

**EFFECT OF TYPE OF SOLVENTS ON ASYMMETRIC POLYETHERSULFONE  
MEMBRANE FOR CO<sub>2</sub>/CH<sub>4</sub> SEPARATION**

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POLYETHERSULFONE MEMBRANE FOR CO<sub>2</sub>/CH<sub>4</sub>  
SEPARATION.**

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**EFFECT OF TYPE OF SOLVENTS ON ASYMMETRIC POLYETHERSULFONE  
(PES) MEMBRANE FOR CO<sub>2</sub>/CH<sub>4</sub> SEPARATION.**

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**A thesis submitted in fulfillment  
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**DECEMBER 2010**

I declare that this thesis entitled “Effect of Type of Solvents on Polyethersulfone (PES) Asymmetric Flat Sheet Membrane for CO<sub>2</sub>/CH<sub>4</sub> Separation” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

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Dedicated to my beloved parents

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## ABSTRACT

This study investigates the influences of solvent on the structure and performances of polyethersulfone asymmetric flat sheet membrane for gas separation. The asymmetric flat sheet membrane were prepared by dry/wet phase inversion process consisting polyethersulfone (PES) as polymer, distillate water as a non-solvent and different solvent type was also added either dimethylformamide(DMF), dimethylacetamide (DMAc) or N-methyl-2-pyrrolidone (NMP). The dope formulated contains 20wt% polymer, 75wt% solvent and 5wt% non-solvent. Asymmetric flat sheet membranes were cast using a conventional casting technique. Methanol were used as the coagulation medium. The membranes are coated with 3wt% of polydimethylsiloxane (PDMS) mixed with 97wt% of n-hexane. The morphological structures of produced membranes were examined using Scanning Electron Microscope (SEM). The SEM images exhibited the best morphological structure was discovered from the membrane produced by using NMP as solvent followed by DMAc and lastly DMF. The Fourier Transform Infrared Spectroscopy (FTIR) analysis also conducted in order to detect the existence of the functional groups in the membrane. The performance of the membrane was examined by conducting the gas permeation test. Pure carbon dioxide ( $\text{CO}_2$ ) and pure methane ( $\text{CH}_4$ ) were used as the test gases by using feed pressure range from 1 to 3 bar. As predicted by the morphological structure, NMP solvent-membrane showed the best performance compared to DMAc solvent-membrane and DMF solvent-membrane. The selectivity of  $\text{CO}_2/\text{CH}_4$  was 1.1358 (at 1 bar), 1.9946 (at 2 bar) and 2.6906 (at 3 bar) for NMP solvent-membrane, 1.0564 (at 1 bar), 1.8974 (at 2 bar) and 1.8958 (at 3 bar) for DMAc solvent-membrane and 0.9141 (at 1 bar), 1.7759 (at 2 bar) and 1.5257 (at 3 bar) for DMF solvent-membrane. Hence, solvent was discovered to affect the morphological structure which will consequently affect the performance of the polyethersulfone asymmetric flat sheet membrane. So, from the study conducted on solvent type, the most suitable solvent to produced high performance polyethersulfone asymmetric flat sheet membrane is NMP.



## ABSTRAK

Kajian ini mengkaji pengaruh pelarut terhadap struktur dan prestasi membrane asimetrik lembar polietersulfon datar untuk pemisahan gas. Membran asimetrik lembar datar disediakan melalui teknik kering / basah inversi fasa proses yang mengandungi polietersulfon (PES) sebagai polimer, air suling sebagai jenis non-pelarut dan pelarut berbeza juga ditambah samada dimetilformamida (DMF), dimetil asetamida (DMAc) atau N-metil-2-pirolidon (NMP). Dop formula tersebut mengandungi polimer 20wt%, 75wt% pelarut dan 5wt non-pelarut. Membran asimetris lembaran datar yang dijadikan menggunakan teknik casting konvensional. Methanol digunakan sebagai medium koagulasi. Membran tersebut dilapisi dengan 3wt% dari polydimethylsiloxane (PDMS) dicampur dengan 97wt% n-heksana. Struktur morfologi membran yang dihasilkan telah diuji dengan menggunakan pengimbas mikroskop electron (SEM). Imej SEM menunjukkan gambar struktur morfologi terbaik yang ditemui di membran yang dihasilkan dengan menggunakan NMP sebagai pelarut diikuti oleh DMAc dan terakhir DMF. Fourier Transform Spektroskopi Inframerah (FTIR) analisis juga dilakukan untuk mengesan kewujudan kumpulan berfungsi dalam membrane. Prestasi membran diperiksa dengan melakukan ujian permeasi gas. Karbon dioksida ( $\text{CO}_2$ ) asli dan metana asli ( $\text{CH}_4$ ) digunakan sebagai gas uji dengan menggunakan pelbagai tekanan dengan jarak dari 1 hingga 3 bar. Seperti yang diramal oleh struktur morfologi, NMP pelarut-membran menunjukkan prestasi terbaik berbanding dengan DMAc pelarut-membran dan DMF pelarut-membran dengan selektivitas  $\text{CO}_2/\text{CH}_4$  adalah 1.1358 (pada 1 bar), 1.9946 (pada 2 bar) dan 2.6906 (pada 3 bar) untuk NMP pelarut-membran, 1.0564 (pada 1 bar), 1.8974 (pada 2 bar) dan 1.8958 (pada 3 bar) untuk DMAc pelarut-membran dan 0.9141 (pada 1 bar), 1.7759 (pada 2 bar) dan 1.5257 (pada 3 bar) untuk DMF solvent-membran. Oleh kerana itu, kesimpulannya pelarut mempengaruhi struktur morfologi yang secara langsung akan menjejaskan prestasi membran asimetrik lembar polietersulfon datar. Daripada kajian yang dilakukan pada jenis pelarut, pelarut yang paling sesuai untuk menghasilkan membrane asimetrik lembar polietersulfon datar berprestasi tinggi adalah NMP.

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## LIST OF ABBREVIATIONS

CO <sub>2</sub>	-	Carbon Dioxide
PES	-	Polyethersulfone
SEM	-	Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
RO	-	Reverse Osmosis
TIPS	-	Thermal Induced Phase Separation
H <sub>2</sub>	-	Hydrogen
N <sub>2</sub>	-	Nitrogen
CH <sub>4</sub>	-	Methane
PSU	-	Polysulfone
P	-	Permeability
D	-	Diffusion Coefficient in Membrane
NMP	-	N-methyl-2-pyrrolidone
DMAc	-	Dimethylacetamide
DMF	-	Dimethylformamide
PDMS	-	Polydimethylsiloxane
P <sub>i</sub>	-	Permeability for Gas component
Q	-	Gas Flowrate
A	-	Area
△P	-	Pressure in System
P <sub>j</sub>	-	Permeability of Another Gas Component
α	-	Selectivity

CSDS	-	Chemical Safety Data Sheet
IR	-	Infrared

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

The separation of acid gases such as CO<sub>2</sub> and H<sub>2</sub>S is of great importance in many industrial areas, such as upgrading of natural gas and greenhouse gas emission reduction. Since CO<sub>2</sub> reduces the energy content and is corrosive to the transportation and storage systems in the presence of water, CO<sub>2</sub> concentration needs to be reduced to less than 2% to reach the U.S. pipeline specification (Baker, 2002). On the other hand, the increasing public concern over global warming has concentrated on the greenhouse gas emission. It is highly desirable to remove and sequester CO<sub>2</sub> from various sources.

For natural gas sweetening, the most common process is amine absorption. However, amine plants are large and heavy, requiring tall structures which present problems for use on offshore platforms. They are very complex and require constant operator supervision and maintenance. Also, the presence of a generator which burns some of the methane is a fire safety hazard on offshore platforms. Compared to other technologies, membrane-based CO<sub>2</sub> capture has the advantages of low energy consumption, low weight and space requirement, simplicity of installation / operation, and high process flexibility. The extent of the benefits from using membrane technology is highly dependent on the nature of the separation problem. Natural gas is typically produced at high pressure which is deal for membrane separation. The carbon dioxide permeates through the membrane leaving a methane stream with essentially no pressure drop (Spillman *et al*, 1990). Membrane systems are extremely reliable since the process is continuous with few control components which can cause a shutdown.

In gas separation membrane process, the ability of a membrane to control the permeation rate of chemical species through it had made it favourable for separating mixture of gases. Preferably, membranes should exhibit high selectivity and high permeability simultaneously. However, current commercial membranes usually suffer for a trade-off between selectivity and permeability, which hinder the large-scale application in the industry.

## **1.2 Problem Statement**

The key to high performance of membrane-based gas separation process is strongly depends on permeability and selectivity. Traditionally, there has been a trade-off between selectivity and permeability; where membrane with higher selectivity tends to exhibit less permeability and vice versa. Higher permeability of membrane will leads to higher productivity and lower capital cost while membrane with higher selectivity will shows more efficient separation process. One of the major problems confronting the use of membrane-based gas separation processes in a wide range of applications is the lack of membranes with high performance. Despite the limitation in achieving both high permeability and selectivity, it is important to select the most compatible combination of polymers and solvents formulation for flat asymmetric membrane that has improvement in the membrane properties for acid gas separation. Therefore, membrane formation process plays an important role and certain factors need proper attention in order to produce a good membrane for gas separation.

## **1.3 Objective of Research**

The main objective of this study is to develop a high performance asymmetric flat sheet membrane for gas separation by study the effect of different solvents used in the formation of the membrane.

## **1.4 Scope of Research**

Several scopes that have been outlined in order to achieve the objective of this study are as follows:

- To fabricate Polyethersulfone (PES) asymmetric membrane in flat sheet form by dry/wet phase inversion.
- To study the effect of different solvents used in the formation of asymmetric flat sheet membrane.
- To characterize the PES asymmetric flat sheet membrane using Scanning Electron Micrograph (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).
- To test the performance of the asymmetric flat sheet membrane in gas separation using single permeation test.

## **1.5 Rationale and Significant**

- High performance membrane for gas separation (acid gas).
  - ✓ Flat asymmetric membrane exhibited greater gas selectivity than the dense membrane.
- Lower operating costs.
  - ✓ The only major operating cost for single-stage membrane system is membrane replacement. This cost is significantly lower than the solvent replacement and energy cost 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.

