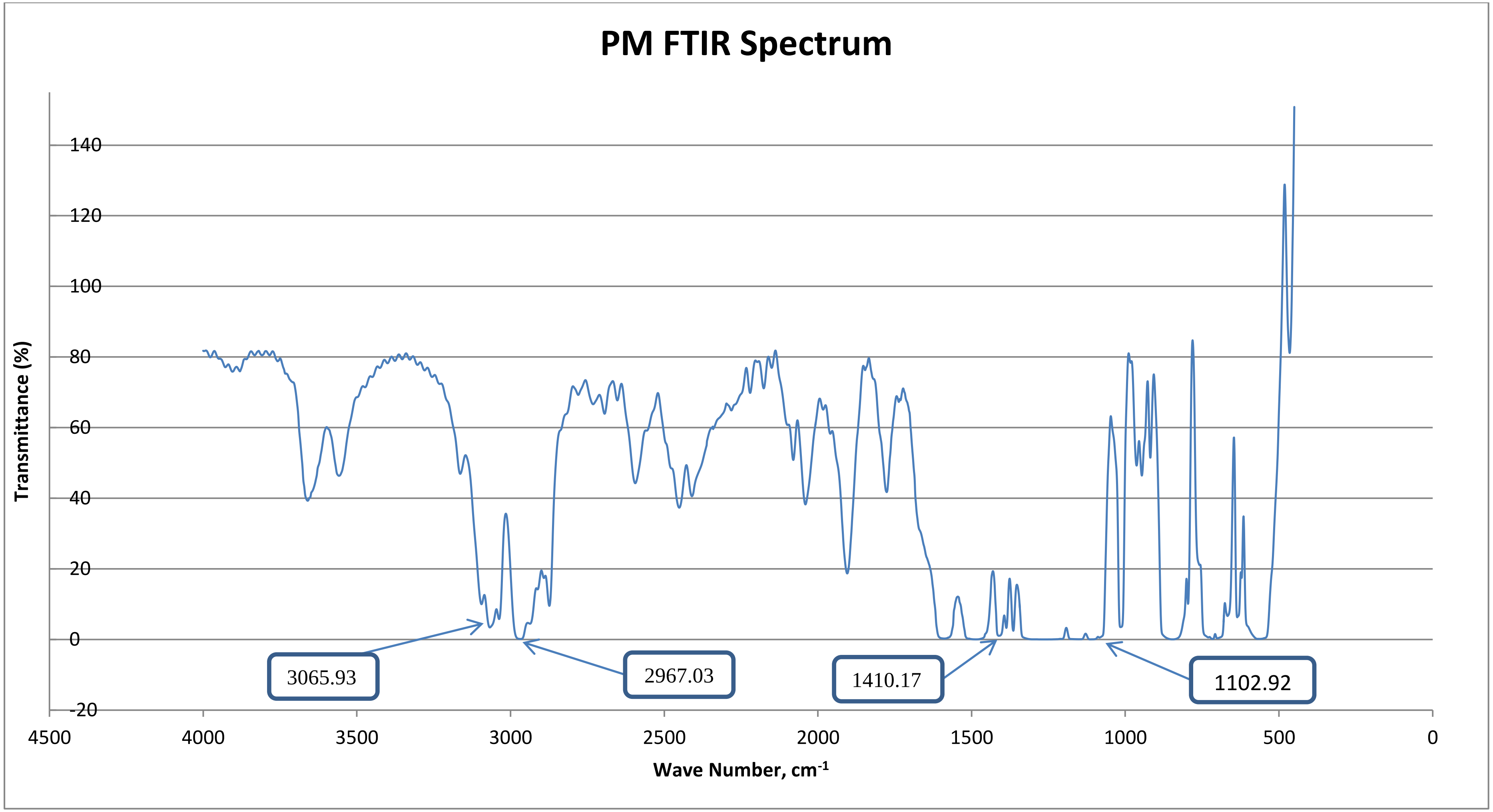


Figure 4-12: FTIR Spectrum of Polymeric Membrane

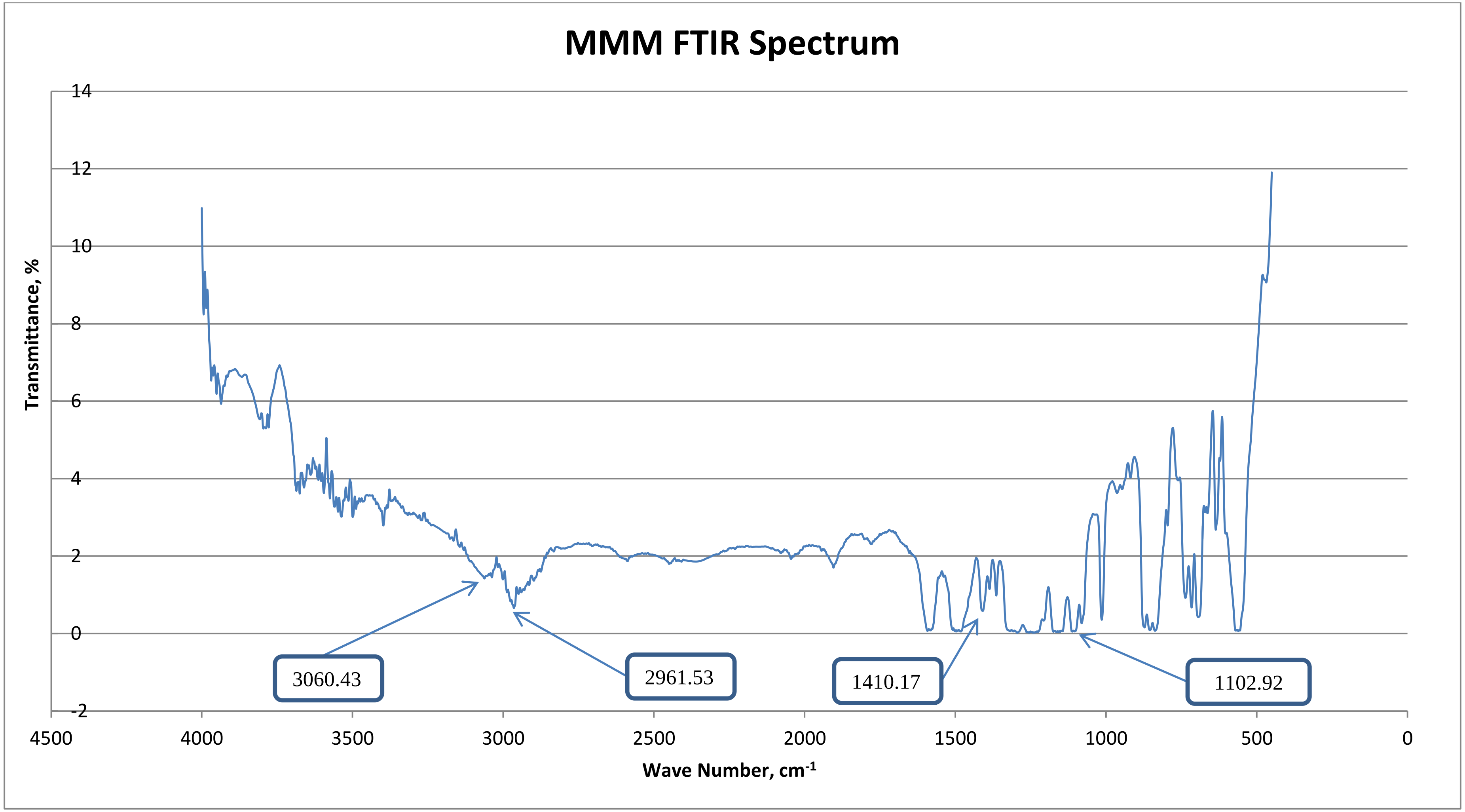


Figure 4-13: FTIR Spectrum