Non Solvent Effect on Polysulfone Membrane for Carbon Dioxide Removal from Natural Gas

By

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

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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Approved by,

____

(Dr. Zakaria Man)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
July 2010

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.

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AINUL YAQIN BINTI JAMIL

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ABSTRACT

Gas separation by selective transport through membranes is one of the fastest growing branches in membrane technology. Polymeric membrane is a type of membrane that is most favorable to be used as the gas separation membrane. In this study Polysulfone has been chose as the material for the membrane fabrication. This is due to the good separation properties, low cost and not easily plasticized by highly sorbing plasticization gases. In order to fabricate the membrane, wet phase inversion process has been used. In this process, polymer material that is polysulfone was dissolved together with the solvent which is Dichloromethane (DCM) and 1-Methyl-2 Pyrrolidone (NMP). Then the polymer solution was casted to get a layer of membrane shape before immersing it in a non-solvent coagulation bath to allow wet phase inversion process to occur. In this study, the non-solvent that is used as a coagulation medium, was varied between ethanol and water. The usage of this different non solvent varied the phase change rate between the non solvent and solvent thus will vary the morphology of the membrane formed. By using water as the non solvent, the internal coagulation rate between the solvent and the non solvent was increased thus produced membrane with large macrovoid in the substructure. Meanwhile by using Ethanol as the non solvent, it will reduce the macrovoid and will increase the selectivity of the membrane. The characteristic of the polysulfone membrane was characterized by using Scanning Electron Microscopy (SEM), Fourier Transform Infra Red (FTIR) test, and Universal Testing Machine (UTM). The gas separation behavior of the membrane was determined by using membrane permeation system with different sets of feed pressure of $CO_2$and CH_4 gases. The separation performance of the membrane was determined by calculating the selectivity and the permeability of the membrane. PSF membrane that used 100% Ethanol as the non solvent showed the promising performance in term of selectivity and permeability. The results showed that the polymer and the non solvent pair controlled the morphology of the membrane and eventually affect the performance of the PSF membrane.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

For many years ago, natural gas is one of the most important asset for Malaysia. According to Oil and Gas Journal, Malaysia had about 83 trillion Cubic Feet of proven natural gas reserves as of January 2009. The composition of natural gas differs for different sources. Basically, methane is the major component in natural gas, comprising typically 75-90% of the total component [Baker, (2004)]. Natural gas may also contain undesirable amount of impurities such as Carbon Dioxide (CO_2) and Hydrogen Sulfide (H_2S). It is usually desirable to remove the impurities to prevent corrosion problems and to increase heating value of the gas.

Table 1-1: Typical Composition of Natural Gas [Handbook of Natural Gas Transmission and Processing, 2006]

Name	Formula	Volume (%)
Methane	CH_4	>85
Ethane	C_2H_6	3-8
Propane	C_3H_8	1-2
Butane	C_4H_{10}	<1
Pentane	C_5H_{12}	<1
Carbon Dioxide	CO_2	1-2
Hydrogen Sulfide	H_2S	<1
Nitrogen	N_2	1-5
Helium	He	<0.5

Existing CO_2 removal technologies such as amine stripping, PSA and TSA consume large space, high capital and operating cost. Since the last two decades, membrane technology has been developed to face those challenges. Based on this technology, CO_2 and other components of natural gas have to pass through a thin membrane barrier. The high permeating component will diffuse through the membrane and separated from the non-permeable component.

Carbon dioxide removal from natural gas using the membrane process has emerged as a promising alternative to the conventional processes because of a number of advantages such as low capital cost, less space requirement, environmental friendliness and low energy consumption [D.Dortmundt et al (1999)]. Development of suitable membranes is the most crucial factor in determining the competitiveness of membrane technology over other separation strategies. Suitable membrane for the CO_2 separation process requires both high permeability and a satisfactory selectivity at the same time [M.Iqbal et al (2008)].

In this study, the gas separation membrane was fabricated by using Polysulfone membrane. Development of the membrane will be using different type of solvent – non solvent mixture to determine the best combination that gives the best performance asymmetric membrane in sweetening the natural gas. The performance of the membrane is determined by its permeability and selectivity. The polysulfone membrane will be fabricated by using the phase inversion technique. In this technique, the polymer solution will loses solvent by evaporation or exchange with other liquid called non-solvent and the precipitation will take place after that. [M.Iqbal et. Al (2008)].

By using different combination of the polymer-solvent-nonsolvent, the morphology of the membrane will be different. This is due to the increase viscosity of the dope solution which can decrease the rate of phase inversion process. [lin et al. (2006)].

1.1 PROBLEM STATEMENT

Polysulfone has satisfactory gas permeabilities and acceptable permselectivities, and it can be used with highly sorbing, plasticizing gases. The demand for polysulfone as a gas separation membrane is very high due to its characteristics and its low price. However, research has been done to improve the performance of the membrane in separating gases. Current research was just only focus in improving the performance by varying the solvent concentration of the polymer solution [M. Iqbal et. al. (2008)]. M.A. Aroon et. al (2010) were successfully proved that when a non- solvent is used as an additive in the polymer –solvent solution, the phase separation behavior during the phase inversion process can be altered and can accelerate the coagulation process. As a result, membranes with a thinner skin layer and more uniform structure can be formed. Meanwhile if varying the non-solvent in the coagulation medium, the microvoid formation in the sublayer of the membrane can also be reduced [Z.G Wang et al (2005)].

1.2 OBJECTIVE OF THE STUDY

i) To develop Polysufone (PSF) membrane with different type of non solvent
ii) To study the characteristics of the membrane formed
iii) To study the permeability of Carbon Dioxide (CO_2) and Methane (CH_4) through the membrane

1.3 RELEVANCY OF THE STUDY

This research is said to be relevant and essential because gas separation by selective transport through polymeric membranes is one of the fastest growing branches of membrane technology. However, the existing polymeric membrane materials are inadequate to be applied in industrial scale thus in industry the demand for a high permeability and selectivity is really high. Thus, by making some modification in the membrane fabrication, by study the effect of the different of non solvent used, it is believed that the membrane will have an excellent property for gas separation work.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE DEFINITION AND ITS MORPHOLOGY

Membrane is defined as selective barrier between 2 phases that has ability to transport one component than the other. Its structure can be homogeneous or heterogeneous, transport can be active or passive and passive transport can be driven by a pressure, concentration or a temperature difference. [M.Mulder, (1996)]. Membrane will act as a filter to separate the gases from the feed into a very rich gas that will pass through the membrane as permeate [C.A Scholes et al. (2008)]. Below is the figure of the schematic membrane gas separation.

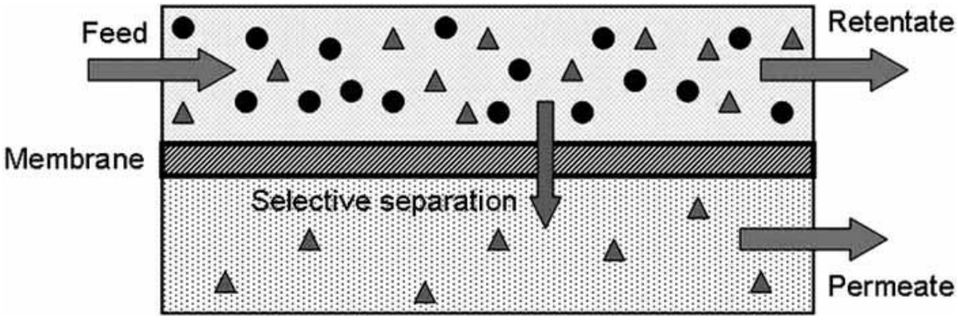

Figure 2-1: Schematic of membrane gas separation [C.A Scholeles et al (2008)]

There is a wide range of membrane application such as for sea water desalination, waste-water treatment, ultrapure water production for semiconductor industry and nitrogen enrichment from air. Each of these applications requires specific type of membrane morphology to ensure the effective separation. Figure 2.2 shows a classification of membrane morphologies.

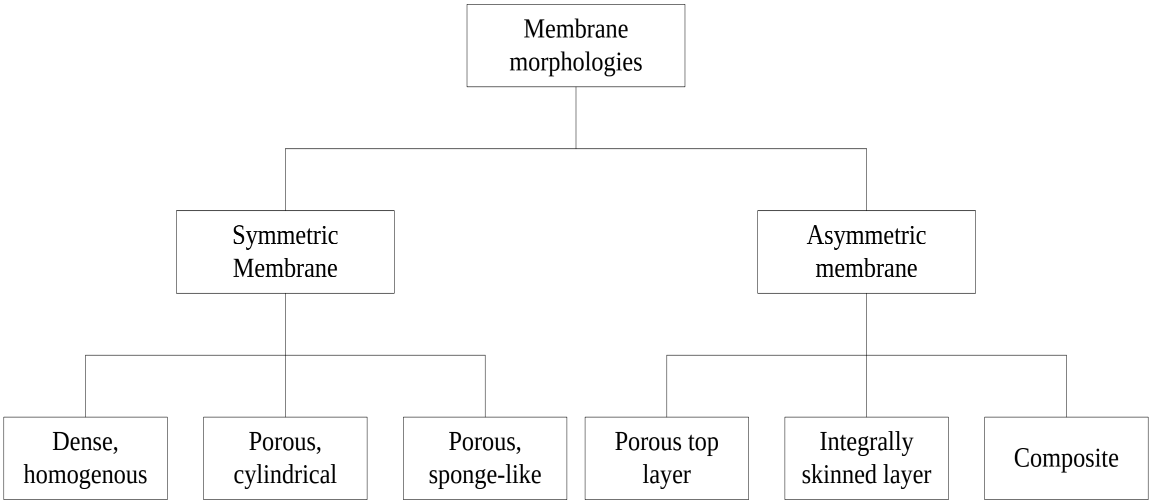

Figure 2-2: Classification of the typical membrane morphologies [M.Iqbal (2007)]

Symmetric membrane refers to the membrane that has essentially same structure and transport properties throughout its thickness [Koros, et al. (1996)]. Meanwhile asymmetric membrane is a membrane constituted of two or more structural planes of non-identical morphologies [Koros, et al. (1996)].

Morphology of membranes plays a major role in determining the performance and application of membrane. High total flux and selectivity is highly desired. Symmetric membrane has advantages in term of selectivity but it is low in total flux of product. Asymmetric membrane is more preferable due to its ability to enhance total flux with sufficient selectivity. Therefore, asymmetric membrane is commercially used at various applications in industry.

2.2 POLYMERIC MEMBRANES

Polymeric membranes are the dense type membrane. Generally, there are 2 types of polymeric membranes which are categorized based on rubbery or glassy polymers. Rubbery polymer is soft and elastic due to the flexibility of the polymer backbone that can rotate freely around the axis while glassy polymer is a rigid polymer as the polymer segments are prohibited from rotating resulted from steric hindrance. Polysulfone and Polyimide are the type of materials used in polymeric membrane fabrication.