- Environmental 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 reinjected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated.
- Good weight and space efficiency
  - ✓ Skid construction can be optimized to the space available and multiple elements can be inserted into tubes to increase packing density. This space efficiency is especially important for offshore environments.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Membrane for Gas Separation**

##### **2.1.1 History of Membrane for Gas Separation**

The history of membrane based gas separations can be traced back over 170 years. In 1829 Thomas Graham observed gaseous osmosis for the air-carbon-dioxide system through a wet animal bladder (Kesting and Fritzsche, 1993). Then, J. K. Mitchell in year 1831 observed that balloons made from India rubber put into gas atmospheres of different composition blew up with different velocities, depending on the nature of the gas (Baker, 1991). Mitchell noted that CO<sub>2</sub> was absorbed by rubber film to a larger degree than other gases, and was led to infer, accordingly, that rubber expanded in volume and hence, porosity was induced in the solid sample which provided a way of penetration of CO<sub>2</sub> molecules.

In 1855, Adolph Fick postulated the concept of diffusion and formulated Fick's First Law of diffusion from the studies on gas transport through nitrocellulose membrane (Baker, 1991). Of course, the significance of Fick's First Law is quite general for many scientific fields, but it is interesting that membranes were the media where it was first established.

Later in 1866, Graham discovered the Graham's law of gas diffusion. Graham's Law describe qualitative about "sorption diffusion" theory for gas transport or permeation through a membrane. In the experiments, gas permeated through the film (natural rubber) into vacuum not into air. Graham established a



series of relative permeation rates across the film for a number of gases that is amazing lose to modern estimates of the corresponding properties then noted that there was no relation between these values and known diffusion coefficients in gases. Therefore, “solution diffusion” mechanism was proposed to describe the mechanism of gas permeate through the rubbery polymer.

Many other important findings in gas permeation research or membrane science more generally, can be attributed to Graham (Graham *et al*, 1866). Graham carried out the first membrane gas separation and obtained oxygen riched air containing 46.6% oxygen. By increasing the pressure of a gas mixture to be separated should be beneficial for obtaining higher fluxes. Graham observed that changes in the thickness of films affects the flux but not the composition of permeate gas. From the study, the effect of temperature on permeation rates is observed; by preparing the first composite membranes and tried to vary deliberately the chemical nature of the membrane material. Graham also described the experiments on hydrogen permeation across membranes made of platinum, palladium, and other metals and concluded that they as well as rubber films behaved like non-porous septa.

In 1891, Kayser demonstrated the validity of Hendry’ law for adsorption of carbon dioxide in natural rubber (Paul and Yampol’skii, 1994). In 1900, Lord Rayleigh measured relative permeabilities of oxygen, nitrogen and argon rubber. Other significant contributions in the understanding of membrane gas transport theory were made by Knudsen in 1908 (Knudsen diffusion defined) and Shakespear in 1917 through 1920 (temperature dependence of gas permeability in membranes). According to Dynes, the process of diffusion of a gas through a rubber film is determined by two more less separate processes. Measurement must be made simultaneously on the permeability, absorption coefficients, and diffusion-constants, as a minimum, any two of these three quantities (Rahman *et al*, 2006).

This method had been used since until in the 1930s and 1940s, R. M. Barrer widely introduced it to experimental practice, so it is often known as the Dynes-Barrer method. A great influence on our knowledge of the thermodynamics and diffusion properties of polymers was exerted by the introduction of McBain microbalances (Paul and Yampol’skii, 1994). This simple instrument made it

possible to obtain abundant information, especially for polymer-vapor systems, on solubility coefficients, sorption isotherms, diffusion coefficients, and sorption kinetics.

### **2.1.2 Gas Separation System**

There are four methods for gas separation in oil and gas industry which are cryogenics distillation, absorption, adsorption and membrane.

#### **2.1.2.1 Cryogenics Distillation**

Cryogenic distillation involves a series of vaporizations and condensations in which the higher boiling species concentrate in the liquid phase which flows down the column and the lower boiling components concentrate in the vapor phase which moves up the column. Heat is removed from the column at the top through a condenser while heat is added at the bottom of the column through the reboiler. Cryogenics is the predominant technology in the separation of atmospheric gases, methane from nitrogen, ethane and ethylene and is also used in hydrogen separations.

#### **2.1.2.2 Absorption**

Absorption is a physical process where a gas is selectively dissolved in a liquid and subsequently recovered through the action of heat, pressure, and/or another chemical. Absorption processes have found major applications in the removal of acid gases such as carbon dioxide and hydrogen sulphide (MacLean *et al*, 1986). The compensating advantage is that separation can often be effected at a more convenient temperature. Absorption comes into its own when the normal boiling points of the components are widely operated, or where one or more of the components have a strong affinity for a particular solvent. Hence its use with carbon dioxide removal from synthesis gas, and for scrubbing carbon dioxide and sulphur compounds from natural gas.

### **2.1.2.3 Adsorption**

This technique uses a porous solid material such as a zeolite, an aluminosilicates material, or a carbon molecular sieve to preferentially adsorb one gaseous species versus others. The adsorbent is packed in carbon steel vessels and a higher pressure is used to adsorb while a lower pressure is used to desorb.

### **2.1.2.4 Membrane**

Membrane which are thin barrier between feed and permeate gas streams have been used to selectively transport fluids since life itself. There have been however, the major technical advances that permit industrial use. The first was the research of Loeb and Sourirajan (1963) where thin asymmetric membranes consists of a thin, dense outside layer was formed on a thick, porous base layer, and were developed from cellulose acetate. This allowed high flux as well as good selectivity. This same principle has been applied to many other polymeric systems. Membranes have been formed into separators by either winding flat sheets into spirally wound modules or taking bundles of hollow fibers and casting epoxy resins on both ends and then encasing the bundle in carbon steel shells with appropriate entrance and exit nozzles (MacLean *et al*, 1986).

### 2.1.3 Comparison between Gas Separation Systems

Each of the four gas separation technologies are summarized with respect to their performance as shown in Table 2.1. Special attention will be given to product quality and general economic considerations.

**Table 2.1:** Comparison of Gas Separation Systems

Process	Advantage	Disadvantage
Cryogenic distillation	<ul style="list-style-type: none"> <li>• Low power consumption</li> <li>• Could produce high purity products.</li> <li>• Could achieve higher recovery compared to other process.</li> </ul>	<ul style="list-style-type: none"> <li>• Unable to economically scale down to very small size.</li> <li>• Consist of highly integrated, enclosed system which does not permit easy handling of widely varying feed streams.</li> </ul>
Adsorption	<ul style="list-style-type: none"> <li>• Could obtain high purity of products.</li> <li>• Can be supplied to remote locations where equipment size is critical.</li> </ul>	<ul style="list-style-type: none"> <li>• Lower recovery of products.</li> <li>• Single relatively pure product.</li> </ul>
Absorption	<ul style="list-style-type: none"> <li>• Excellent for CO<sub>2</sub> and H<sub>2</sub>S removal</li> </ul>	<ul style="list-style-type: none"> <li>• High partial pressure needed for physical solvents</li> <li>• Low partial pressure needed for chemical solvent slow purity of acid gas</li> </ul>
Membrane	<ul style="list-style-type: none"> <li>• Versatility</li> <li>• Simplicity</li> <li>• Stable at high pressure</li> <li>• Could achieve high purity of product.</li> </ul>	<ul style="list-style-type: none"> <li>• Possible recompression of permeate.</li> <li>• Medium purity.</li> </ul>

#### **2.1.4 Advantages of Membrane for Gas Separation**

Membrane process is most favorable separating system since it combined several beneficial features that make them attractive for industrial applications. The features are described briefly below:

- 1) Separation is on basis of molecular size, which means that the separation process could be carry out at ambient or modest temperature. Thermally sensitive solutes can be treated without damage. Other environmental stresses, such as imposed by chemical additives and high shear can also be avoided or minimized (Baker, 2002).
- 2) Membrane separation process did not require any phase change and any latent heat. Thus, it could save lost of energy consumption (Baker, 2002).
- 3) Membrane devices are almost always compact and modular, especially if membrane is provided in a bundle of hollow fibers and spiral wound that occupies high area per unit volume (Spillman and Sherwin, 1990). This factor also leads towards weight and space efficiency, which is important in transportation or offshore platform applications.
- 4) Membrane process is environmental friendly because it produces no waste. In fact, one of the major accomplishments of membrane processes is that they provide a means for recovering value from previously discarded effluents (Baker, 2002).
- 5) Membrane devices could be easily scale up from pilot to commercial size, which allows pilot scale tests with a single module and then direct scale-up by simply using many multiples of this unit (Baker, 2002).

## **2.2 Membrane Classification**

Typically, there are two types of membrane structure namely, symmetric and asymmetric. The different between these two structures were the physical and chemical properties.

### **2.2.1 Symmetrical Membrane**

Symmetrical membranes have a uniform composition structure throughout, and they can be porous or dense. The resistance to mass transfer in these membranes are determined by the total membranes thickness. A decrease in membrane thickness results in an increased permeation rate (Strathmann, 1986).

#### **2.2.1.1 Microporous Membrane**

The simplest form of microporous membrane is a polymer film with cylindrical pores or capillaries. However, more commonly microporous membranes have a more open and random structure with interconnected pores. They are very similar in structure and function to conventional filters. However in contrast with conventional filters, these pores are extremely small (Strathmann, 1986).

#### **2.2.1.2 Non-porous, Dense Membrane**

This type of membranes consists of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rates within the membrane, which are determined by their diffusivity and solubility in the membrane material. Thus, this type of membranes can separate permeants of similar size if their concentration in the membrane material differ significantly (Strathmann, 1986).

### 2.2.1.3 Electrically-Charged Membranes

These types of membranes are also referred to as ion-exchange membranes. They can be dense or microporous, but most commonly are very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. Separation is achieved mainly by exclusion of ions of the same charge as the fixed ions on the membrane structure, and is affected by the charge and concentration of ions in the solution. This type of membranes is used for processing electrolyte solution in electrodialysis.

### 2.2.2 Asymmetric Membranes

Asymmetric membranes are used primarily for pressure driven membrane processes, such as ultrafiltration and gas separation. Their structure consist of a very thin (0.1 to 2.0 $\mu\text{m}$ ) polymer layer on highly porous 100 to 200 $\mu\text{m}$  thick sublayer (Strathmann, 1986). This means that this membrane consist two layer; a thin, dense and nonporous skin layer that perform the separation, supported by on a finely microporous substrate that made from the same material that only provides the mechanical strength (Baker, 2002). The sublayer only acts as a support and does not affect the separation characteristics or the permeation rate of the membrane in pressure driven processes. To obtain high permeation rates, the selective layer of gas separation membranes must be extremely thin (Baker, 2002). Since the permeation rate in ultrafiltration or gas separation processes is inversely proportional to the thickness of the thin barrier layer, asymmetric membranes exhibit much higher permeation rates than symmetric structures of comparable thickness. Another advantage of asymmetric membranes is the membranes are surface filters retaining all the rejected materials at the surface where they can be removed by shear forces applied by the feed solution moving parallel to the membrane surface (Costello, 1994). Ideal asymmetric membrane for gas separation should meet the following requirement. (Paul and Yampol'skii, 1994).