of Mixed Matrix Membrane

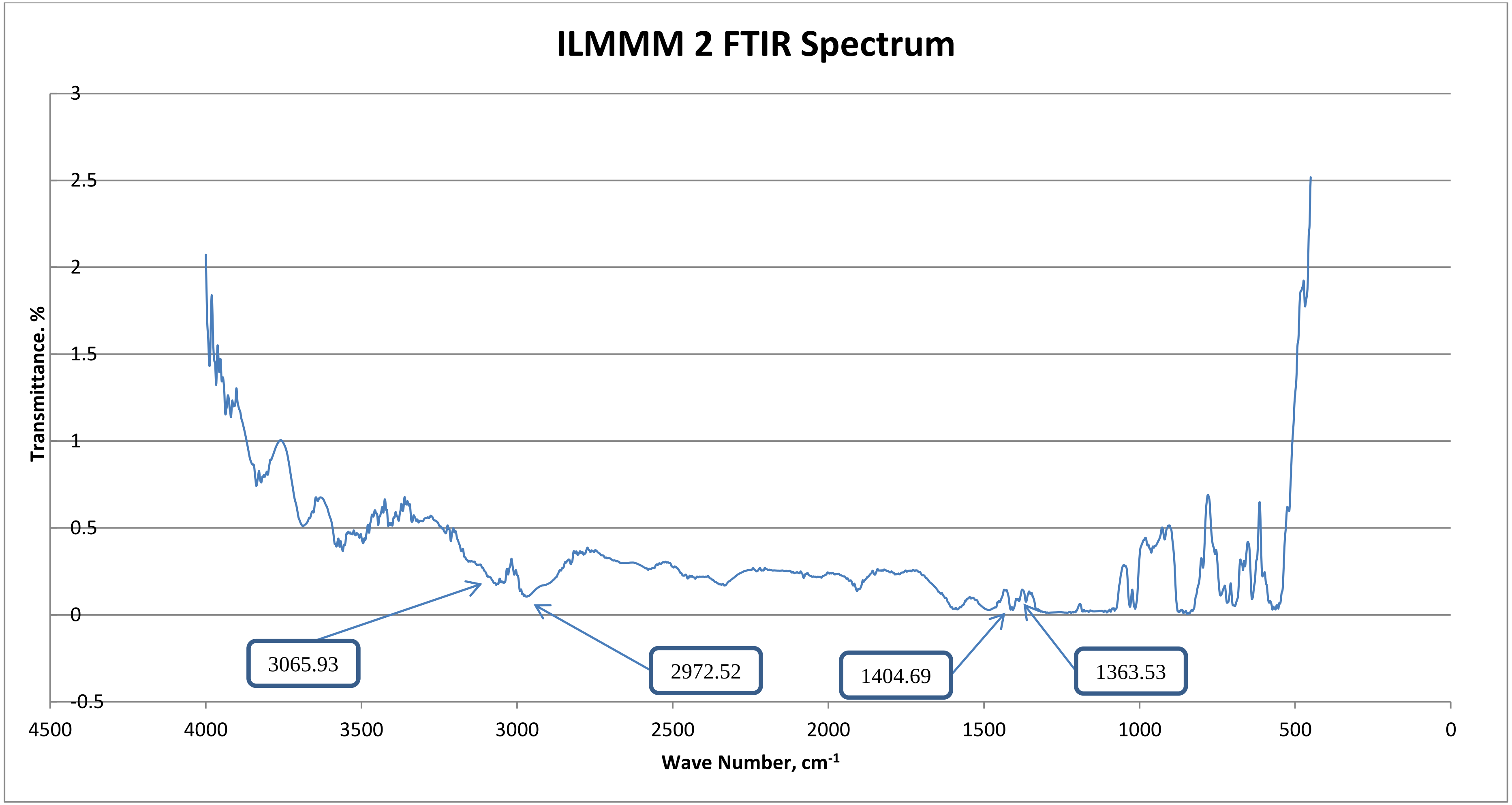


Figure 4-14: FTIR Spectrum of Ionic Liquid Mixed Matrix Membrane 2

4.3. Phase 3 – Membrane Performance

Performances of membrane were conducted only for selected membranes which were PM, ILMMM 2 and ILMMM 3. The results of the performance are shown below.