2.2.1 Permeability of polymeric membranes

Gas transport through polymeric membrane is based on the 'solution-diffusion' mechanism: [H. Wang et al. (2002)].

$$P = DS$$

$$P = N\ell / p_2 - p_1 \quad \text{where,}$$

P = gas permeability, D = diffusion coefficient, S = solubility coefficient, N = permeation flux, ℓ = membrane thickness, p_2 = upstream pressure, p_1 = downstream pressure [T.S Chung et al. (2007)]

The ability of a membrane to separate two molecules for example A and B is the ratio of their permeabilities, called membrane selectivity,

$$\alpha_{AB} = P_A / P_B$$

An upper limit for the performance of polymeric membranes in gas separation was predicted by Roberson in early 1990. [Roberson LM. (1991)]. The performance of various membrane materials available for the separation of O_2/N_2 is captured in figure below :

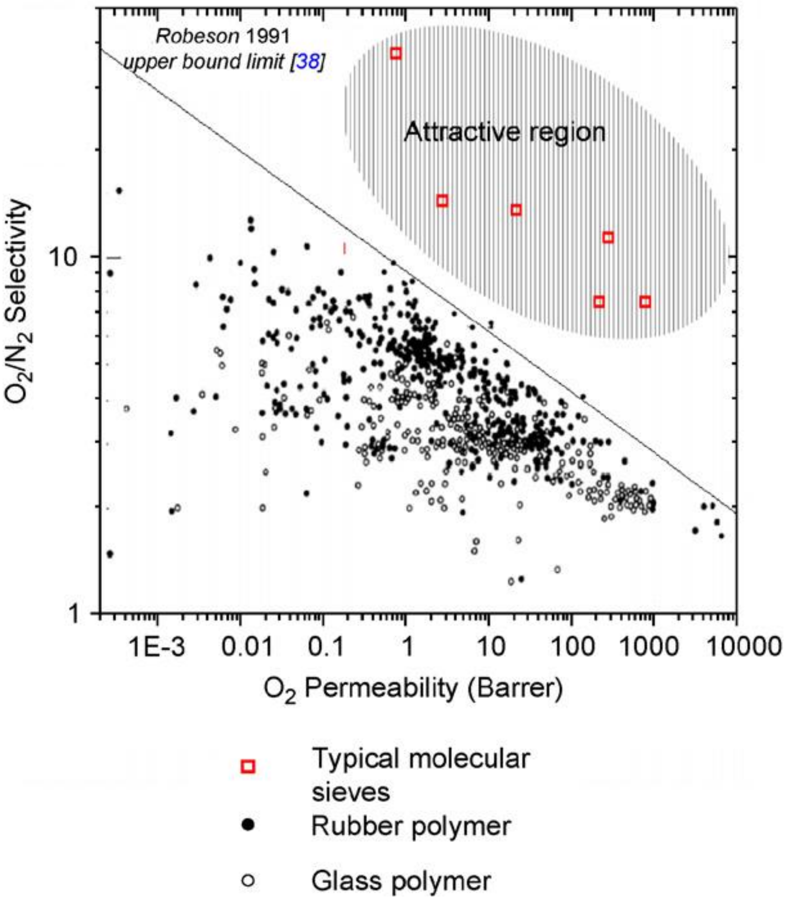

Figure 2-3: Relationship between the O_2/N_2 selectivity and O_2 permeability for polymeric membranes and inorganic membranes [Roberson L.M (1991)]

2.3 INORGANIC MEMBRANE

Inorganic membrane poses attractive characteristics such as high solvent – resistant properties, thermal and pore structure stability [K.Li (2007)]. Most importantly, membrane failure due to the swelling induced plasticization would not happen with inorganic membrane. Inorganic membranes are commonly formed from metals, ceramic or pyrolized carbon. However, despite of all the advantages of the inorganic membrane, the application of inorganic membranes is still limited due to the high cost of fabrication, the complication of handling and lack of technology to form continuous and defect – free membrane. [G.Ciobanu et al.(2008)]. Thus, to overcome the limitation between the polymeric membrane and the organic membrane mixed matrix membrane has been introduced.

2.4 MIXED MATRIX MEMBRANE

Mixed matrix membrane has been introduced in order to improve the limitation of polymeric membrane such as failure due to the swelling induced plasticization. Mixed matrix membrane has an excellent mechanical strength due to the combination of the inorganic membrane materials such as metals and ceramic with the polymeric membrane materials. Mixed matrix membrane has inorganic filler embedded in the polymer matrix as shown in figure 2.4. Many studies have reported that, mixed matrix membrane may exhibit substantially increased permeability and selectivity that are far beyond the properties of pure polymer membrane [A.F. Ismail et al. (2007)].

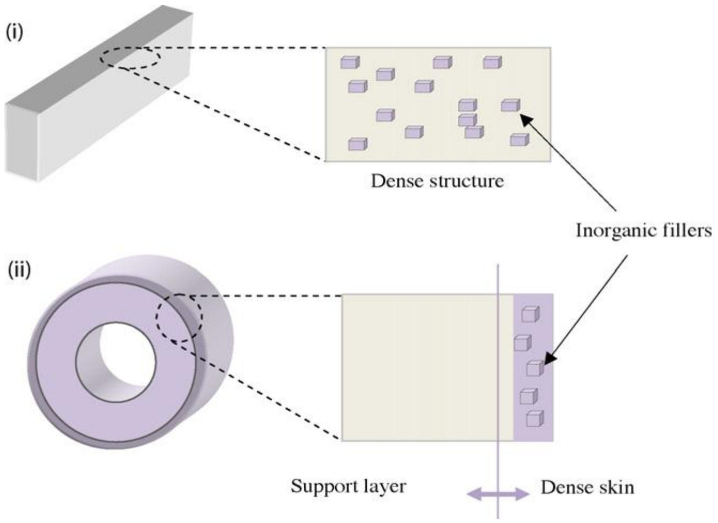

Figure 2-4: Schematic of polymer/inorganic filler mixed matrix membrane [A.F. Ismail et al. 2007]

The investigation of mixed matrix membrane for gas separation was first reported in 1970s with the discovery of a delayed diffusion time lag effect for CO_2 and CH_4 when adding 5A zeolite into rubbery polymer polydimethyl siloxane (PDMS). [Paul DR and Kemp DR (1973)]. In this work Paul and Kemp found that the addition of 5A into the polymer matrix caused very large increases in the diffusion time lag but had only minor effects on the steady state permeation.[T.S Chung et al. (2007)].

2.5 DEVELOPMENT OF DIFFERENT TYPE OF POLYMERIC MEMBRANE

2.5.1 Polysulfone

Polysulfone is one of the most favorable materials used in polymeric membrane fabrication. This is due to the economical advantage of this material. PSF has a very low price which is eg: $ 15/kg PSF Udel P-1700 [G.C Kapantaidakis et (1995)]. In addition PSF has a promising gas permeabilities and good permselectivities. It also can be used for CO_2 gas which is considered as a highly sorbing and plasticizing gas.

Plasticization is a phenomenon that is a not favorable which occurred to the membrane used for gas separation. During plasticization, the interaction between the adjacent polymers chain will reduce which can be called as swelling. Thus, the separation performance will be change resulting in the membrane failure. [C.A Scholes et al. (2009)].

2.5.2 Polyimide

Polyimide is also a promising polymer material for gas separation membrane fabrication. The special property of this material is it has a high glass transition temperature. [Rezac et al (1997)]

However, polyimide is very susceptible to plasticization gas such CO_2 [G.C Kapantaidakis et al. (1995)]. Polyimide material is also very expensive as compared to other type of polymer material. Thus it makes polyimide is not favor to be chose as the membrane material for this study.

2.6 NON SOLVENT USED IN MEMBRANE FABRICATION

Generally most of the solvent and non-solvent used in membrane fabrication can vary the membrane morphology and thus can affect the gas separation properties of the membrane. The example of non solvent used in membrane fabrication is Methanol, Ethanol, Buthanol and Glycerol. By adding the non solvent in casting solution, the macrovoid formation in the sub layer of the membrane formed can be reduced [M.A Aroon et al. (2009)]. Macrovoid, a large pore, can often be observed in asymmetric membrane. However this structure only suitable for ultra filtration process and was found very useful in drug delivery system but for gas separation and reverse osmosis process, this macrovoid structure is not favorable. [Z.G Wang et al. (2005)]

The macrovoid structure can be avoided by reducing the fluidity of the casting solution. This step may lower the phase inversion rate. Thus, to achieve this objective, the casting solution viscosity need to be increased by increasing polymer concentrations or adding additives such as low molecular weight component and other polymer. [Z.G Wang et al (2005)]. The type of secondary polymer that is often used as an additive are PVP (poly N-vinyl-2-pyrrollidone) or PEG (polyethylene glycol).

A detail study had been done by Buennta et al on preparation of a type of membrane using different solvent – nonsolvent pairs. Several parameters have been have been investigated in their study, which they have studied the effect of solvent and polymer concentration, composition of coagulation bath, the exposure before the coagulation on the morphology of the membrane.

Based on the report from Ismail and Lai, the larger solubility parameter difference used in phase inversion technique between the solvent and the coagulant, a less porous and closed-cell substructure of asymmetric PSF membrane will be formed. Thus, by using the non solvent which has the higher solubility parameter in PSF polymer solution, the porous substructure in the membrane can be reduced and the gas separation performance of the membrane can be increased.

2.7 PREPARATION OF THE MEMBRANE

2.7.1 Phase inversion technique

The phase inversion process is the best known method for the preparation of synthetic polymeric membrane. Phase inversion process involves a phase separation in a polymer solution either by temperature change or by immersing the polymer in a non-solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process). [S.P Nunes and K.V.Peinemann (2001)]. Technically it is a process in which an initially homogenous casting solution becomes thermodynamically unstable due to external effects [Yip and McHugh, (2006)]. Phase separation of casting solution can be induced by four different techniques as illustrated in Figure 2.5. [Baker, (2004)].

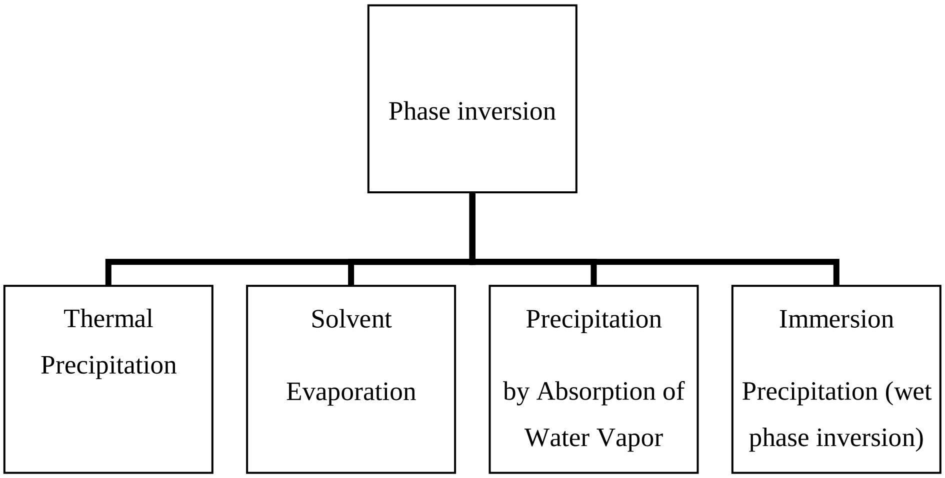

Figure 2-5: Method of inducing phase inversion process during membrane fabrication

a) Immersion Precipitation

In the wet phase inversion technique, the polymer solution will be immersed in a non solvent coagulation bath. The properties of the membrane can be varied by changing the non solvent solution or the composition of the coagulation bath. [D-J Lin et al (2006)]. From the previous study, a few modifications have been conducted to vary the formation of the membrane by manipulating the dope solution. As for example, by changing the casting temperature, adding the non-solvent in the dope solution and by using additives [D-J Lin et al (2006)].