- 1) The selective skin layer should defect free so that gas transport takes places exclusively by solution diffusion not by poorly selective flow through process.

- 2) The selective layer should be as thin as possible to maximize the gas fluxes.
- 3) The supporting substructure should not contribute any resistance to gas transport.
- 4) The substructure should provide sufficient mechanical strength to support the delicate selective layer in high pressure operation.

#### **2.2.2.1 Thin Film Composite Membrane**

This membrane consists of a thin dense film of highly cross-linked polymer formed on the surface of a thicker microporous support. The dense polymer layer is extremely thin, on the order of 0.1 mm or less, so membrane permeability is high. Because it is highly cross-linked its selectivity is also high.

#### **2.2.2.2 Liquid Membrane**

Liquid membranes have become increasingly significant in the context of facilitated transport that utilizes carriers to selectively transport components such as metal ions at a relatively high rate across the membrane interface. Generally, formation of a thin film is not a problem. Difficulty is encountered, in maintaining and controlling this film and properties during a mass separation process (Strathmann, 1986).

### **2.3 Membrane Module**

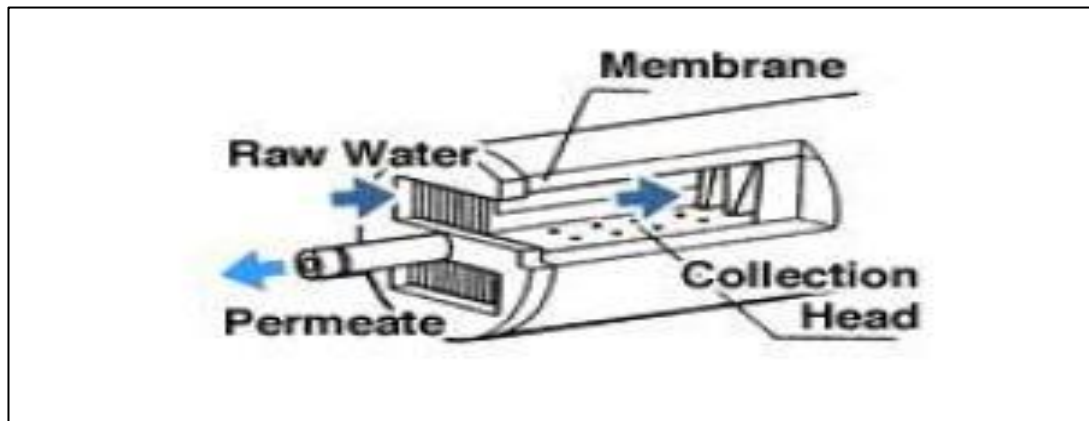
Large membrane areas are normally required in order to apply membranes on a technical scale. A module was defined as the smallest unit into which the membrane area is packed. At certain flow rate and composition, a feed enters the module. Both the feed composition and flow rate inside the module change as a function of distance. This was due to the ability of membrane which is able to transport one component more readily than other. There are four major types of modules



normally used in membrane separation processes which are plate and frame, spiral wound, tubular and hollow fiber module (Mulder, 1996).

### 2.3.1 Plate and Frame Module

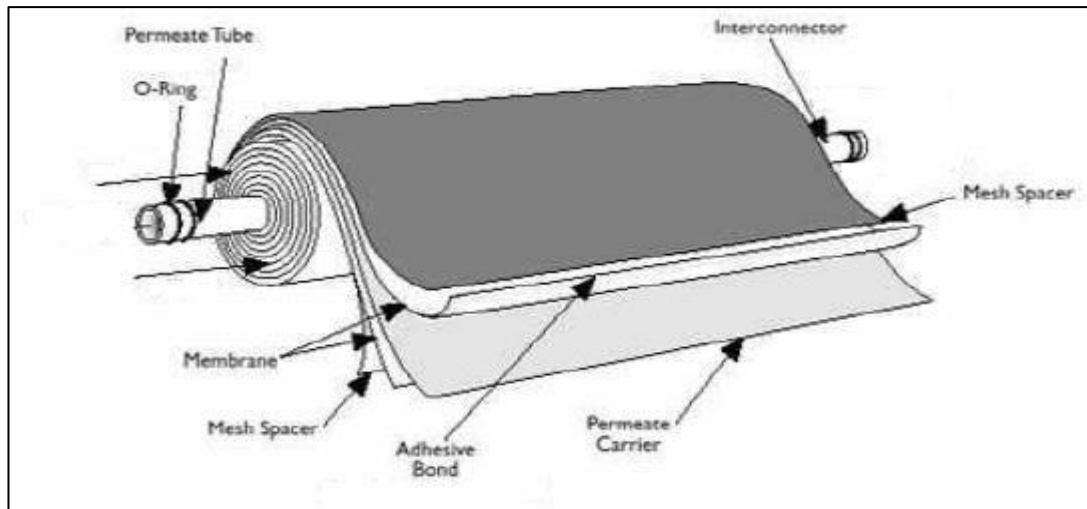
Plate and frame module can be described as simple and easy maintenance. Two membrane are placed in a sandwich-like fashion with the feed side was faced each other. In each compartment; feed and permeate, the suitable spacer membrane support plates are stacked alternately (Wang *et al*, 2006).



**Figure 2.1:** The Structure of Plate and Frame Membrane Module (Yoshihito *et al*, 1992)

### 2.3.2 Spiral Wound Module

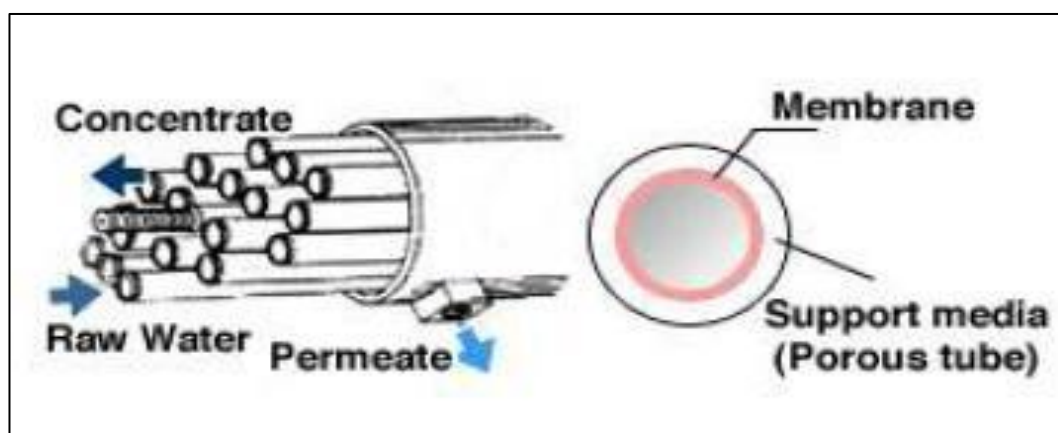
Spiral wound membrane module was formed using a flat sheet membrane. It consists of two layers of membrane, placed into a permeate collector fabric. The membrane envelope was wrapped around a centrally placed permeate drain. This causes the packing density of the membrane to be higher. The feed channel is placed at moderate height to prevent plugging of the membrane unit. Spiral membranes are only used for nanofiltration and reverse osmosis (RO) application (Holding, 1998).



**Figure 2.2:** Structural of Spiral Wound Membrane Module (Yoshihito *et al*, 1992)

### 2.3.3 Tubular Module

Tubular membranes are not self supporting membrane. It was made of special material and located on the inside of a tube. This module acts as the supporting layer for the membrane. The flow of a tubular membrane was usually inside out due to the location of tubular membranes is inside a tube. Tubular membranes have a diameter of about 5 to 15 mm and due to this size, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low, which result in high priess per module (Baker, 1991).



**Figure 2.3:** Tubular Module Diagram (Yoshihito *et al*, 1992)

### 2.3.4 Hollow Fiber Module

Hollow fiber membrane has diameter below  $0.1\mu\text{m}$  which means the chances of plugging was very high. The membranes can only be used for the treatment of water with low suspended solid content. The packing density of a hollow fiber membrane was very high. Hollow fiber membranes always used merely for nanofiltration and reverse osmosis (RO) (Wang *et al*, 2006).



**Figure 2.4:** Hollow Fiber Membrane Module (Wang *et al*, 2006)

## 2.4 Membrane Formation Technique

In the membrane field, the term phase inversion is commonly used to describe the phase separation process. Membrane can be prepared by phase inversion techniques and can be categorized into four different techniques that is thermal precipitation, air casting of dope solution, precipitation from the vapour phase and immersion precipitation (Baker, 2002).

### 2.4.1 Thermal Precipitation

For thermal induced phase separation (TIPS) technique, it is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying.

### **2.4.2 Air Casting of Dope Solution**

In the air casting technique process, the polymer is dissolved in a mixture of a volatile solvent and less volatile non-solvent. During the evaporation of the solvent, the solubility of the polymer decreases and then phase separation take places.

### **2.4.3 Precipitation from the Vapour Phase**

In the precipitation from the vapor phase process, phase separation of the polymer solution is induced by penetration of non-solvent vapor in the solution.

### **2.4.4 Immersion Precipitation**

In the immersion precipitation case, a polymer is cast as a thin film on a support or extruded through a die, and is subsequently immersed in a nonsolvent bath. Precipitation can occur because of the good solvent in the polymer solution is exchanged with nonsolvent in the coagulation bath (Fleming, 1988). Among these techniques, immersion precipitation is widely used to produce commercial gas separation membranes and other membrane based-separation. Immersion precipitation technique is divided into three categories: wet phase inversion technique, dry phase inversion technique and dry/wet phase inversion technique.

#### **2.4.4.1 Wet Phase Inversion Technique**

The wet phase separation technique is the most common method for preparation and production of polymeric membrane. A cast thin layer of a polymer solution is immersed in a liquid non-solvent for polymer that is miscible with polymer solvent. The exchange of the solvent from thin layer of polymer solution with a non-solvent from the coagulation bath produces thermodynamic instability in now ternary membrane forming system. The thermodynamic instability is resolved by the separation into polymer-rich phase forms a solid membrane matrix while the

polymer-lean phase leaves a porous structure by leaching out the system (Fleming, 1988).