Table 4-1: Permeability of Carbon Dioxide across PM, ILMMM 2 and ILMMM 3 at Different Pressure

	PM	ILMMM 2	ILMMM 3
Pressure (bar)	Permeability (GPU)		
2	8.00	26.36	27.72
4	7.00	25.10	26.00
6	7.50	23.00	24.56
8	7.50	19.00	23.46

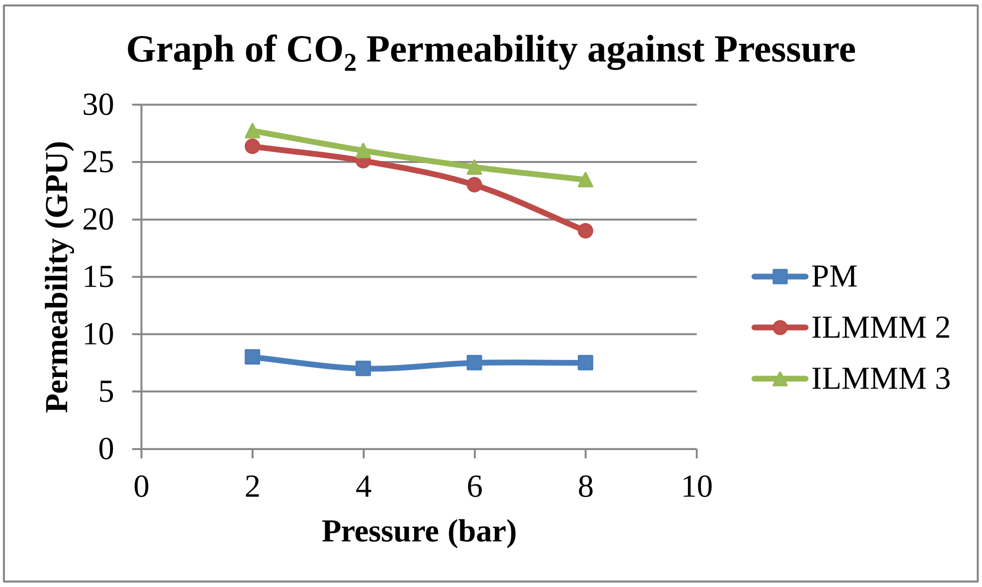


Figure 4-15: Graph of Carbon Dioxide Permeability against Pressure for Polymeric Membrane, Ionic Liquid Mixed Matrix Membrane 2 and Ionic Liquid Mixed Matrix Membrane 3

Fig. 4-15 shows the graph of CO_2 permeability against pressure for three membranes which are Polymeric Membrane, Ionic Liquid Mixed Matrix Membrane 2 and Ionic Liquid Mixed Matrix Membrane 3.. The blue line with square-shaped markers shows the permeability of CO_2 across the polymeric membrane at different pressure. As the pressure increases from 2 bar to 8 bar, the permeability slightly decreases. Meanwhile, the red line with circle-shaped markers shows the permeability of CO_2 at different pressure for ILMMM 2. It can be observed that the permeability of CO_2 also decreases as the pressure increases. But, the permeability of CO_2 at 2 bar for ILMMM 2 is 330% of permeability of CO_2 for PM at the same pressure. Also, the permeability line which is green in colour and with triangular-shaped markers shows the permeability of CO_2 at different pressure across the ILMMM 3. This trend for this permeability is that as the pressure increases, the permeability across the membrane decreases slightly too. The permeability of CO_2 across ILMMM 3 at 2 bar is 27.72 GPU which is 350% higher than the permeability of CO_2 across PM at the same pressure. The trend shows that as the CMS content increases, the permeability of CO_2 also increases.