In several recent papers, the fabrication of the membrane by using phase inversion technique with different of solvent and non solvent used has showed that the characteristic of the membrane formed can be changed [M.Iqbal (2007)]. The formation of asymmetric membrane is mainly controlled by both thermodynamics of the casting solution and the kinetics of transport properties [J.Ren et al (2010)].

b) Thermal precipitation

By using this method, a prepared film is cast from a hot, one – phase polymer solution, followed by cooling to precipitate the polymer. The cooled film is separated into two phase region; polymer-matrix phase and membrane pore-phase. The initial composition of the polymer solution will determine the pore volume of final membrane but the cooling rate of the solution greatly influences the pore size of the final membrane. Rapid cooling will produce small pores [Ruthven, (1997)].

c) Polymer precipitation by Absorption of Water Vapor

In this technique, water vapor is required to induce phase separation during membrane fabrication process. The casting solution that consists of polymer, volatile solvent and non-volatile solvent is cast onto a continuous stainless steel belt. The cast film is passed along the belt through a series of chambers. During circulation, the film loses the volatile solvent by evaporation and simultaneously absorbs water vapor from the atmosphere. After precipitation, the membranes are passed into an oven to dry the remaining solvent. The membrane formed is usually used for microfiltration purpose [Baker, (2004)].

d) Polymer precipitation by solvent evaporation

This is one of the earliest methods of making microporous asymmetric membrane [Baker, (2004)]. A polymer is dissolved into a two-component solution mixture consisting of a volatile solvent such as acetone and less volatile non-solvent typically water or alcohol. The solution is then cast onto a glass plate. The volatile solvent is allowed to evaporate at certain period of times so the casting solution is enriched with the less volatile non-solvent. The non-solvent enriched casting solution will precipitate to form the membrane structure.

There are many factors that affect the porosity and pore size of membrane formed through this method. Fine pores membrane will be formed for a short evaporation time. Larger pores membrane is produced if the evaporation step is prolonged. Porosity is mainly affected by non-solvent composition of the casting solution. Increasing non-solvent composition will increase the porosity of membrane and vice versa [Ruthven, (1997)].

A ternary phase diagram is commonly used to describe membrane-forming system involving a polymer, solvent(s) and non-solvent(s) by using dry/wet phase inversion process. This ternary phase diagram can be divided into three regions which are stable, metastable and unstable region. In the stable region, all components of the casting solution exist in one state and are homogenously miscible with each other. In the unstable region, the casting solution will spontaneously separate into two phases, polymer-rich and polymer-poor phase before the membrane structure is fixed. While in the metastable region, the homogenous casting solution will be thermodynamically unstable but it will not normally precipitate unless well nucleated [Baker, (2004)].

Each region in the phase diagram is confined by a particular curve. The stable region and metastable region are separated through a binodal curve while a spinodal curve separatea between metastable and unstable regions. The ternary phase diagram is illustrated in Figure 2.6.

Phase separation of an initially stable solution can be the result of two mechanisms: nucleation and growth or spinodal decomposition [Koros and Pinnau, (1994)]. Nucleation and growth decomposition mechanisms occur in the metastable region. Hence, a homogenous casting solution will become unstable through nucleation and growth mechanism if the final composition of membrane finally stops at metastable region as illustrated by line ABCD in Figure 2.6.

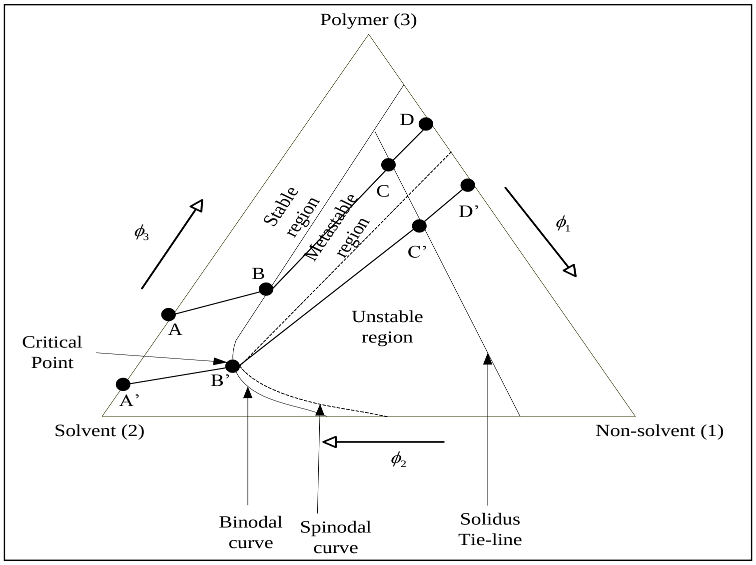

Figure 2-6: Figure Ternary phase diagram of membrane formation system.

At point A, the casting solution exists in stable and homogeneous solution. It will enter the metastable region and starts to become unstable at point B. This solution will undergo phase separation through nucleation and growth mechanism as the membrane structure is fixed, point C, through solidification of casting solution in metastable region. The final composition of nucleation and growth-decomposed membrane is located at point D which determines the overall porosity of membrane.

In case of nucleation and growth mechanism, membrane structure is formed based on the formation of the nuclei. The nuclei will evolve to form droplet and finally becomes porous structures of membrane. This mechanism will produce membrane with closed cell morphology if the average composition or concentration of final membrane is larger than the critical point (CP). On the other hand, if the average composition or concentration of final membrane is less than the critical point (CP), the membrane structure produced from nucleation and growth mechanism will be powdery and low integrity. This is because the nucleation of polymer-rich phase is dispersed in the polymer-poor phase.

In addition to nucleation and growth mechanism, the final membrane structure may be formed through spinodal decomposition mechanism. In this mechanism, the casting solution will be separated instantaneously into two phases, polymer-rich phase and polymer-poor phase. The instantaneous separation of casting solution leads to interconnectivity of these two phases to form an open cell thus forming an interconnected. This structure is attractive for gas separation membrane [Koros and Pinnau, (1994)]. Membrane formation through spinodal decomposition mechanism occurs once the homogenous casting solution enter the unstable region directly without passing through the metastable region as shown by line A’B’C’D’ in Figure 2-6.

CHAPTER 3

METHODOLOGY

3.1 MEMBRANE FABRICATION AND DEVELOPMENT

After understanding the theoretical concept of membrane fabrication and phase inversion process, the steps to develop the membrane can be worked out. All the chemicals and materials needed in the membrane development have been listed.

3.1.1 Equipment / Apparatus

Equipment that will be used throughout the experimental works has been listed in the following table:

Table 3-1: List of equipment used

No.	Equipment	Usage / Significant
1.	Laboratory heater and magnetic stirrer	• To mix the polymer (PSF) with the solvent in a high temperature to prepare the dope solution
2.	Bath Sonication	• To remove gas bubbles that are formed while stirring the dope solution • To ensure that the solution is well mixed
3	Coagulation Bath	• For wet phase inversion process (Dope solution that has been casted on the glass plate will be immersed inside the nonsolvent solution here)
4	Casting knife	• To cast the membrane into a layer shape
5	Dryer	• To dry the membrane

3.1.2 Materials / Chemicals

Chemicals that will be used in the experimental works have been listed as per the table :

Table 3-2: List of Chemicals used

No	Chemicals	Usage / Significant	Suppliers
1.	Polymers	• Polysulfone (PSF)	• Huntsman
2.	Solvent	• Dichloromethane (DCM) • 1-Methyl-2-Pyrrolidone (NMP)	• Merck • Merck
3.	Non Solvent	• Ethanol • Water (H_2O)	• Merck • In-house tap water

3.2 EXPERIMENTAL WORKS / PROCEDURES

The membrane will be fabricated with different sets of non solvent concentration. The quantity of the solvent and the polymer will be the same for the whole samples. The concentration of the non solvent is varied in order to find a membrane which provides the best gas permeability and selectivity. The combination of the polymers and non solvent concentration are tabulated in the following table:

Table 3-3: Variation of compositions for each membrane samples

Membrane	Concentration (percentage %)				
	Polymer	Solvent		Nonsolvent	
	Polysulfone	DCM	NMP	Ethanol	H_2O
1	15	42.5	42.5	100	0
2	15	42.5	42.5	0	100
3	15	42.5	42.5	70	30
4	15	42.5	42.5	50	50

3.2.1 Membrane preparation

The Polysulfone was dried for 24h prior to use in the oven to eliminate all the moisture. The casting solution was then prepared by dissolving 15% of the Polysulfone in 42.5% of dichloromethane (DCM) and 42.5% 1-methyl-2-pyrrolidone (NMP). The solution was stirred on the hot plate at 35^{o}C for 24h to prepare a clear solution. The solution was then degassing for 4h followed by casting onto a glass plate using a casting knife with a gap setting of 500mm at ambient temperature. The glass plate was then immersed in a coagulation bath for 2h to allow the phase separation process. The coagulation solution will be using different concentration of the non-solvent solution. The membrane was peeled out from the glass plate and then washed with tap water and allowed to dry in the open air for 16h.

3.3 METHOD TO STUDY THE CHARACTERISTICS OF THE MEMBRANE FORMED

After the fabrication process is done and membrane is fully developed, the characteristics of the membranes are tested by using the following equipment:

Table 3-4: Equipment used to study membrane characterization

Equipment	Purpose / Explanation
SEM	• Scanning Electron microscope. SEM uses electrons instead of light to form an image • To analyze the morphology of each membrane. Specimens of the membrane is taken to examine the morphology of the surface and cross sections • Samples should be dry because SEM utilizes vacuum conditions and uses electron to form an image
FTIR	• To measure the molecular interactions between the polymer blends of different composition. • A drop from each different dope solutions prepared was used for the testing • The procedure to examine is to put a drop of dope solutions on potassium bromide pellets and then these coated pellets were dried under vacuum
UTM	• Universal testing machine. This machine is used to determine the tensile properties of the membrane samples. • The same size of the membrane samples need to be prepared and tested to keep the consistency

3.4 GAS PERMEABILITY STUDY

The permeability evaluation of the membrane samples will be checked by using a membrane permeation system. The assembly unit consists up of permeation cell having stainless steel paired disk tightened together with nut bolts having lower one fixed in which the circular sample to be tested is placed.

To start with the experiment, the system should be fully evacuated from residual gases or dust which may had been settled earlier by using vacuum pump for at least half an hour. The permeation of the CO_2 and CH_4 gases at ambient conditions was calculated by bubble flow meter attached to the assembly at feed pressures of 2, 4, 6, 8 and 10 bar.