#### **2.4.4.2 Dry Phase Inversion Technique**

Flat sheet skinned asymmetric membrane are generally made by a casting solution consisting of polymer, solvents and non-solvent. If the non-solvent components are less volatile to the solvent components, evaporation will ultimately produce a critical non-solvent concentration that causes the membrane to be transform from a single phase to a two phase structure. If the solvents and non-solvents components are removed solely by evaporation, membrane formation is defined as a dry phase inversion process (Pinnau, 1988).

#### **2.4.4.3 Dry/Wet Phase Inversion**

Asymmetric flat sheet Polyethersulfone (PES) membrane can be prepared using a simple dry/wet phase inversion method. The flat sheet membrane was prepared by casting a dope solution on a glass plate by using a pneumatically controlled casting machine with appropriate shear rate. The asymmetric membrane was then quenched immediately and smoothly in an aqueous bath at room temperature and remained there for two whole days for solvent-nonsolvent exchange process to occur. After that, the membrane was immersed in an alcohol nonsolvent bath for a day and then dried at room temperature for another day (Pinnau, 1988).

### **2.5 Polymeric Membrane**

Polymeric membranes are being increasingly used to effect separations of gas streams in a variety of applications. Examples of such applications would include the generation of medium purity nitrogen from compressed air, the recovery of hydrogen from refinery purged gases and the removal of carbon dioxide from produced natural gas streams. In many cases the polymers employed for the fabrication of the

membrane are glassy amorphous materials characterized by high glass transition temperatures, good mechanical strength and an acceptable combination of gas permeability and selectivity properties.

The permeability of a polymer to gases depends upon both the physical properties of the polymer and the gases concerned. For a particular gas the nature of the polymer and its interaction with the gas will clearly determine the transport behaviour. Factors which relate to the molecular structure of the polymer, such as polarity, hydrogen bonding, cohesive energy density, chain flexibility and crystallinity will all have an influence on the transport process (Crank and Park, 1968). It is evident that in correlating gas solubility and diffusivity with polymer structural properties it is difficult to isolate these many inter-relating factors. The selectivity of a polymer to a particular gas mixture is a still more complicated issue, because gases behave competitively in glassy polymer systems.

In developing a clearer understanding of factors affecting glassy polymer gas selectivity, careful studies for pure gas sorption and permeation are required. Analysis of competitive gas sorption and transport behaviour should result in the development of a clearer appreciation of the interrelationship between polymer structural factors and gas separation behaviour.

### **2.5.1 Material for Polymeric Membrane**

Any polymeric material will separate gases to some extent. However, proper selection of the polymeric material comprising the membrane is extremely important since it determines the ultimate performance of the gas separation module. In the early period, rubbers and, to a lesser extent, other polymers of natural origin served as the traditional test objects. Studies on rubbers established trends for the effect of the structure, molecular mass and crosslink density of the polymer. The advent of the era of synthetic and semi-crystalline polyolefins and other vinylic-type polymers that took place in the late 1950s and 1960s was accompanied by intense interest for packaging applications, where their barrier properties to gases are critical. Gas sorption

and diffusion measurements were also widely and effectively used as a probe of polymer structure or morphology.

In the early 1970s interest moved to the glassy state of polymers and, on the other hand, to the direct search for advanced materials for gas separation membranes. The rate of publication, the diversity of polymers investigated, and the number of groups involved in research has increase enormously since the time. Simultaneously, since the 1960s interest in non traditional types of membrane materials, such as media providing coupled or facilitated transport by means of free or fixed carriers, had emerged. Membrane processes involve very different processes and hence it might be expected that a number of very different membranes is necessary. The most important membrane qualities to be considered are (Rautenbach and Albrecht, 1989) are:

- High selectivity
- High permeability
- Mechanical strength
- Temperature stability
- Chemical resistance

### **2.5.2 Gas Transport in Polymer Material**

Separation of gases through membrane is the result of differences in the transport rate of chemical species through the membrane interphase. The transport rate is determined by the driving force of forces acting on the individual components and their mobility and concentration within the interphase. The mobility and concentration of the gas mixture within the interphase will determine how large a flux is produced by a given driving force. These driving forces are hydrostatic pressure, concentration difference and electrical potential difference.

### **2.5.2.1 Permeation**

Gas mixtures can be separated by porous and non-porous membranes. Membrane performance can be characterized by two main parameters, which are the flux of the gas through membrane (permeability) and the separation efficiency of the membrane (selectivity). The permeabilities of different components in membrane depend on the mechanism by which the components are transported. Generally, gas transport through polymeric membrane is modeled by sorption-diffusion mechanism. This mechanism is so named because transports occur when gas molecules from upstream gas phase first sorb into the membrane, then diffuse across it and finally desorb on the downstream gas phase side (Mahajan, 2000). In order to increase the permselectivity of the membrane, it is require adjusting the diffusivity and the solubility of the penetrants. The solubility selectivity is dependent on the relative condensability of gas penetrants and penetrants-membrane medium interactions, whereas diffusivity selectivity is dependent on the relative differences of the diffusion coefficients of gas penetrants through the membrane material (Vu, 2001).

### **2.5.2.2 Sorption**

The sorption coefficient describes the amount (or concentration) of gas that is taken up by a membrane material at a given pressure or fugacity at equilibrium (Vu, 2001). For glassy polymer, this quantity is modeled by the dual-mode sorption model.

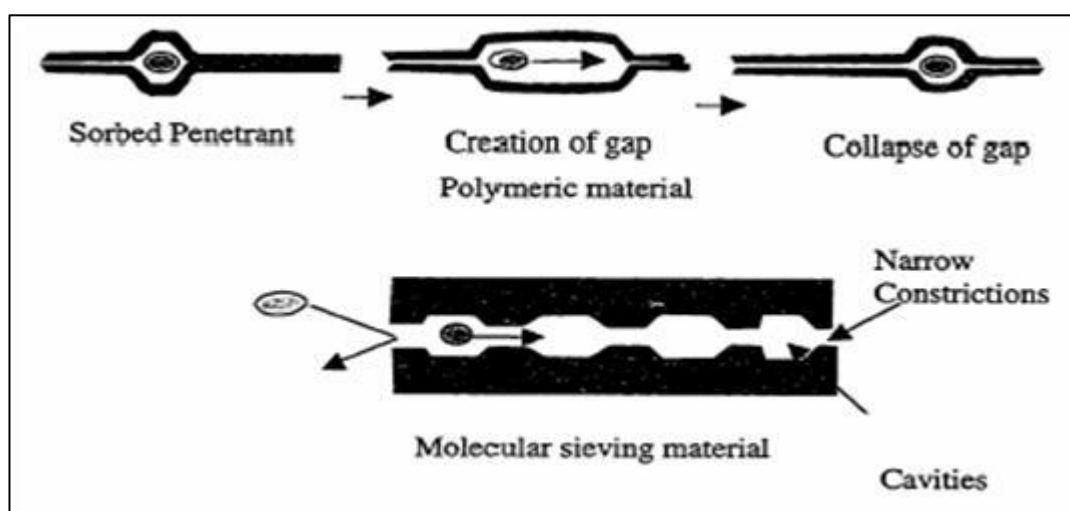
### **2.5.2.3 Diffusion**

Diffusion coefficient is defined as a quantity that measures the mobility of the penetrant molecules in the membrane. For polymers, the diffusion rate is affected by the penetrant size, the packing and mobility of polymer chains, and the cohesive energy of the polymer (Crank and Park, 1968). The diffusion of gas through polymer occur when the polymer provide an opening for the sorbed penetrants to move into, with the subsequent collapsed of the sorbed cage that was previously occupied by the penetrant. This opening resulted from the thermally induced motion of the polymer



segment. Thus, the rate of gas diffusion depends on the concentration of the opening that is adequately large to accept the diffusing molecules (Mahajan, 2000).

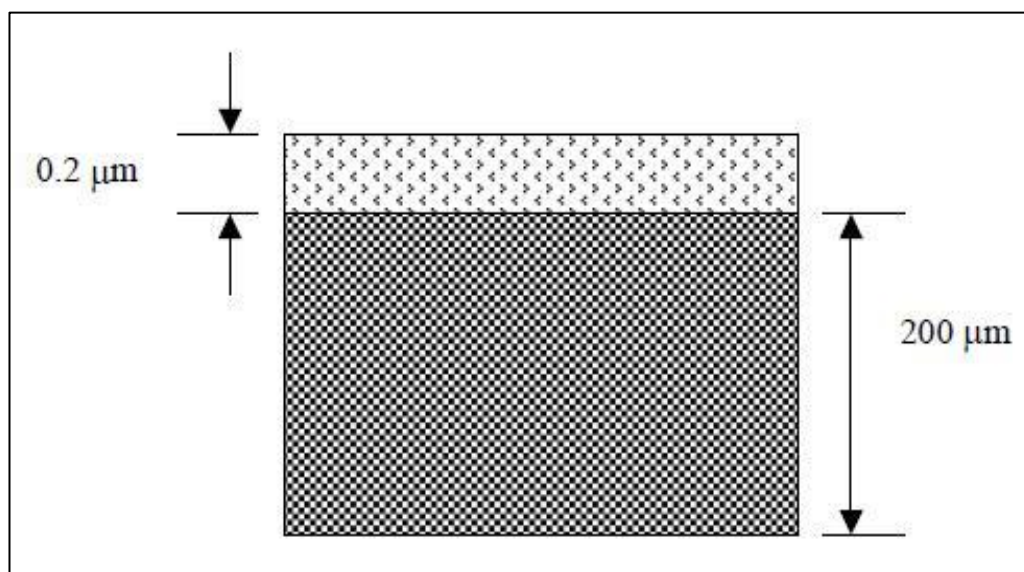
For gas separation, diffusion is a function of both the difference in diffusive jump lengths between the penetrants and the frequency of sufficiently-sized gaps. The size and frequency of these gaps differ for differently sized penetrants because of the different gap sized necessary for a penetrants to execute a diffusive jump. As shown in Figure 2.5, the diffusive jumps of gas penetrants in polymer can only occur when gaps of sufficient size are available (Vu, 2001).