Table 4-2: Permeability of Methane across PM, ILMMM 2 and ILMMM 3 at Different Pressure

	PM	ILMMM 2	ILMMM 3
Pressure (bar)	Permeability (GPU)		
2	2.16	5.27	10.27
4	2.46	5.58	9.70
6	2.68	5.35	10.54
8	2.88	4.80	10.77

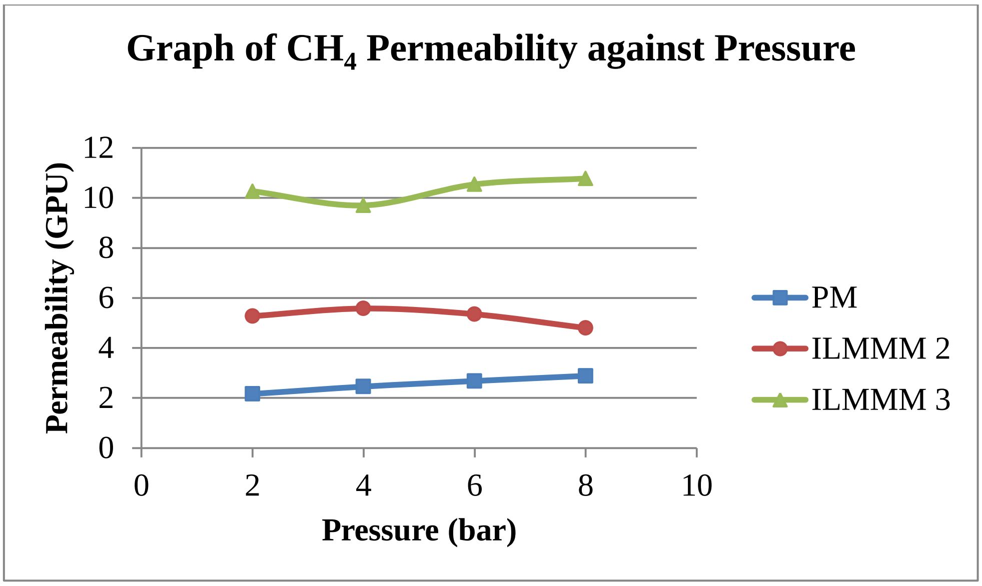


Figure 4-16: Graph of Methane Permeability against Pressure for Polymeric Membrane, Ionic Liquid Mixed Matrix Membrane 2 and Ionic Liquid Mixed Matrix Membrane 3

Fig. 4-16 shows the graph of CH_4 permeability against pressure. The blue line with square-shaped markers shows the permeability of CH_4 across the polymeric membrane at different pressure. As the pressure increases from 2 bar to 8 bar, the permeability slightly increases. Meanwhile, the red line with circle-shaped markers shows the permeability of CH_4 at different pressure for ILMMM 2. It can be observed that the permeability of CH_4 at first increases, but after the pressure increases starting from 4 bar, the permeability decreases. Moreover, the permeability of CH_4 at 2 bar for ILMMM 2 is only 240% higher than that of permeability of CO_2 for PM at the same pressure. Also, the permeability line which is green in colour and with triangular-shaped markers shows the permeability of CH_4 at different pressure across the ILMMM 3. This trend for this permeability is that as the pressure increases, the permeability across the membrane decreases but then increases at 5 bar until at the pressure of 8 bar. The permeability of CH_4 across ILMMM 3 at 2 bar is 10.27 GPU is 475% of the permeability of CH_4 across PM at the same pressure.

Table 4-3: Selectivity of Carbon Dioxide/Methane across PM, ILMMM 2 and ILMMM 3 at Different Pressure

	PM	ILMMM 2	ILMMM 3
Pressure (bar)	Selectivity $\left(\frac{P_{CO_2}}{P_{CH_4}}\right)$		
2	3.70	5.00	2.70
4	2.85	4.50	2.68
6	2.80	4.30	2.33
8	2.60	3.96	2.18