3.4.1 Gas Permeability Calculations

Permeability of gases was measured by considering the time taken to flow certain amount of gas volume in bubble soap flow meter. As an example, for a membrane, time taken to flow X ml of CH_4 was t seconds at p bar feed pressure. The effective area of membrane is A cm^2 and testing temperature is 25^oC. Hence the permeability of CH_4 gas can be determined as follows:

CH_4 volumetric flow rate = Q,

This volumetric flow rate, Q, is corrected to standard temperature and pressure

(STP), Q_{STP}, as follows:

$$\frac{V_{(STP)}}{V_{300K}} = \frac{273K}{300K}$$

$$Q = \frac{V}{t}$$

$$\frac{Q_{(STP)}}{Q_{300K}} = \frac{273K}{300K}$$

$$\begin{aligned} Q_{STP} &= \frac{273K}{300K} \times Q_{300} \\ &= \text{cm}^3\,(STP)/s \end{aligned}$$

CH_4 flux, J_{CH_4} ,is, therefore,

$$\begin{aligned} J_{CH4} &= \frac{Q_{STP}}{A} \\ &= cm^3 (STP)/cm^2.s \end{aligned}$$

Once CO_2 flux, J_{CH_4} , was determined, the CH_4 permeability be calculated using the following formula:

$$\begin{aligned} \frac{P}{} &= \frac{J_{CH_4}}{\Delta p} \times l \\ &= \frac{\dfrac{cm^3\,(STP)}{cm^2.s} \times cm}{1\,bar \times 76 \dfrac{cmHg}{bar}} \\ &= X \quad \frac{cm^3 (STP)}{cm^2.cmHg.s} \times cm \\ &= X\ Barrer \end{aligned}$$

The permeability of membrane is commonly expressed in unit of Barrer.

$$1\ \text{Barrer} = 10^{-10}\ \frac{cm^3 (STP) cm}{cm^2 \sec cmHg}$$

Particularly for asymmetric membranes, it is more convenient to use the terminology "permeance" rather than permeability. Permeance, (P/l), or also known as pressure normalized flux, is defined permeability, P_i, per effective thickness of asymmetric membranes, l. Permeance of membrane is expressed in unit of GPU.

$$1 \text{ GPU} = 10^{-6} \frac{cm^3(STP)}{cm^2 \sec cmHg}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 GAS PERMEATION TEST

4.1.1 Effect of non-solvent used on the gas selectivity

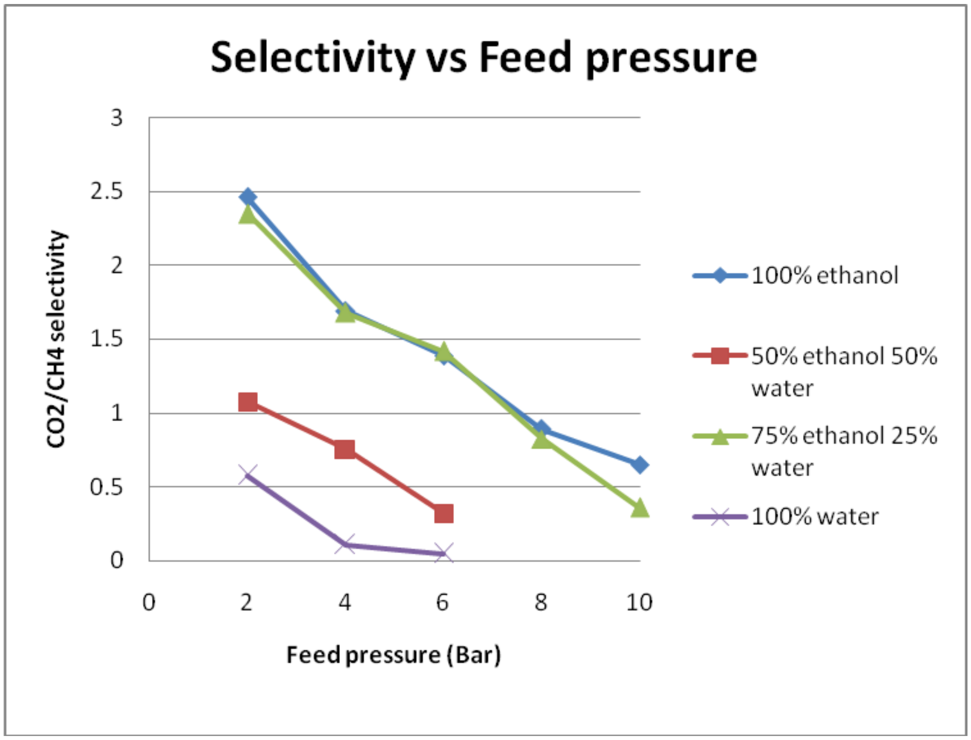

Figure 4-1: Selectivity of Carbon Dioxide over Methane

From the result, it shows that the ideal selectivity of Carbon Dioxide over Methane is given by membrane that used pure ethanol as the non-solvent and the lowest selectivity is observed for membrane that used pure water as non- solvent. This is due to higher porosity and macrovoid substructure in the membrane that is prepared from pure water. The higher macrovoid in the structure could enhance the CH_4 and CO_2 permeances.

The presence of pores on the membrane surface layer will create sufficient space for both gases to pass through the membrane surface and it can be concluded that there was no separation at all for membrane that used pure water as the non-solvent. Thus selectivity is less for membrane that used water as non solvent compared to membrane that used Ethanol.

The same condition also has been studied by Lai et. al in the development of Poly Methyl Methacrylate (PMMA) membrane. The morphology of the membrane can be control by adjusting non solvent content in casting solution which it can suppress the macrovoids in the polymeric membrane. D.Wang et. al has reported that the ideal selectivity for Carbon Dioxide over Nitrogen for silicon coated asymmetric membrane has been achieved after using the combination of 50% propanol and 50% of water as a non-solvent used in the coagulation bath.

From result in figure 4.1 it is also showed that high selectivity is also being achieved by using the combination of 75% ethanol and 25% water as the non solvent. According to D.Wang et. al water is a strong non-solvent for PSF membrane while ethanol vice versa. A strong non solvent may increase internal coagulation rate and internal diffusion rate between the non solvent and solvent used for the membrane fabrication thus induced a large macrovoid in the surface of the membrane formed. However a good combination between the solvent and non-solvent used can greatly reduced the big macrovoid formation in the membrane surface thus will increase the separation property. For PSF membrane the used Ethanol and water as a non-solvent and DCM as a solvent, 75% Ethanol and 25% water is the best combination of non solvent to produce a good gas separation membrane.

From the results, Even though pure Ethanol is the best non solvent used to give the ideal selectivity for gas separation membrane, the usage of pure Ethanol as a non solvent in PSF production for commercial purpose is unrealistic as it has a high price. From the experimental results, by addition 25% of water in the pure ethanol solution, almost ideal selectivity can also be achieved. Water is widely known as cheap and easily obtained material. Therefore, the addition of water into Ethanol as Non solvent will reduce the consumption of Ethanol as well as reduce the cost of fabrication.

4.1.2 Effect of feed pressure to the CH_4 permeability

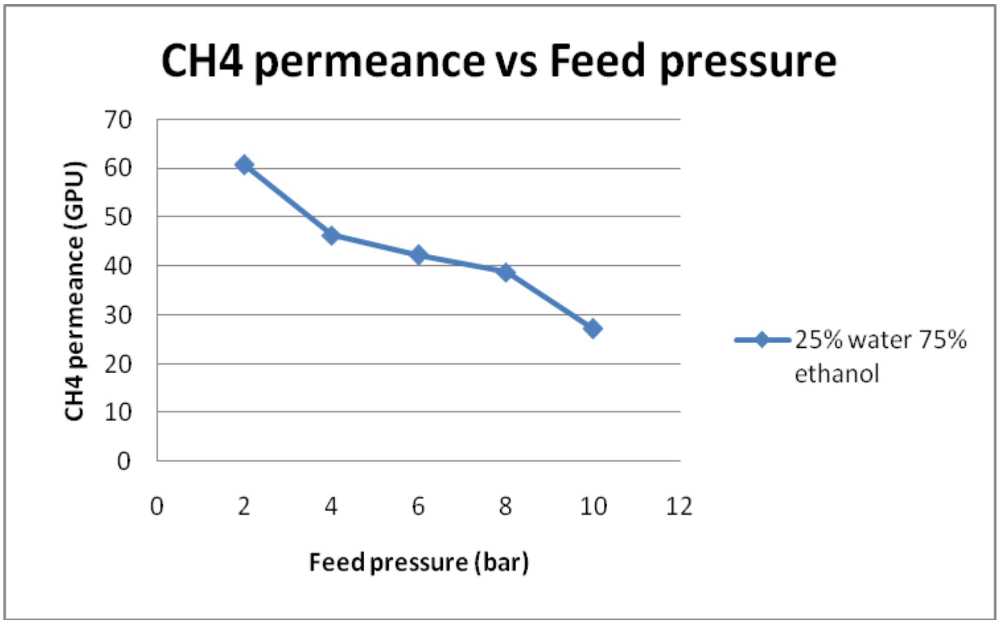

Figure 4-2: Permeability of Methane for membrane used 25% water and 75% ethanol as non solvent

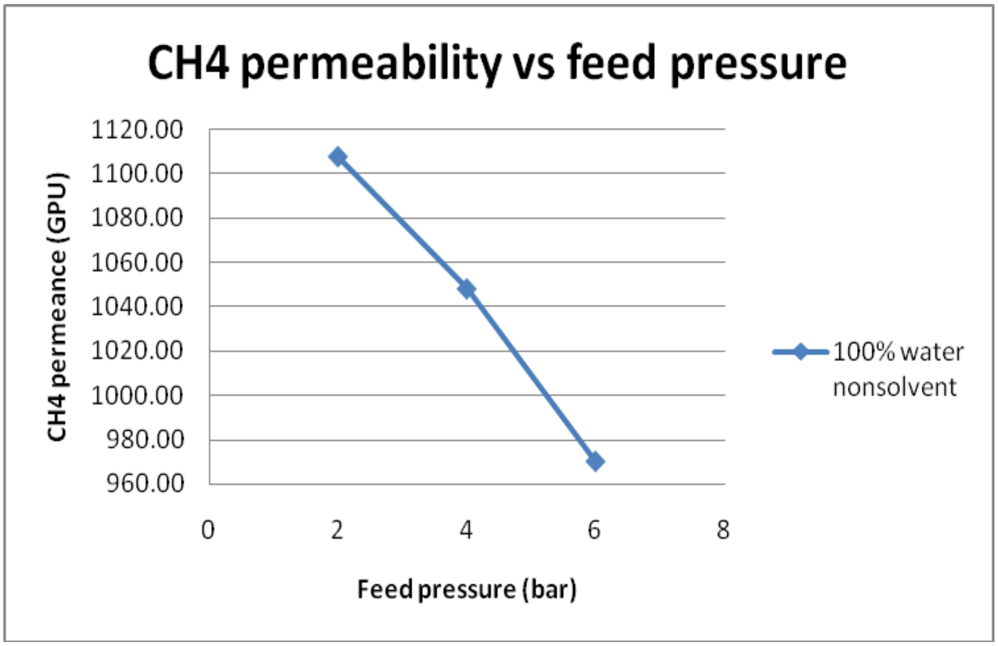

Figure 4-3: Permeability of Methane for membrane use 100% water as non solvent

Figure 4.2 and figure 4.3 has shown the experimental results for permeability of Methane on 2 different membranes. From the observation, the gas permeability is keep decreasing by increasing of the feed pressure. This is typical behavior of CH_4 transport mechanism through dense membrane due to solution diffusion mechanism as reported by previous researchers [Lin and Chung, (2001)]. The decreasing permeability of Methane for both membranes may also due to compaction of PSF-H_2O and PSF-Ethanol-H_2O membrane as CO_2 pressure increase.

From the graph it is also showed that the permeance of CH_4 gas is higher in PSF-H_2O membrane compared to PSF-Ethanol-H_2O membrane. This is because PSF-H_2O has more porous substructure with the presence of macrovoid as compared to PSF-Ethanol-H_2O membrane. High porosity substructure of PSF-H_2O membrane makes the membrane becomes less restricted, thus allowing the gas to diffuse more easily across the structure of the membrane.