**Figure 2.5:** Transport of penetrant through polymer and molecular sieves (Mahajan, 2000)

## 2.6 Asymmetric Membrane

Asymmetric membrane consists of two structurally distinct layers, one of which is a thin, dense, selective skin or barrier layer and the other a thick, porous matrix layer whose chief function is to provide a physical support for the thin skin. The skin layer performs the separation with a high flux because it is thin and with a high selectivity due to its high density. The porous sublayer provides the mechanical strength that the gases permeate without resistance (Baker, 1991). Two general classes of asymmetric membrane are universally recognized, integrally skinned and thin-film composite. Figure 2.6 shows asymmetric membranes consist of an extremely thin and dense surface layer ( $0.1\mu\text{m}$  to  $1\mu\text{m}$ ) supported on a much thicker porous sublayer ( $100\mu\text{m}$  to  $200\mu\text{m}$  of the same material), first developed by Loeb and Sourirajan, in which skin and substructure layers were of the same material and were prepared from the same solution at the same time (Guang-Li, 1993; Ismail and Yean, 2003; Srathman, 1986; Wang and Minhas, 1991; Chung and Hu, 1997).



**Figure 2.6:** A schematic illustration of the structure of integrally-skinned asymmetric membranes

Formation of asymmetric membrane is probably most interesting from a fundamental standpoint and most practical for commercialization. However, a major drawback with the asymmetric membrane is the presence of pinhole and other defects in the dense barrier, which lower its separation properties. These defects,

caused by gas bubbles, dust particles and support fabric imperfections, are often difficult to eliminate. These defects may not significantly affect the performance of asymmetric membrane used in liquid separation operations, such as reverse osmosis, but can be disastrous in gas separation applications (Baker, 1991).

A solution to this problem was proposed by Henis and Tripodi, who coated the surface of polysulfone asymmetric membranes with highly permeable silicone rubber (Henis and Tripodi, 1981). Coating may be regarded as a standard procedure to repair gas separation membranes that is widely used to repair any defects or pores that may arise in the active layer of a gas separation membrane. It is believed that coating material can plug membrane defects and also prevent simple convective gas flow through defects. In other words, the purpose of coating with silicone is to fill any surface pinholes or imperfection.

The Skin layer can be considered to be essentially defect-free if the transport properties of asymmetric membranes were predominantly determined by solution diffusion mechanism. Since the skin during membrane formation is relatively difficult to eliminate, therefore, silicone- coated membranes are commonly utilized in industrial membrane gas separation processes (Ismail *et al.*, 2003). This technique is used to repair any defects or pores that may occur in the active layer of a gas separation membrane. So, for each silicone- coated gas separation membrane with selectivity is 80 % or greater than intrinsic for the polymer film, a defect-free skin layer is formed (Ismail and Lai, 2004).

### **2.6.1 Characteristic of Asymmetric Membrane**

As mentioned before, asymmetric membrane consists of a thin skin layer supported by an open sublayer. Characteristics of such a structure are:

#### **1) Porosity of the top layer**

This property largely determines the type of the process in which the membrane can be used. A pore-free top layer gives pervaporation or gas separation properties, while an open top layer gives an ultrafiltration or a microfiltration membrane.

#### **2) Thickness of the top layer**

The thickness of the top layer determines the permeation rate and for most of the separation process this permeation rate is reduced with an increasing skin thickness.

#### **3) Porosity of the sublayer**

The desired sublayer only serves as a mechanical support for the top layer and does not give any additional transport resistance. This means that it should have a regular structure and a high porosity with sufficient interconnection of the pores.

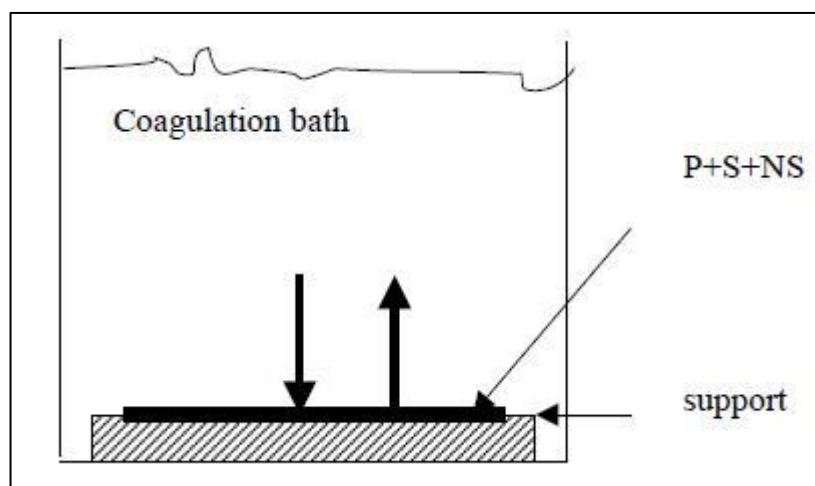
#### **4) Presence of macrovoids**

During membrane formation by immersion precipitation, often large conical voids are formed, called macrovoids (Van't Hoff, 1988). They are initiated just below the top layer and depending on the circumstance under which the membrane is made they can have dimension ranging from about 1 $\mu$ m to 100  $\mu$ m or more. When the membranes have to be used at high pressure, microvoids may give rise to ruptures in the thin top layer.

## 2.6.2 Asymmetric Membrane Fabrication Technique

### 2.6.2.1 Flat Sheet Casting Technique

Flat sheet casting is the oldest technique used to form membranes and involves a number of stages. The dope solution is prepared by dissolving a polymer in a suitable solvent or a mixture of solvents and non-solvent to form a homogeneous dope solution. The dope is then cast over a suitable base or support (e.g. glass plate or nonwoven polyester) by a casting knife. The casting knife consists of a steel blade resting on two runners arranged to form a precise gap between the blade and the support. This gap, which can vary from 50 to 500  $\mu\text{m}$ , determines the thickness of the membrane produced. The cast film undergoes a partial evaporation of solvent or mixture of solvents before immersion into a coagulation bath. The partial evaporation may result in solidification and pre-orientation of the skin. When the film is immersed in the coagulation bath the phase separation is completed. Water is often used as a non-solvent for many types of polymers for gas separation. Parameters influencing membrane structure and properties include solvent/non-solvent, polymer concentration, evaporation time, humidity, temperature and composition of the casting solution.



**Figure 2.7:** Schematic Preparation of flat sheet membrane by immersion precipitation

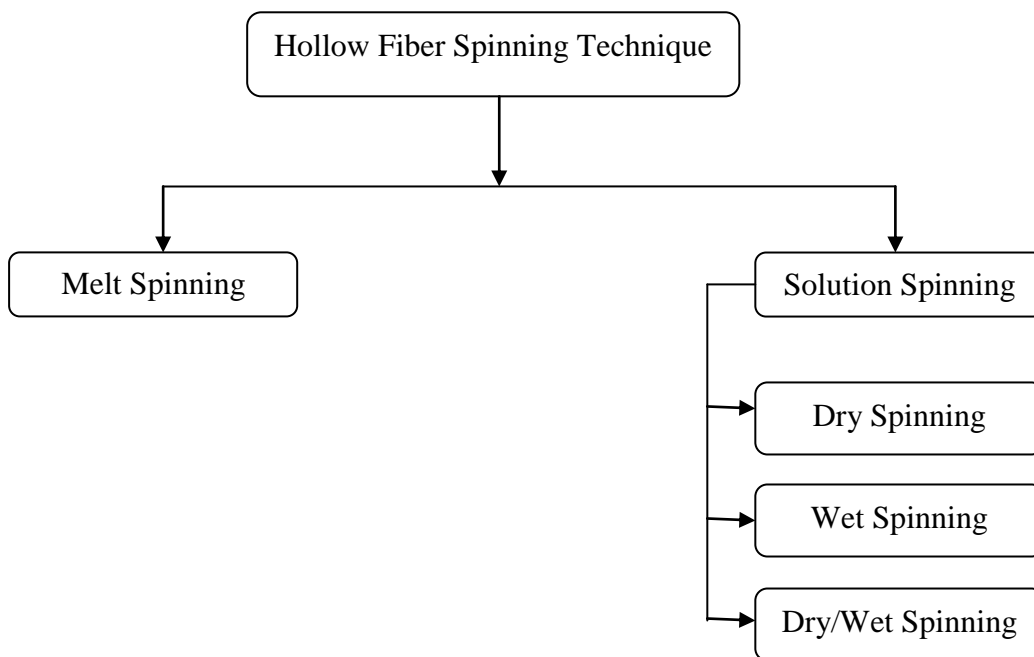
The membranes obtained after precipitation can be used directly or subjected to drying or post treatment techniques to enhance the selectivity. The resultant membranes are used in plate-and-frame and spiral wound systems. In flat sheet membrane preparation, there is only one interface between polymer solution and non-solvent bath and penetration of non-solvent starts from the 'free' side of the membrane (the side not connected to the support) as depicted in Figure 2.7. The composition at the 'support' side remains constant until the non-solvent has reached the bottom of the film. Since the volume of the non-solvent bath is large compared to the polymer film, the composition of the former can be assumed constant.

It should be mentioned that there are situations where penetration of non-solvent may occur from both sides in a flat film. An example is the production of large sheets of membranes in a casting machine, where a porous support is covered with a thin film of the polymer solution and immersed in a non-solvent bath. In flat sheet membranes, macrovoids formation occurs from only one side and it is not opposed by non-solvent penetration from the other side (Van't Hoff, 1988). A top layer is formed at the 'bath side' (interface with the coagulation bath). Under this top layer nuclei of a diluted phase are formed. The diffusion process will only be disturbed when gelation of the surrounding phase occurs, or after the 'support side' boundary is reached.

#### **2.6.2.2 Hollow Fiber Spinning Technique**

Spinning is a physical process involving the extrusion of a polymer solution through an annular spinneret to form a hollow fiber. The term spinning originates from the production of man-made textile fibers that involves similar principles. Hollow fiber spinning is a tricky practical process and generally involves four main steps namely, solution formulation, extrusion, coagulation and treatment of the coagulated fibers. Similar to flat sheet casting, a number of processing parameters influence the structure and hence the separation performance of hollow fiber membranes.

Hollow fiber membranes can be fabricated in the form of dense and asymmetric structures. These structures differ only in the method used to solidify the gel filament. A dense structure is usually fabricated by melt spinning while solution spinning (phase inversion) yields asymmetric membranes. The major techniques used in the fabrication of hollow fiber membranes are summarised as depicted in Figure 2.8.



**Figure 2.8:** Hollow Fiber Spinning Technique

## **2.7 Factor Affecting Gas Permeation in Membrane**

### **2.7.1 Pressure**

When the dilute solutions pass through the membrane, the fluxes will increase, but after the optimum pressure the purity of the fluxes become low because the pressure will destroy the membrane structure. So, particle that larger than the membrane pores also can pass through the membrane.