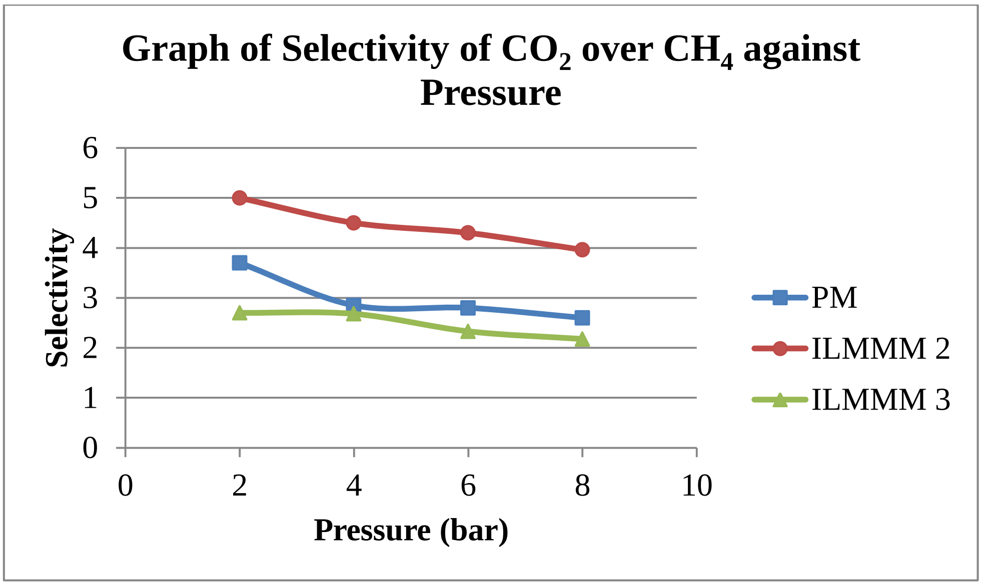


Figure 4-17: Graph of Carbon Dioxide/Methane Selectivity against Pressure for Polymeric Membrane, Ionic Liquid Mixed Matrix Membrane 2 and Ionic Liquid Mixed Matrix Membrane 3

Fig. 4-17 shows the graph of selectivity of carbon dioxide over methane at different pressure for PM, ILMMM 2 and ILMMM 3. The blue line with square-shaped markers shows the selectivity across PM at 4 different pressures. As the pressure increases, the selectivity gets lower. The red line with circle-shaped markers shows the selectivity of ILMMM 2 also at different pressures. The trend is like this, the selectivity decreases along with increasing pressure. The green line with triangular shape markers shows the selectivity of carbon dioxide over methane for ILMMM 3.

The same trend pattern also can be observed from the line. As the pressure increases, the selectivity decreases. Among the three lines, it can be concluded that the ILMMM 2 has the highest selectivity among the other membrane.

Based on the three membranes performances that have been conducted, although ILMMM 3 has the highest permeability of CO_2 across the membrane, ILMMM 2 has the highest permeability of CH_4, but the overall indicator still refers to the selectivity of carbon dioxide over methane across the membrane. ILMMM 2 has the optimum composition of DCM, PSU, [(emim)(CF_3SO_3)] and CMS for this project. It has the highest selectivity of carbon dioxide over methane as compared to the other membrane tested.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

As a conclusion, all of the objectives stated earlier have been achieved. The six membranes have been fabricated. The characterizations for all the membranes also have been conducted. Based on FESEM images result, the polymer, PSU and the inorganic filler, CMS were good in term of polymer-sieve contact. Meanwhile, the addition of [(emim)(CF_3SO_3)] into mixed matrix membrane has shifted the peaks characteristics of functional group of mixed matrix membrane in FTIR analysis. The performances of the membrane were conducted only for selected one. It can be summarized that, as the CMS compositions in the membrane increases, the selectivity increases but stop increasing at ILMMM 3. The optimum composition for the selectivity of carbon dioxide over methane to be optimum, is at ILMMM 2 composition.

5.2. Recommendations

There are several recommendations for this project.

i. The performance of each membrane must be conducted to really understand the effect of inorganic filler variation in the membrane.
ii. The FESEM image must be clearer and magnified with the same magnification and microscope distance.
iii. SEM in better than FESEM should be used when comparing the morphology of the membranes.

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