The permeability results for PSF-H_2O membrane were only obtained until feed pressure reached 6 bar. The membrane starts to break after the pressure was increased to 8 bar. This situation may occur due to porous substructure of the membrane thus reduce the rigidity of the particular membrane.

4.2 SEM IMAGES

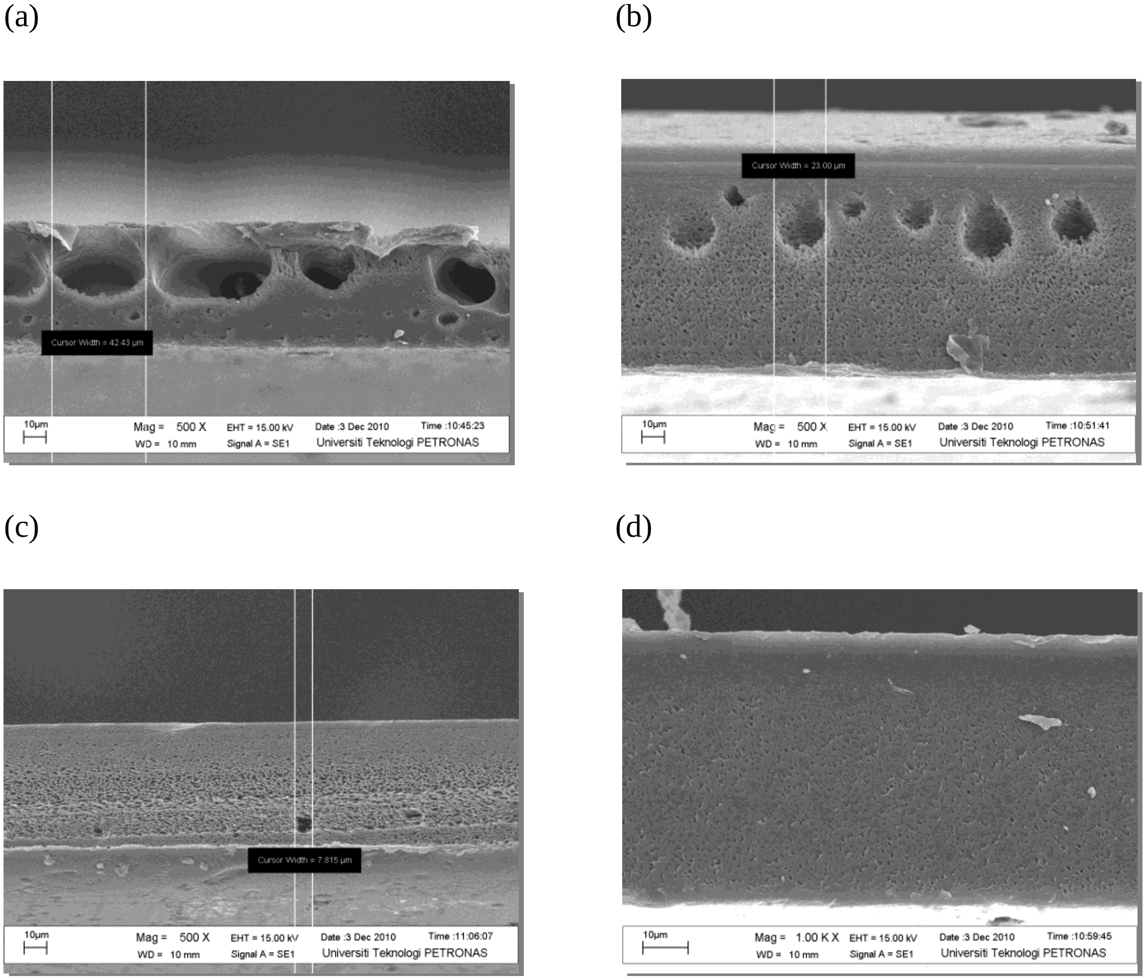

Figure 4-4: SEM images of the cross sections of the membranes. (a) PSF-nonsolvent 100% water; (b) PSF-nonsolvent 50%water+50%ethanol; (c) PSF-nonsolvent 25% water + 75% Ethanol; (d) PSF-nonsolvent 100% Ethanol

SEM pictures were taken to study the structure of the membrane. Different morphologies of PSF membranes were observed due to the variation of demixing rate of the polymer-solvent solution. The larger macrovoid formation was observed in figure 4.4 (a) for PSF membrane that used 100% water as non-solvent. As water is the stronger non solvent, it may increase the internal coagulation rate and internal diffusion rate between the solvent thus will increase the formation of the macrovoids. The same behavior was also reported by D. Wang et. al.

Picture 4.4 (b) has shown the cross sectional surface of PSF membrane that used 50% water + 50% Ethanol as non solvent. The number of macrovoid formation was reduced compared to (a). The combination of water which is a strong non solvent and Ethanol which is the weaker non solvent may slower the coagulation rate thus will reduce the macrovoid formation.

Picture 4.4 (c) showed PSF membrane that used 25% water and 75% Ethanol as the non solvent. The number of macrovoid formation is reducing as the percentage of Ethanol is higher.

While picture 4.4 (d) showed PSF membrane that used 100% Ethanol as the non solvent. The macrovoid structure is very small and it is hard to distinguish even though with using higher magnification compared to the others. The coagulation rate is reduced with the use of ethanol as Ethanol is a weaker non solvent compared with water.

The usage of Ethanol as non-solvent is favored as it may reduce the size of the macrovoid thus can increase the performance of the membrane.

4.3 FTIR SPECTROSCOPY TEST PROPERTIES

FTIR spectroscopy of PSF membranes was employed to identify the composition of PSF in the molecular level. Appendix B shows the FTIR spectroscopy results of PSF-NMP-DCM with various non-solvent compositions. Sulfone groups (SO_2) of PSF shows the stretching vibration at 1105, 1300 cm^{-1}. While the CH_3 group from Dichloromethane (DCM) which is the solvent appears at 1376cm^{-1}. This results shows that DCM and NMP are compatible with PSF polymer at molecular level.

4.4 TENSILE PROPERTIES

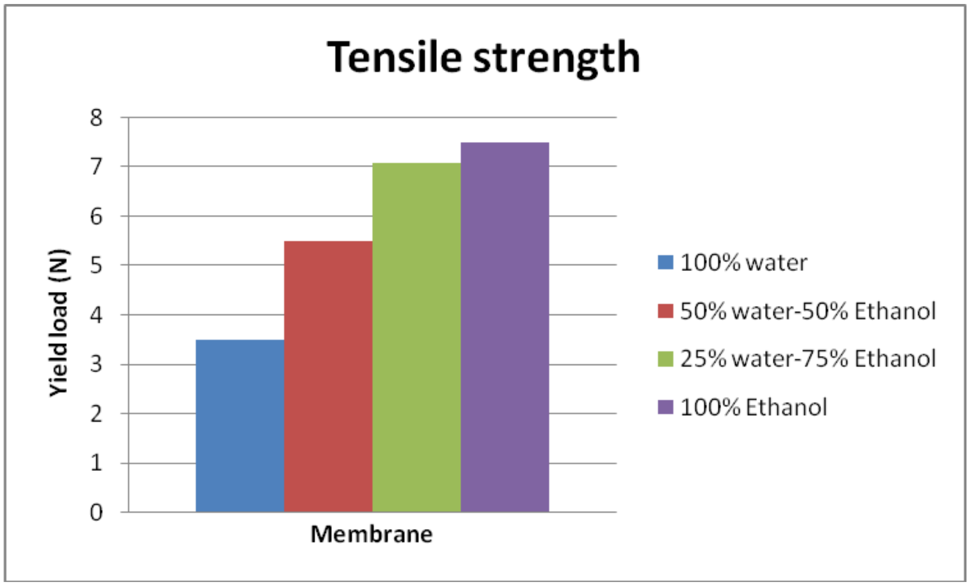

Figure 4-5: Comparison of yield load for each membrane before necking

Figure 4.4 it shows the comparison results for tensile test for each membrane which used different non-solvent in phase inversion technique. The detail tensile test results for each membranes is per attached in the appendix C. Membrane which used 100% ethanol as the non-solvent exhibit the higher load at yield. The load at yield is the maximum stress that a material can withstand before necking, which is when the specimen's cross section starts to significantly contract. PSF membrane that used 100% Ethanol as non-solvent is much more flexible compared to other composition thus it is more resists to deformation and tougher. However PSF membrane that used 25% Water and 75% Ethanol as non solvent also exhibit the same behavior. PSF membrane with this non solvent composition has 7.1N as its Yield load and it’s comparable with PSF membrane that used 100% Ethanol as the non-solvent. For membrane that used 100% water as the non solvent, that type of membrane experienced necking after the load has reached 3.5N. This membrane has the lowest load at yield as it has lots of porous structure thus make it easily deform. Therefore, from the tensile stress results, it shows membrane that used 100% ethanol has the highest tensile strength following by membrane that used 75% ethanol and 25% water.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The effect of various non-solvent used in PSF membrane fabrication on morphology and separation characteristic have been investigated. Membranes were prepared based on wet phase inversion method.

PSF membrane prepared from 25% water and 75% Ethanol showed the best performance in gas separation behavior. Increasing the water content in the non-solvent solution would change the membrane morphology. Higher water concentration produced macrovoid and highly porous substructure. This might occur due to larger solubility parameter difference between solvent mixtures and Ethanol while more water amount was added in the Ethanol bath leading to fast exchange rate between solvent of casting solution with coagulant. Consequently, faster demixing mechanism took place when water was present in the Etanol bath. Thus, the macrovoid formation in the membrane substructure will increase.

Membrane with larger macrovoid formation has lower separation performance. Macrovoid will increase the permeability of all the gasses that passed through the membrane thus will reduce the selectivity of the membrane.

Even though some of the membrane prepared in this study, has showed unexpectedly very low selectivity, it is still showing the higher CO_2 permeance as compared to other PSF membrane that have been reported by previous researches.

The permeability and selectivity results revealed that PSF membrane that used 100% Ethanol as non solvent show promising performance. The addition of 25% water in the Ethanol solution is still acceptable and gives the comparable performance to the membrane that used pure Ethanol as the non solvent.

5.1 RECOMMENDATION

Based on this work, some recommendations for future works have been suggested to improve gas separation behavior the PSF membrane.

The gas separation behavior of the membrane should be observed by using the mixture of gases in order to simulate the real situation in natural gas separation process instead of by passing through the membrane only one type of gas per time. In this study only one type of gas can be passing through the membrane due to the restriction of the equipment used.

The PSF polymer materials can be blended together with other type of polymer so that the morphology, characteristics and gas separation behavior of the membrane can be improved.

The addition of other in-organic material such as zeolite, silica and carbon molecular sieve (CMS) during preparation of PSF membrane also be done in order to enhance the membrane performance in separating natural gases.