### **2.7.2 Temperature**

Flux increases proportionally with temperature due to reduce kinematics viscosity. Increased flux leads to an increased rate of fouling. Also temperature increases the chemical activity and foulant deformation, which can accelerate foulant layer densification, resulting in an increased hydraulic resistance. Ultimately, flux in a fouling system is reduced at a higher rate from a temperature increase, and may actually stabilize at a lower value than would occur at lower temperatures.

### **2.7.3 Flow Rate**

For every different concentration, when the flow rate of process is increase, the diffusion through the membrane will totally increase. Thus, the fluxes will also increase.

### **2.7.4 Concentration**

The increasing of solute concentration when operating time it will cause the polar increase, thus the effects of fluxes will decrease.



## 2.8 Current Status of Gas Separation Membranes

Membranes offer lower energy cost and viable economics at low volume, simplicity of operation, portability, compactness and mechanical reliability. Polyethersulfone membrane-based separation, for example has grown to represent about one-third of new liquid-nitrogen production capacity for small users. Membrane separations are not as competitive for large units or where high purity is required. Most of today gas separation membranes are formed into hollow-fiber modules due to their low production cost. Currently, only eight or nine polymer materials have been used to make at least 90% of the total installed gas separation membrane-based systems. Table 2.2 show the principal gas separation markets, producers and membrane systems (Koros, 1991).

**Table 2.2:** Principal Gas Separation Markets, Producers and Membrane Systems

Company	Market	Membrane Material Used	Module Type
Permea	Large gas companies	Polysulfone	Hollow fiber
Medal (Air Liquide)	Nitrogen separation	Polyimide /polyaramide	Hollow fiber
IMS (Praxair)	Hydrogen separation	Polyimide	Hollow fiber
Grace Membrane System (GMS)	CO <sub>2</sub> , H <sub>2</sub> and natural gas separations	Tetrabromopolycarbonate	Spiral wound
Separex	CO <sub>2</sub> , H <sub>2</sub> and methane	Cellulose acetate	Spiral wound
Ube Industries	CO <sub>2</sub> and vapor recovery	Polyimide	Hollow fiber
GKSS licensees	H <sub>2</sub>	Silicone rubber	Plate frame
Cynara (Natco)	CO <sub>2</sub>	Cellulose acetate	Hollow fiber

## 2.9 Research and Development of Membrane for Gas Separation

The study findings in membrane for gas separation by various authors and researchers are shown in table below.

**Table 2.3:** Research and Development in Membrane for Gas Separation

No	Author	Membrane/Gas Separation Properties	Study Findings
1.	Krishna & Baten, 2007	-12 different zeolite (AFI,MOR,TON,FER,LTL,MFI,ISV,BEA,FAU,LTA,CHA, & DDR).	-CO <sub>2</sub> /CH <sub>4</sub> membrane permeation selectivity for all the zeolite=1 to 1000 roughly. -The sorption selectivity CO <sub>2</sub> /N <sub>2</sub> for all the zeolite=0.5 to 800 -Self diffusivity between CO <sub>2</sub> and N <sub>2</sub> =0.1 to 1.0 -CO <sub>2</sub> /N <sub>2</sub> membrane permeation selectivity for CH <sub>4</sub> =10 to 100
2.	Wang & Kamiya, 1995	Polysulfone membrane/CO <sub>2</sub>	-The sorption equilibrium obeys the dual-mode model. -The diffusion coefficient is concentration dependent and its temperature dependence can be well expressed by Arrhenius equation. -The partial molar volume of CO <sub>2</sub> is smaller than in rubbery polymers and no appreciable temperature dependence in the range of 15-75°C

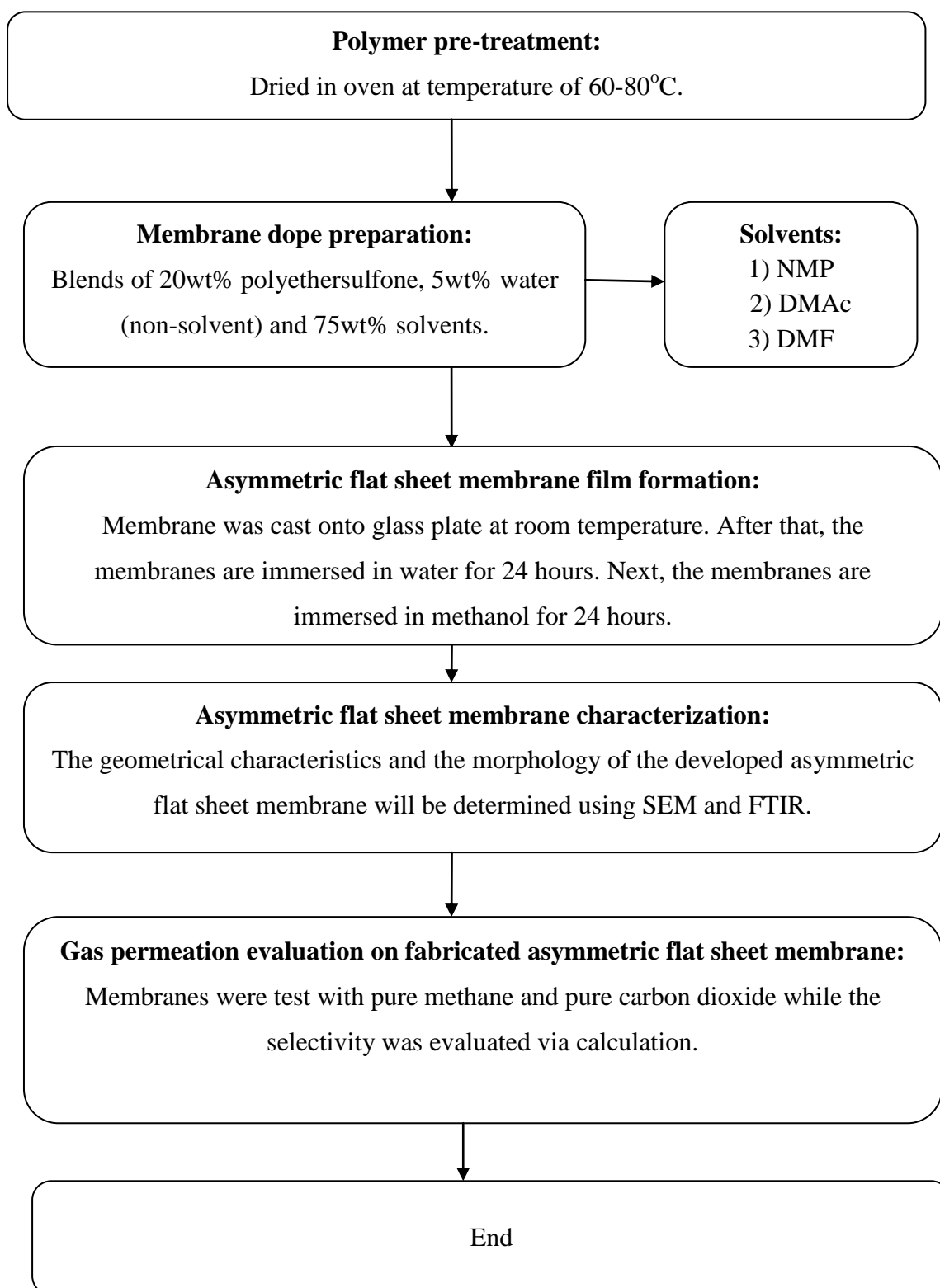
3.	Ettouney & Majeed, 1997	Silicone rubber and polysulfone membrane/ $\text{CO}_2$ , $\text{N}_2$ , $\text{O}_2$ , & $\text{CH}_4$	<p>-Feed flow rate used are <math>3.33 \times 10^{-5}</math>, <math>6.67 \times 10^{-5}</math>, <math>1 \times 10^{-4}</math> and <math>1.33 \times 10^{-4}</math>.</p> <p>-Absolute pressure used in the experiment is 239.2, 377, 514.9 and 790.6 kPa.</p> <p>-High permeability is in <math>\text{CO}_2</math> mixture, followed by the pure gas and the lowest is found in the air gas mixture.</p> <p>-Permeability of the polysulfone membrane, faster species is reduced in mixture with slower species (<math>\text{CO}_2</math> against <math>\text{O}_2</math>, <math>\text{N}_2</math> or <math>\text{CH}_4</math>) and (<math>\text{O}_2</math> against <math>\text{N}_2</math> or <math>\text{CH}_4</math>).</p> <p>-Permeability of species is only affected by presence of faster permeating species such as <math>\text{CO}_2</math> or <math>\text{O}_2</math>.</p> <p>-<math>P_{\text{CO}_2/\text{PSU}} = 1.1 \times 10^{-6}</math> to <math>3.3 \times 10^{-7}</math></p> <p>-<math>P_{\text{CH}_4/\text{PSU}} = 1.4 \times 10^{-8}</math> to <math>3.5 \times 10^{-8}</math></p> <p>-<math>S_{\text{CO}_2/\text{CH}_4} = 23</math> to 32.4</p>
4.	Xu <i>et al.</i> , 1997	<p>-Poly (phenylenethioetherimides)s (PPTI), 2,2-bis(3,4-decarboxyphenyl) hexafluoropropane dianhydride (6FDA), poly(1,4-phenylenethioether)(PPT) or poly(1,4-phenylenesulfide)</p> <p>-<math>\text{CO}_2</math>, <math>\text{O}_2</math>, <math>\text{N}_2</math>, <math>\text{CH}_4</math> (at temperature of <math>35^\circ\text{C}</math>).</p>	<p>-6FDA/PPTI-4 polyimide shows higher permeability and selectivity towards <math>\text{CO}_2/\text{CH}_4</math> system than PPT.</p> <p>-<math>P_{\text{CO}_2}</math> 6FDA/PPTI=6.62-23.11</p> <p>-<math>P_{\text{CH}_4}</math> 6FDA/PPTI=0.22-0.66</p> <p>-<math>D_{\text{CO}_2}</math> 6FDA/PPTI=1.53-3.54</p> <p>-<math>D_{\text{CH}_4}</math> 6FDA/PPTI=0.19-0.39</p> <p>-<math>S_{\text{CH}_4}</math> 6FDA/PPTI=0.71-1.29</p> <p>-<math>S_{\text{CO}_2}</math> 6FDA/PPTI=2.98-4.96</p> <p>-<math>P_{\text{CO}_2}/P_{\text{CH}_4}</math> 6FDA/PPTI=25.42-34.79</p> <p>-<math>D_{\text{CO}_2}/D_{\text{CH}_4}</math> 6FDA/PPTI=6.09-9.07</p> <p>-<math>S_{\text{CO}_2}/S_{\text{CH}_4}</math> 6FDA/PPTI=3.84-4.18</p>

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Research design**

This chapter covers the type of materials used to fabricate the asymmetric flat sheet membrane as well as the experimental procedures and methods used to test this new membrane. Basically, there are two main steps involve in asymmetric flat sheet membrane formation. They are (1) preparation of the membrane dope solution and (2) casting the membrane dope solution to form an asymmetric flat sheet membrane film. The selection of suitable membrane material also plays an important role in achieving the best performance in membrane separation process. Figure 3.1 shows the research design for this study.