CHAPTER 6

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APPENDIX A

Gas permeation test results

Membrane 1- Non solvent used (100% ethanol)

Run	P(bar)	t co2 (s)	t ch4 (s)	A (cm2)	V (cm3)	QCO2	QCH4	(P/l) CO2	(P/l) CH4	(P/l) CO2 (GPU)	(P/l) CH4 (GPU)	Selectivity (CO2/
1	2	8.45	20.45	13.5	1	0.107692	0.044499	5.24816E-05	2.16856E-05	52.4816	21.6856	2.42
2	2	8.49	20.42	13.5	1	0.107185	0.044564	5.22344E-05	2.17174E-05	52.2344	21.7174	2.41
3	2	8.46	21.7	13.5	1	0.107565	0.041935	5.24196E-05	2.04364E-05	52.4196	20.4364	2.57
Average		**8.47**	**20.85667**	**13.5**	**1**	**0.107481**	**0.043666**	**5.23785E-05**	**2.12798E-05**	**52.37853333**	**21.2798**	**2.46**
1	4	4.32	7.61	13.5	1	0.210648	0.11958	5.13275E-05	2.91373E-05	51.3275	29.1373	1.76
2	4	4.44	6.99	13.5	1	0.204955	0.130186	4.99403E-05	3.17217E-05	49.9403	31.7217	1.57
3	4	4.3	7.48	13.5	1	0.211628	0.121658	5.15663E-05	2.96437E-05	51.5663	29.6437	1.74
Average		**4.3533333**	**7.36**	**13.5**	**1**	**0.209077**	**0.123808**	**5.09447E-05**	**3.01676E-05**	**50.9447**	**30.16756667**	**1.69**
1	6	1.49	2.09	13.5	1	0.610738	0.435407	9.92102E-05	7.07288E-05	99.2102	70.7288	1.40
2	6	1.48	1.92	13.5	1	0.614865	0.473958	9.98806E-05	7.69913E-05	99.8806	76.9913	1.30
3	6	1.46	2.15	13.5	1	0.623288	0.423256	1.01249E-04	6.87550E-05	101.249	68.755	1.47
Average		**1.4766667**	**2.053333**	**13.5**	**1**	**0.616297**	**0.444207**	**0.000100113**	**7.21584E-05**	**100.11**	**72.16**	**1.39**
1	8	0.85	0.78	13.5	1	1.070588	1.166667	1.30432E-04	1.42138E-04	130.432	141.2138	0.92
2	8	0.89	0.73	13.5	1	1.022472	1.246575	1.24570E-04	1.51873E-04	124.57	151.873	0.82
3	8	0.81	0.75	13.5	1	1.123457	1.213333	1.36873E-04	1.47823E-04	136.873	147.823	0.93
Average		**0.85**	**0.753333**	**13.5**	**1**	**1.072172**	**1.208858**	**0.000130625**	**0.000147278**	**130.63**	**146.9699333**	**0.89**
1	10	15.64	10.04	13.5	50	2.909207	4.531873	2.83548E-04	4.4170297E-04	283.548	441.70297	0.64
2	10	15.72	10.23	13.5	50	2.894402	4.447703	2.82105E-04	4.33499E-04	282.105	433.499	0.65
Average		**15.68**	**10.135**	**13.5**	**50**	**2.901805**	**4.489788**	**0.000282827**	**0.000437601**	**282.8265**	**437.600985**	**0.65**

Membrane 2- Non Solvent used (25% Water + 75% Ethanol)

Run	P(bar)	t co2 (s)	t ch4 (s)	A (cm2)	V (cm3)	QCO2	QCH4	(P/l) CO2	(P/l) CH4	(P/l) CO2 (GPU)	(P/l) CH4 (GPU)	Selectivity (CO2/
1	2	3.18	7.27	13.5	1	0.286164	0.125172	1.39456E-04	6.10000E-05	139.45	61	2.29
2	2	3.05	7.34	13.5	1	0.298361	0.123978	1.45400E-04	6.04182E-05	145.4	60.4182	2.41
3	2	3.09	7.33	13.5	1	0.294498	0.124147	1.43518E-04	6.05007E-05	143.518	60.5007	2.37
Average		**3.11**	**7.313333**	**13.5**	**1**	**0.293008**	**0.124432**	**0.000142791**	**6.06396E-05**	**142.79**	**60.640**	**2.35**
1	4	2.89	5.02	13.5	1	0.314879	0.181275	7.67249E-05	4.41703E-05	76.7249	44.1703	1.74
2	4	2.86	4.55	13.5	1	0.318182	0.2	7.75297E-05	4.87329E-05	77.5297	48.7329	1.59
3	4	2.82	4.82	13.5	1	0.322695	0.188797	7.86294E-05	4.60031E-05	78.6294	46.0031	1.71
Average		**2.856667**	**4.80**	**13.5**	**1**	**0.318585**	**0.190024**	**7.7628E-05**	**4.63021E-05**	**77.628**	**46.3021**	**1.68**
1	6	2.46	3.23	13.5	1	0.369919	0.281734	6.00908E-05	4.57657E-05	60.0908	45.7657	1.31
2	6	2.45	3.78	13.5	1	0.371429	0.240741	6.03360E-05	3.91067E-05	60.336	39.1067	1.54
3	6	2.46	3.51	13.5	1	0.369919	0.259259	6.00908E-05	4.21149E-05	60.0908	42.1149	1.43
Average		**2.456667**	**3.506667**	**13.5**	**1**	**0.370422**	**0.260578**	**6.01725E-05**	**4.23291E-05**	**60.17**	**42.33**	**1.42**
1	8	3.41	2.98	13.5	1	0.266862	0.305369	3.25124E-05	3.72038E-05	32.5124	37.2038	0.87
2	8	3.53	2.87	13.5	1	0.25779	0.317073	3.14072E-05	3.86298E-05	31.4072	38.6298	0.81
3	8	3.46	2.73	13.5	1	0.263006	0.333333	3.20426E-05	4.06108E-05	32.0426	40.6108	0.79
Average		**3.466667**	**2.86**	**13.5**	**1**	**0.262553**	**0.318592**	**3.19874E-05**	**3.88148E-05**	**31.99**	**38.815**	**0.82**
1	10	453.84	157.28	13.5	50	0.100256	0.289293	9.77150E-06	2.8196197E-05	9.7715	28.196197	0.35
2	10	457.18	164.81	13.5	50	0.099523	0.276075	9.70011E-06	2.69079E-05	9.70011	26.9079	0.36
3	10	452.16	168.72	13.5	50	0.100628	0.269678	9.80781E-06	2.62844E-05	9.80781	26.2844	0.37
Average		**454.3933**	**163.6033**	**13.5**	**50**	**0.100136**	**0.278349**	**9.75981E-06**	**2.71295E-05**	**9.76**	**27.13**	**0.36**

Membrane 3 – Non Solvent used (100% water)

Run	P(bar)	t co2 (s)	t ch4 (s)	A (cm2)	V (cm3)	QCO2	QCH4	(P/l) CO2	(P/l) CH4	(P/l) CO2 (GPU)	(P/l) CH4 (GPU)	Selectivity (CO2,
1	2	6.89	4.08	13.5	10	1.320755	2.230392	6.43643E-04	1.08694E-03	643.643	1086.94	0.59216
2	2	6.95	3.97	13.5	10	1.309353	2.292191	6.38086E-04	1.11705E-03	638.086	1117.05	0.57122
3	2	7.02	3.96	13.5	10	1.296296	2.29798	6.31723E-04	1.11987E-03	631.723	1119.87	0.56410
Average		**6.95**	**4.003333**	**13.5**	**10**	**1.308801**	**2.273521**	**0.000637817**	**0.001107954**	**637.817**	**1107.953333**	**0.575672**
1	4	97.68	11.34	13.5	50	0.465807	4.012346	1.13501E-04	9.77667E-04	113.501	977.667	0.1161
2	4	97.36	10.15	13.5	50	0.467338	4.482759	1.13874E-04	1.09229E-03	113.874	1092.29	0.1043
3	4	97.72	10.32	13.5	50	0.465616	4.408915	1.13454E-04	1.07430E-03	113.454	1074.3	0.1056
Average		**97.58667**	**10.60333**	**13.5**	**50**	**0.466253**	**4.30134**	**0.00011361**	**0.001048085**	**113.6097**	**1048.085667**	**0.10840**
1	6	164.89	7.62	13.5	50	0.275942	5.971129	4.48248E-05	9.69969E-04	44.8248	969.969	0.0462
2	6	171.33	7.53	13.5	50	0.265569	6.042497	4.31399E-05	9.81562E-04	43.1399	981.562	0.0440
3	6	169.15	7.71	13.5	50	0.268992	5.901427	4.36959E-05	9.58646E-04	43.6959	958.646	0.0456
Average		**168.4567**	**7.62**	**13.5**	**50**	**0.270168**	**5.971684**	**4.38869E-05**	**0.000970059**	**43.89**	**970.06**	**0.0452**

Membrane 4 – Non Solvent used (50% water + 50% ethanol)