**Figure 3.1:** Research design flowchart

## **3.2 Material selection**

In asymmetric flat sheet membrane formation, selection of suitable polymer and solvent is an important aspect. This section will discuss about the selection of the materials and the attractive criteria that had been fulfilled by this materials.

### **3.2.1 Polymer selection**

#### **3.2.1.1 Polyethersulfone (PES)**

Polyethersulfone were selected as the polymer to be use in this study. PES contains sulfone and ether groups in the main chain. PES is a tough and rigid resin similar to conventional engineering plastics at room temperature. The greatest characteristic of PES is that it has by far better high-temperature properties than conventional engineering plastics. Specifically, PES remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200°C. This polymer several excellent properties:

- ✓ High chemical resistance.
- ✓ Stable to oxygen and to thermal degradation.
- ✓ Good electrical insulation properties, which make it preferable to be use in electrical/electronic industries.
- ✓ Have high mechanical values.
- ✓ Excellent resistance to combustibility.

PES are unaffected by hydrocarbon and aqueous acids and bases, and only slightly affected by alcohols and detergent solutions. Table 3.1 shows the physical properties of Polyethersulfone (PES).

**Table 3.1:** Physical Properties of Polyethersulfone (PES).

Physical Properties	Descriptions
Density	1.37gcm <sup>-3</sup>
Flammability	V-0 at 0.4mm
Limiting Oxygen Index	34-41%
Radiation Resistance	Good Fair
Water Absorption-Equilibrium	2.2%
Water Absorption-Over 24 hours	0.4-1%
Resistance to Ultraviolet	Fair
Coefficient of Thermal Expansion	55 x 10 <sup>-6</sup> K <sup>-1</sup>
Heat Deflection Temperature-0.45MPa	> 260°C
Heat Deflection Temperature-1.8MPa	203°C
Lower Working Temperature	-110°C
Thermal Conductivity at 23°C	0.13-0.18Wm <sup>-1</sup> K <sup>-1</sup>
Upper Working Temperature	180-220°C
Dielectric Constant at 1MHz	3.7
Dielectric Strength at 25µm Thick	232 KVmm <sup>-1</sup>
Elongation at Break	20-150%
Initial Tear Strength	7.5-16.9gµm <sup>-1</sup>
Permeability to Oxygen at 25°C	0.4 x 10 <sup>-13</sup> cm <sup>3</sup> .cm cm <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup>
Permeability to Water at 38 °C	1200 x 10 <sup>-13</sup> cm <sup>3</sup> .cm cm <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup>
Specific Heat	1.1 kJ.kg <sup>-1</sup> K <sup>-1</sup>

### 3.2.2 Solvent selection

#### 3.2.2.1 N-methyl-2-pyrrolidone (NMP)

NMP solvent is N-methyl-2-pyrrolidone, the lactam of 3-methylaminobutyric acid. NMP is chosen as the solvent because it has good chemical stability, high solvency and high boiling point. Having no active hydrogen, this remarkably stable

heterocyclic compound is classified as an aprotic solvent and is uniquely suitable as a chemical reaction medium. Its low flammability, low volatility, biodegradability, low aquatic toxicity and recyclability make it suitable as a replacement for hazardous solvents. Table 3.2 shows the physical properties of N-methyl-2-pyrrolidone (NMP).

**Table 3.2:** Physical Properties of N-methyl-2-pyrrolidone (NMP).

Physical Properties	Description
Molecular Formula	C <sub>5</sub> H <sub>9</sub> NO
Molar Mass	99.13 g/mol
Density	1.028 g/cm <sup>3</sup>
Melting Point	-24°C
Boiling Point	202-204°C

### 3.2.2.2 Dimethylformamide (DMF)

DMF solvent is Dimethylformamide, is the organic compound with the formula (CH<sub>3</sub>)<sub>2</sub>NC(O)H. DMF is one of the solvent that is will be use in this study. DMF is a common solvent for chemical reactions. Pure DMF is odourless whereas technical grade or degraded DMF often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid. DMF is a polar (hydrophilic) aprotic solvent with high boiling point. Table 3.3 shows the physical properties of Dimethylformamide (DMF).

**Table 3.3:** Physical Properties of Dimethylformamide (DMF)

Physical Properties	Description
Molecular Formula	C <sub>4</sub> H <sub>9</sub> NO
Molar Mass	87.12 g/mol
Density	0.97 g/cm <sup>3</sup>
Melting Point	-20°C
Boiling Point	164-166°C



### 3.2.2.3 Dimethylacetamide (DMAc)

DMAc solvent is dimethylacetamide, is the organic compound with the formula  $\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$ . DMAc is also one of the solvent that will be use in this study. DMAc is a clear oily liquid miscible in all proportion with water; melting point  $-20^\circ\text{C}$ , boiling point  $165^\circ\text{C}$  at 1013 hPa. It is dissolved in most organic solvents except aliphatic hydrocarbon. DMAc is produced from acetic acid and dimethylamine. DMAc is a dipolar aprotic solvent with a high boiling point. DMAc is a good reaction medium and catalyst. It is also used as an extraction agent for gases and oils. Table 3.4 shows the physical properties of Dimethylacetamide (DMAc).

**Table 3.4:** Physical Properties of Dimethylacetamide (DMAc)

Physical Properties	Description
Molecular Formula	$\text{C}_3\text{H}_7\text{NO}$
Molar Mass	73.09 g/mol
Density	$0.944\text{ g/cm}^3$
Melting Point	$-61^\circ\text{C}$
Boiling Point	$153^\circ\text{C}$

### 3.2.3 Coagulation Medium

#### 3.2.3.1 Methanol

Methanol also known as methyl alcohol, wood alcohol, wood naphtha or wood spirits is a chemical with formula  $\text{CH}_3\text{OH}$ . It is the simplest aliphatic alcohol and is the first member of the homologous series. Methanol is a colourless liquid, completely miscible with water and organic solvents and is very hygroscopic. Methanol has an agreeable odour and a burning taste. Methanol has a melting point

97°C, boiling point 65°C and relative density 0.8. Table 3.5 shows the physical properties of Methanol.

**Table 3.5:** Physical Properties of Methanol

Physical properties	Description
Molecular Formula	CH <sub>4</sub> O
Molar Mass	32.04 g/mol
Density	0.7918 g/cm <sup>3</sup>
Melting Point	-97°C
Boiling Point	64.7°C

### 3.2.4 Non-solvent

#### 3.2.4.1 Water

Non-solvent that is used in dope solution formulation is water. Water is the chemical substance with chemical formula H<sub>2</sub>O: one molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. Water is a good solvent and is often referred to as the universal solvent. Substances that dissolve in water are known as hydrophilic substances while those that do not mix well with water are known as hydrophobic substances. Table 3.6 shows the physical properties of water.

**Table 3.6:** Physical Properties of Water

Physical Properties	Description
Molecular Formula	H <sub>2</sub> O
Molar Mass	18.01528 g/mol
Density	1000kg/m <sup>3</sup>
Melting Point	0°C
Boiling Point	99.98°C

### 3.3 Penetrants

In this study, pure carbon dioxide and pure methane will be use. Table 3.7 shows the properties of the penetrants.

**Table 3.7:** Properties of the penetrants

	<b>Methane</b>	<b>Carbon dioxide</b>
<b>Formula</b>	CH <sub>4</sub>	CO <sub>2</sub>
<b>Molecular weight</b>	16.043 g/mol	44.010 g/mol
<b>Melting point</b>	-182.5 °C	-78 °C
<b>Boiling point</b>	-161.6 °C	-57 °C

### 3.4 Coating Solution

#### 3.4.1 Polydimethylsiloxane (PDMS)

Polydimethylsiloxane (PDMS) belongs to a group of polymeric organosilicon compound that are commonly reffered to as silicones. PDMS is the most widely used silicon based organic polymer and it is particularly known for its unusual rheological properties. PDMS is optically clear and in general, is considered to be inert, non-toxic and non-flammable. It is occasionally called dimethicone and is one of several type of silicone oil (polymerized siloxane). Table 3.8 shows the physical properties of Polydimethylsiloxane (PDMS).

**Table 3.8:** Physical Properties of Polydimethylsiloxane (PDMS)

<b>Physical Properties</b>	<b>Description</b>
Molecular Formula	(C <sub>2</sub> H <sub>6</sub> OSi) <sub>n</sub>
Specific Heat	1.46 kJ/kg.K
Density	965 kg/m <sup>-3</sup>

Poison Ratio	0.5
Thermal Conductivity	0.15 W/m.K

### 3.4.2 n-Hexane

n-hexane is a very volatile aliphatic hydrocarbon. It is a constituent in the paraffin fraction of crude oil and natural gas and is also used as an industrial chemical and laboratory reagent. Laboratory grade n-hexane contains approximately 99% n-hexane. Hexane is a commercial and industrial product consisting of a mixture of hydrocarbons with six carbon atoms and includes n-hexane and its isomers 2-methylpentane and 3-methylpentane as well as small amounts of other hydrocarbons. Table 3.9 shows the physical properties of n-hexane.