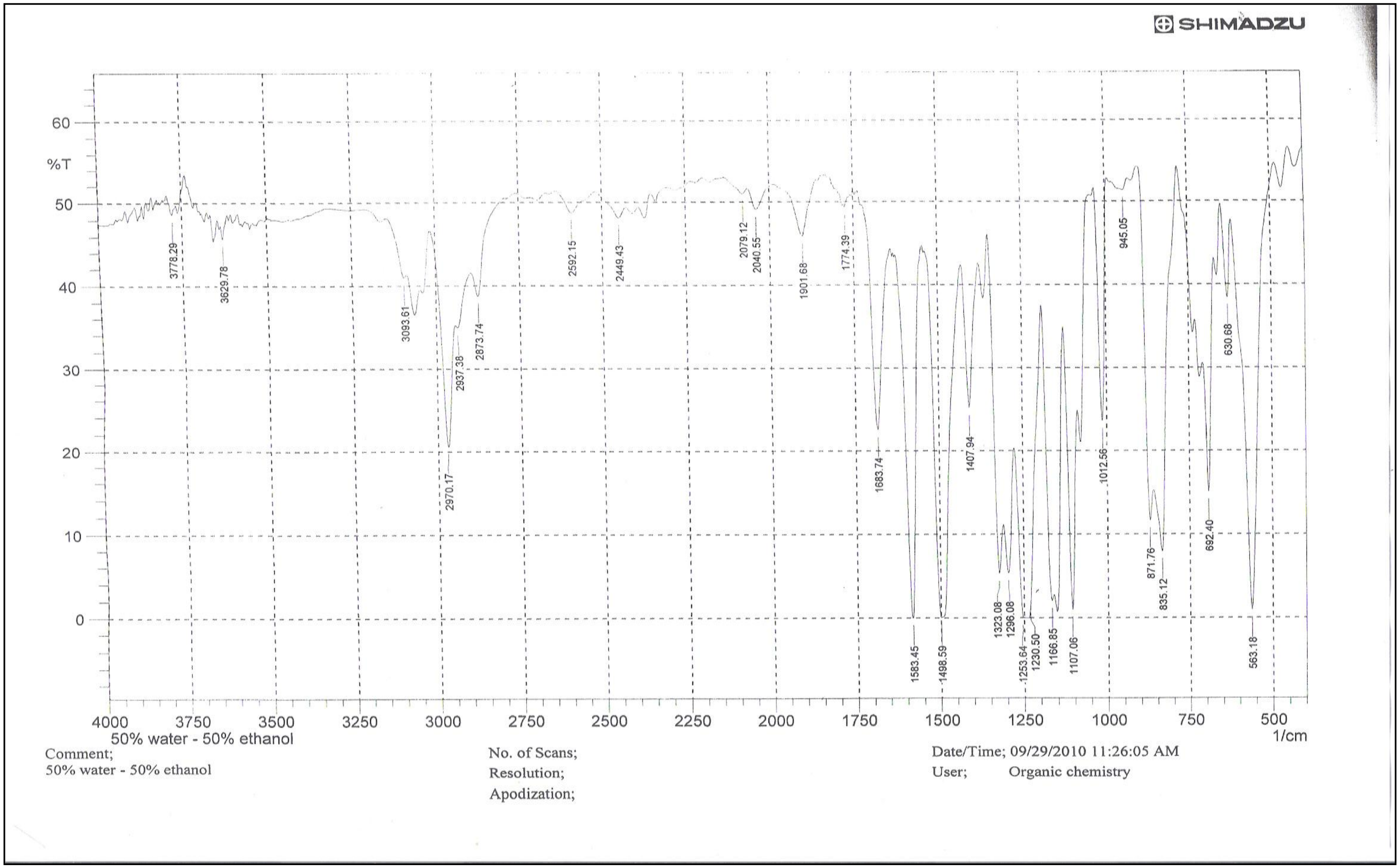
Run	P(bar)	t co2 (s)	t ch4 (s)	A (cm2)	V (cm3)	QCO2	QCH4	(P/l) CO2	(P/l) CH4	(P/l) CO2 (GPU)	(P/l) CH4 (GPU)	Selectivity (CO2,
1	2	5.81	6.89	13.5	1	0.156627	0.132075	7.63287E-05	6.43643E-05	76.3287	64.3643	1.18589
2	2	5.79	6.09	13.5	1	0.157168	0.149425	7.65924E-05	7.28193E-05	76.5924	72.8193	1.05181
3	2	5.83	5.88	13.5	1	0.156089	0.154762	7.60669E-05	7.54200E-05	76.0669	75.42	1.00858
Average		**5.81**	**6.286667**	**13.5**	**1**	**0.156628**	**0.145421**	**7.63293E-05**	**7.08679E-05**	**76.329**	**70.868**	**1.077065**
1	4	3.57	3.0	13.5	1	0.254902	0.308475	6.21106E-05	7.51644E-05	62.1106	75.1644	0.8263
2	4	3.59	2.68	13.5	1	0.253482	0.339552	6.17646E-05	8.27369E-05	61.7646	82.7369	0.7465
3	4	3.61	2.51	13.5	1	0.252078	0.36255	6.14224E-05	8.83406E-05	61.4224	88.3406	0.6953
Average		**3.59**	**2.713333**	**13.5**	**1**	**0.253487**	**0.336859**	**6.17659E-05**	**8.20806E-05**	**61.766**	**82.08063333**	**0.75250**
1	6	5.02	1.57	13.5	1	0.181275	0.579618	2.94469E-05	9.41549E-05	24.4469	94.1549	0.2596
2	6	5.07	1.86	13.5	1	0.179487	0.489247	2.91565E-05	7.94749E-05	29.1565	79.4749	0.3669
3	6	5.05	1.71	13.5	1	0.180198	0.532164	2.92719E-05	8.64464E-05	29.2719	86.4464	0.3386
Average		**5.046667**	**1.713333**	**13.5**	**1**	**0.18032**	**0.533676**	**2.92918E-05**	**8.66921E-05**	**27.625**	**86.69**	**0.3187**

APENDIX B

FTIR SPECTROSCOPY

TEST RESULTS

1. Membrane 1 – nonsolvent (50% water + 50% ethanol)

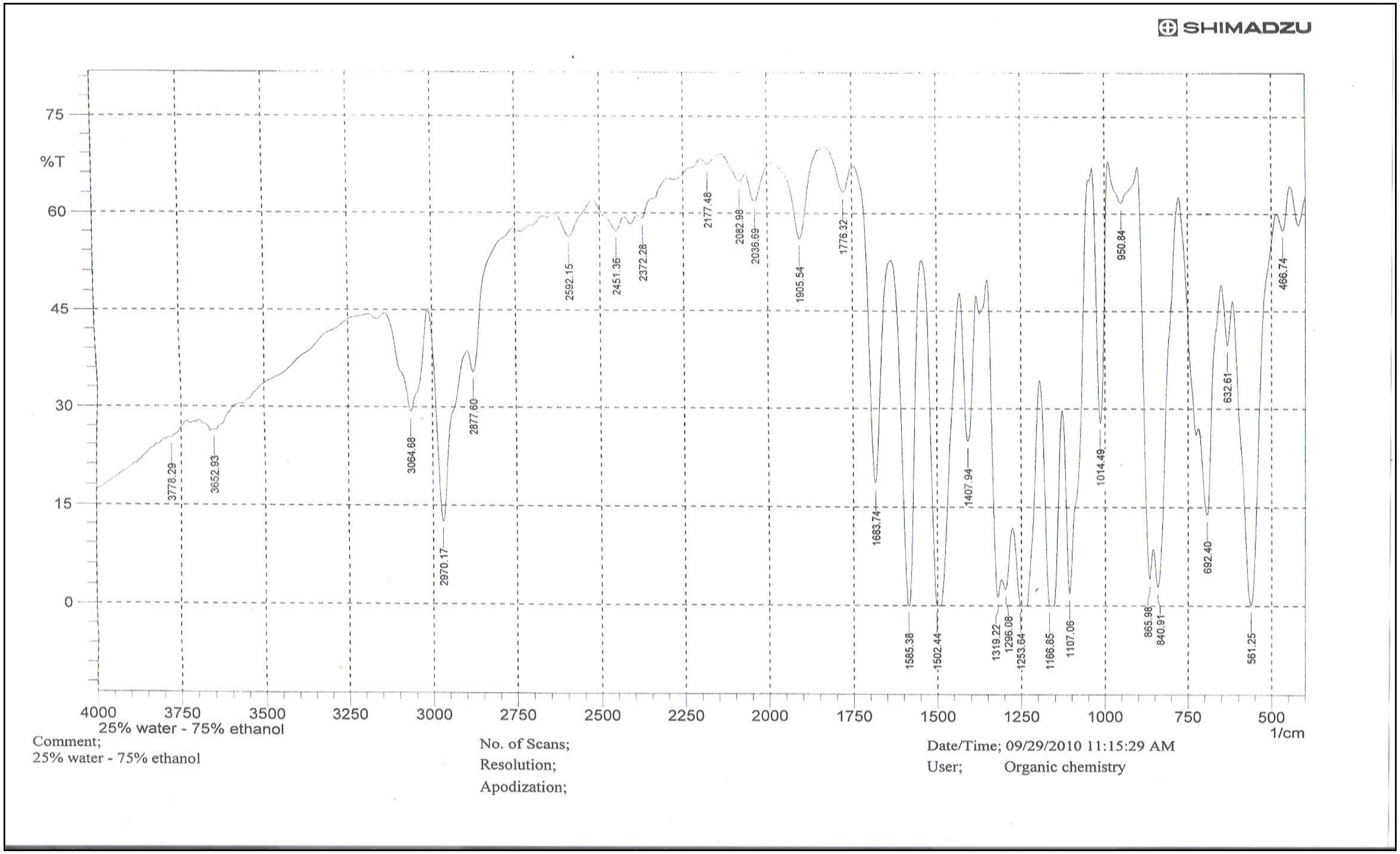


Comment;
50% water - 50% ethanol

No. of Scans;
Resolution;
Apodization;

Date/Time; 09/29/2010 11:26:05 AM
User; Organic chemistry

2. Membrane 2 – Non solvent used (25% Ethanol + 75% Water)



Comment;
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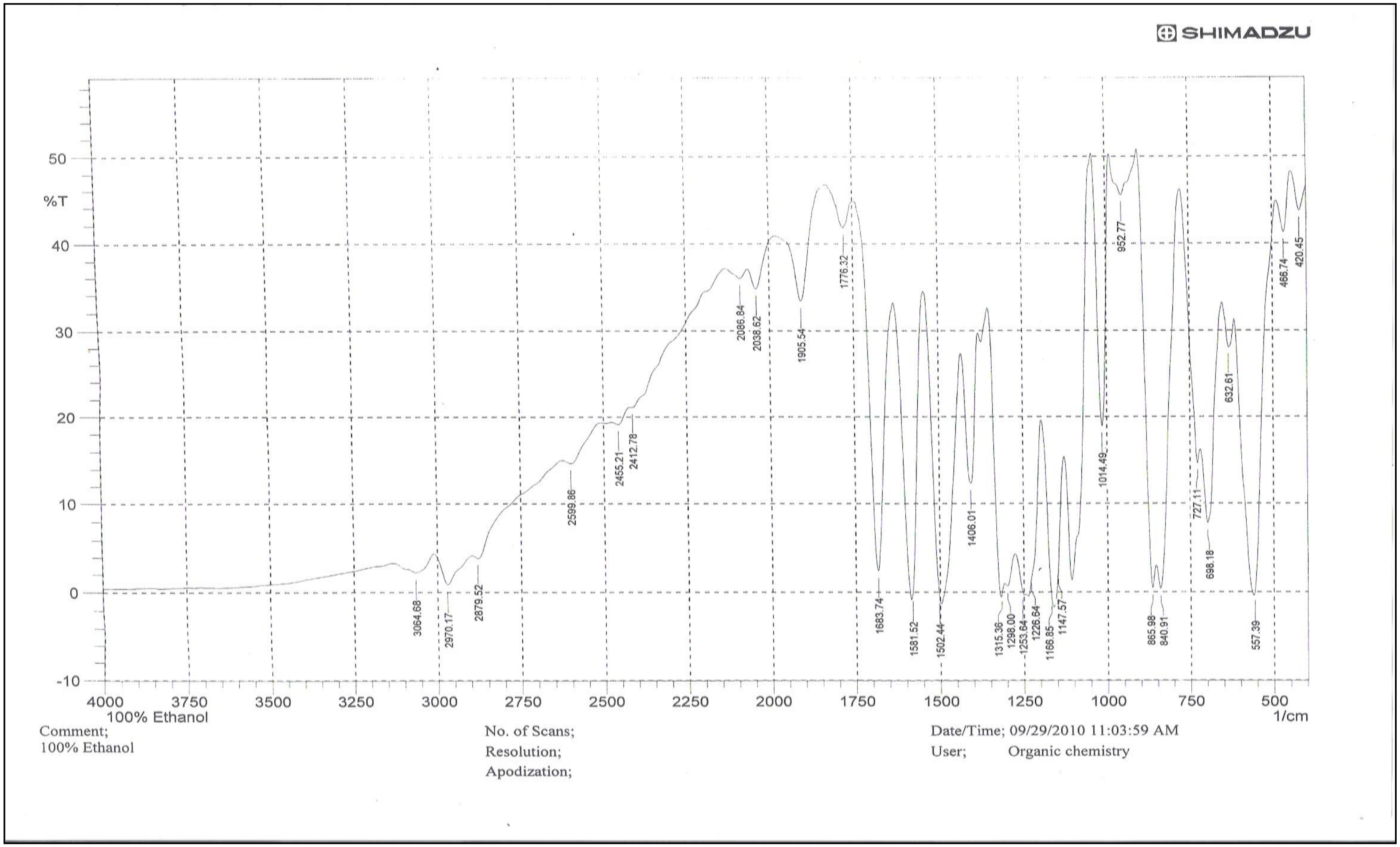
Date/Time; 09/29/2010 11:15:29 AM
User; Organic chemistry

3. Membrane 3 – Non solvent used (100% Ethanol)



Comment;
100% Ethanol

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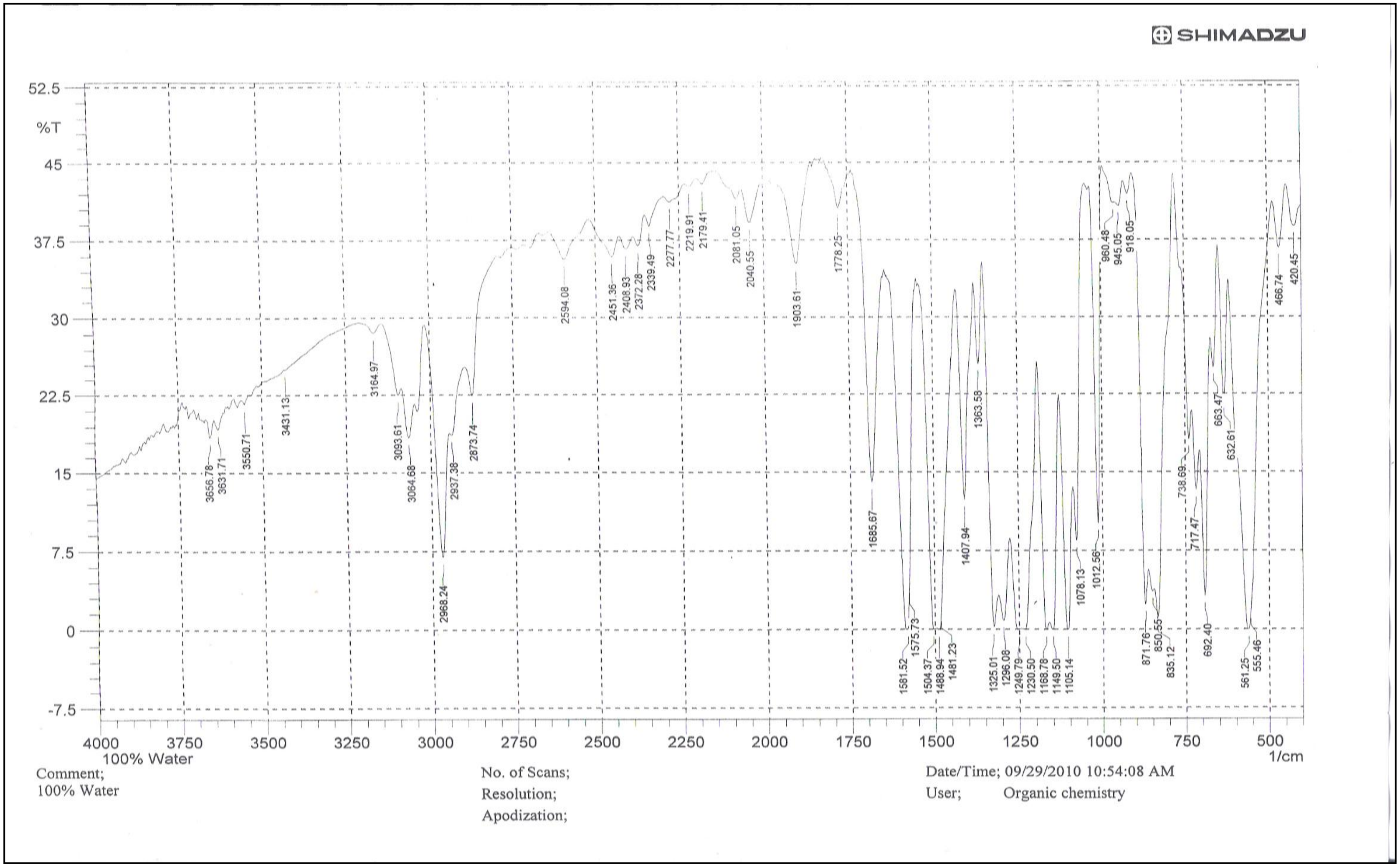
Apodization;

Date/Time; 09/29/2010 11:03:59 AM
User; Organic chemistry

4. Membrane 4 – Non solvent used (100% water)



Comment;
100% Water

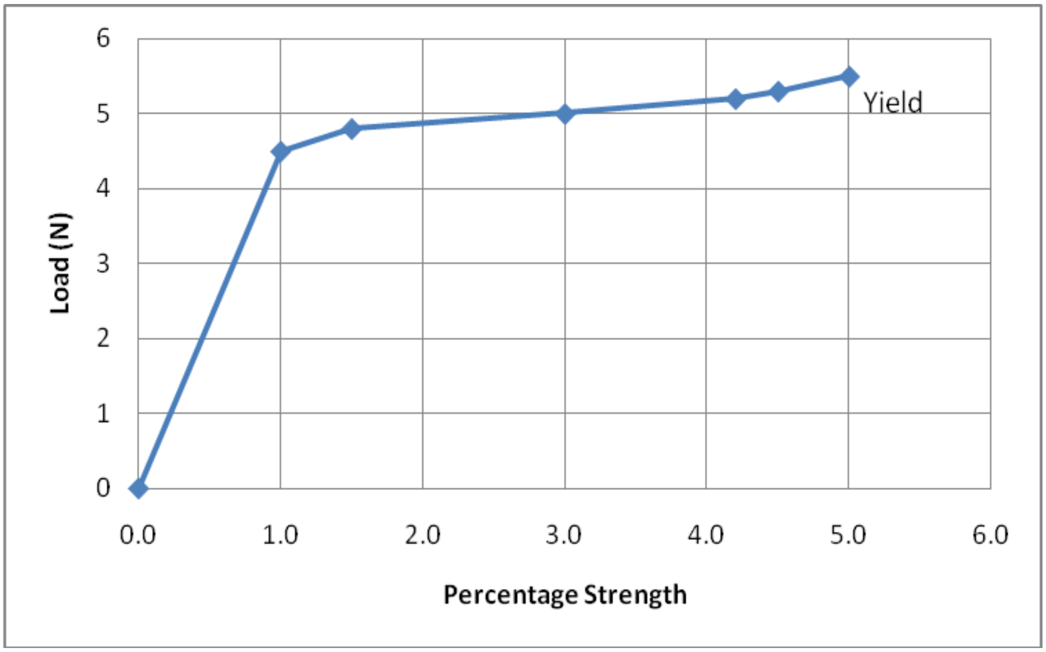
No. of Scans;
Resolution;
Apodization;

Date/Time; 09/29/2010 10:54:08 AM
User; Organic chemistry

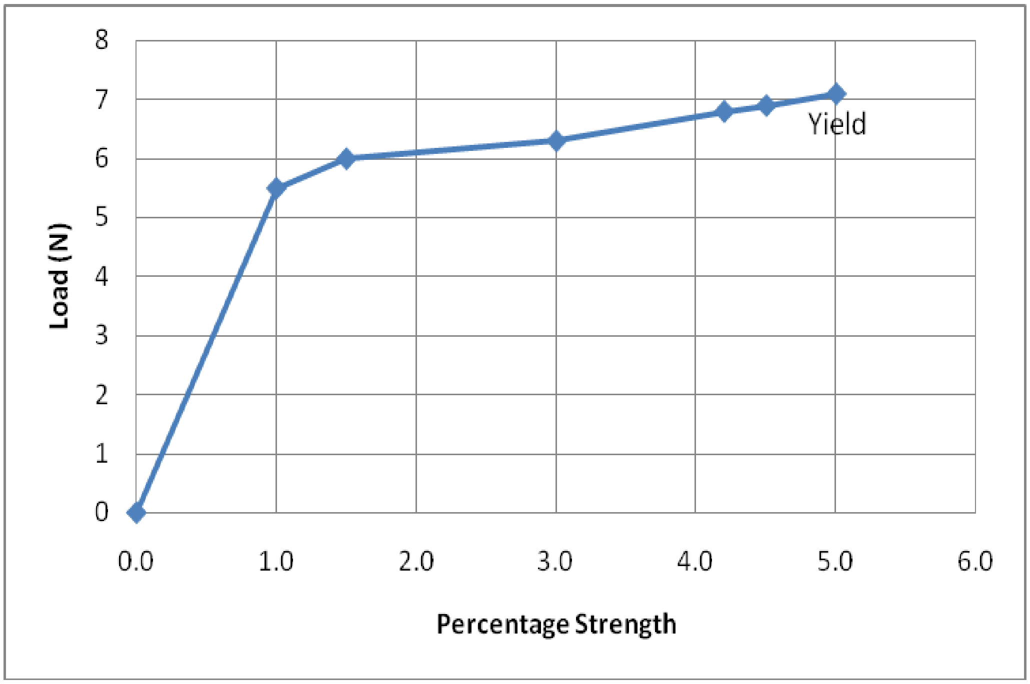
APENDIX C

TENSILE
TEST RESULTS

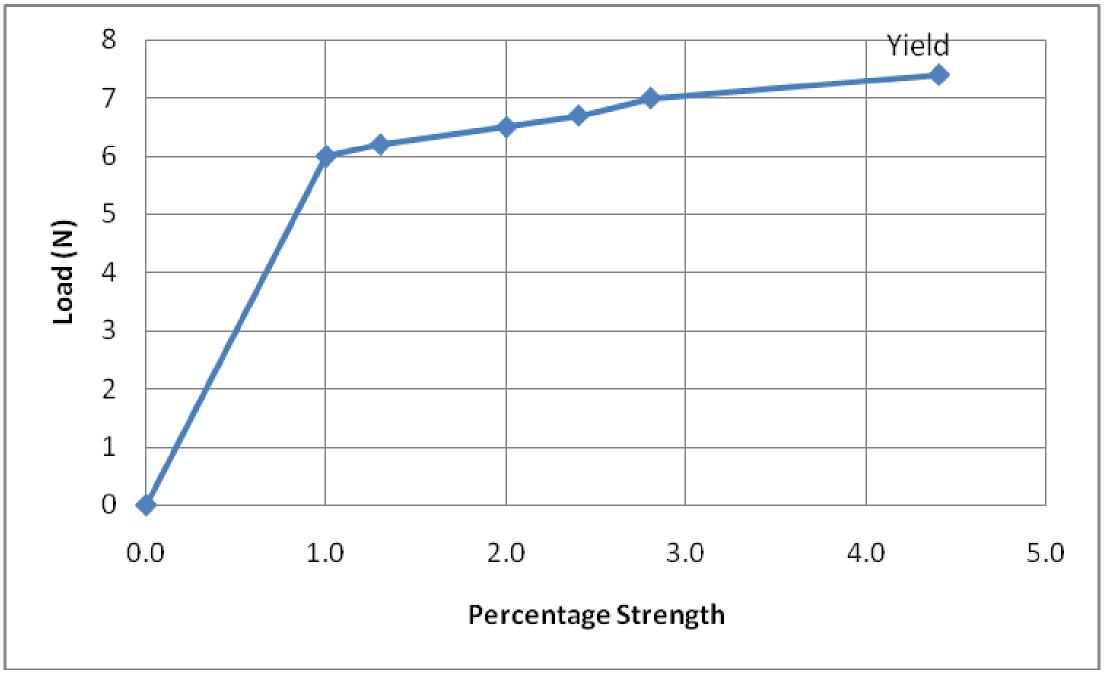
1. Membrane 1 – nonsolvent (50% water + 50% ethanol)



2. Membrane 2 – Non solvent used (25% Ethanol + 75% Water)



3. Membrane 3 – Non solvent used (100% Ethanol)



4. Membrane 4 – Non solvent used (100% water)