**Table 3.9:** Physical Properties of n-Hexane

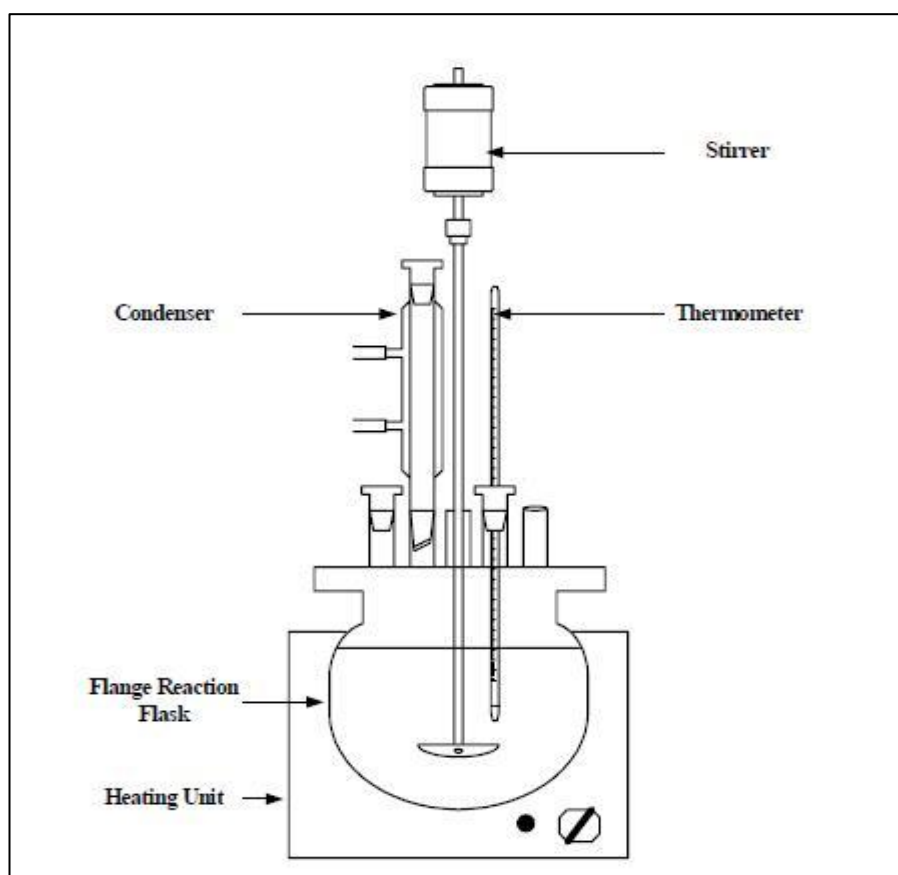
Physical Properties	Description
Molecular Formula	$C_6H_{14}$
Molar Mass	86.10 g/mol
Density	$0.66 \text{ g/cm}^3$
Boiling Point	$68.95^\circ\text{C}$
Melting Point	$-95.3^\circ\text{C}$

### 3.5 Dope solution preparation

In asymmetric flat sheet membrane formation, the dope solution should contain three main materials which are (i) polymer (ii) solvent and (iii) non-solvent. Initially, the polymer was dried in a vacuum condition at  $80^\circ\text{C}$  for at least 24 hours. This drying process is done to remove moisture content during storage. These polymers then dispersed into NMP/DMF/DMAc solvent. The slurry solutions were stirred for 4 hours to homogeneously distribute the polymer particles in the solution. The round bottom solution vessel was used to prepare the solution. The function of

stirrer is to make sure that the polymer, solvent and non-solvent can mix well in order to form a homogeneous solution. The thermometer measured the temperature during the mixing process. The processing temperature should be controlled in a suitable and optimum temperature range by the heater and the condenser.

In this study, the dope solution was prepared in a controlled temperature of 60°C to 80°C, which is the working temperature of the solvents. In order to remove all the water vapor from the polymer and equipment, they had been heated in the oven respectively at least for overnight before the solution was prepared. The existence of water in the polymer solution will influence the purity as well as quality of a polymer solution. The dope solution is now ready to go through membrane casting process. The same steps are repeated to prepare the dope solution by using different solvent. Figure 3.2 show the apparatus setup for dope solution preparation.



**Figure 3.2:** Dope Solution Preparation Vessel (Cheer, 2002)

### **3.6 Asymmetric Flat Sheet Membrane Film Formation**

Using manually casting block, Polyethersulfone membrane was prepared according to dry/wet phase separation process followed by the immersion in a non-solvent bath and membrane drying. Casting process was conducted at room temperature ( $30^{\circ}\text{C}\pm 2$ ). A small amount of dope solution was poured onto a glass plate with a casting block gap setting of  $0.4\mu\text{m}$ . To remove the membrane film from the glass plate, the glass plate and the membrane are immersed into water to initiate delamination and slightly peel the membrane film from the glass plate. After that, the membrane is transferred and immersed into the coagulation medium with water as the coagulant medium for one day. Finally, it is washed with methanol for one day. Then, it was dried for at least two days at room temperature. This was done in order to remove any residual organic compound left in the membrane.

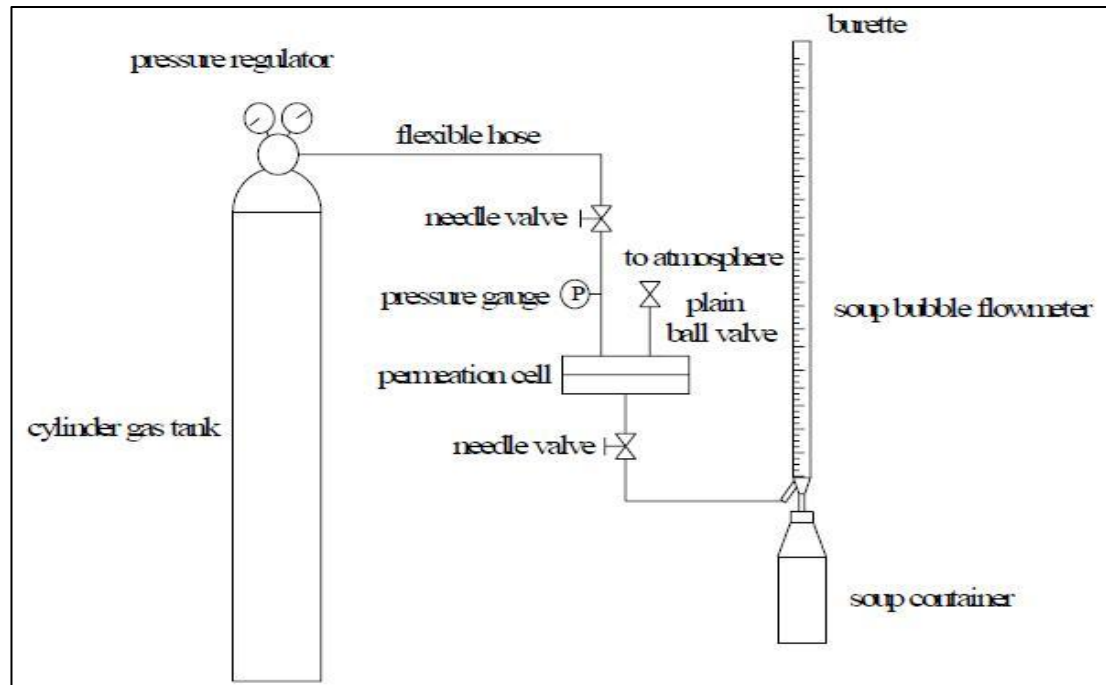
### **3.7 Membrane Coating with Polydimethylsiloxane (PDMS)**

3wt% of coating solution was prepared by dissolving Polydimethylsiloxane (PDMS) (Sylgard-184) in n-hexane. The membrane was cut into a circular disc in a range of  $24\text{-}25\text{ cm}^2$  in area. The solution was slowly pouring onto the top layer of the membrane for 5 minutes. Then, it was removed and allowed to cure at room temperature for 24 hours before it can be used for gas permeation test.

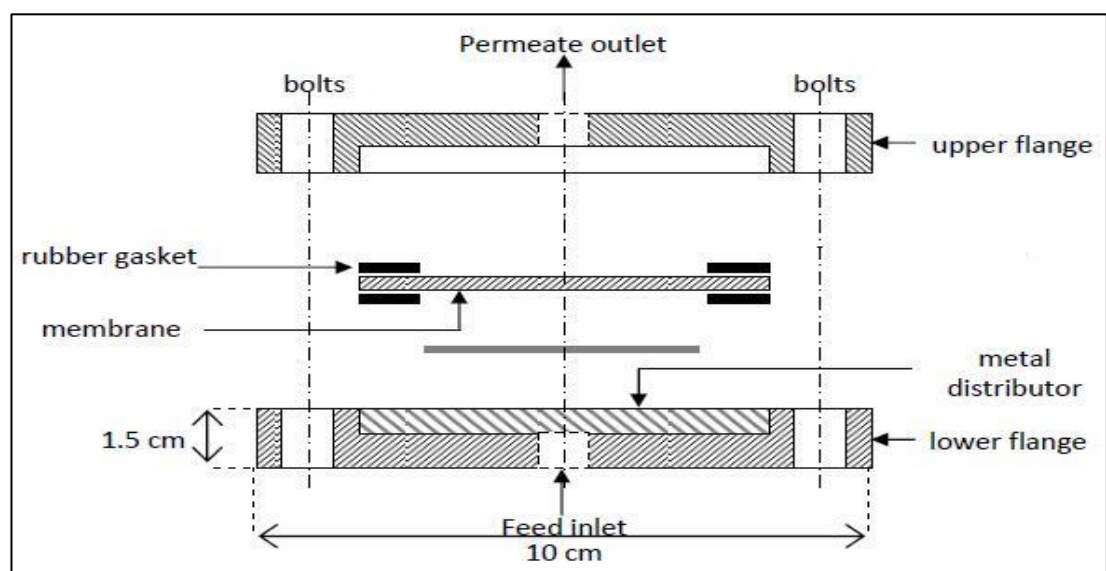
### **3.8 Gas Permeation Test**

The coated asymmetric flat sheet membrane is tested on pure gas  $\text{CO}_2$  and  $\text{CH}_4$ . Pure gas permeation test is done to examine the separation ability of a fabricated membrane under ideal conditions. The membrane was firstly cut into a small circle to be pleated and folded around the permeate core. The fitting of the gas hose and permeability unit is ensured to be suiting each other to avoid gas leakage. The pure gas will be tested at pressure in the range of 1 bar to 3 bar. The  $\text{CO}_2$  permeability test is being conducted once the permeability unit have ready by flowing the  $\text{CO}_2$  gas through the membrane fitted in it. The time of the first bubble

formed and volume difference of the soap water by each membrane was taken. Figure 3.3 shows the gas permeation test apparatus and Figure 3.4 shows the cross-sectional view of assembled permeation cell and gas flow direction.



**Figure 3.3:** Gas Permeation Test Apparatus (Cheer, 2002)



**Figure 3.4:** A cross-sectional view of assembled permeation cell and gas flow direction (Cheer, 2002)

The permeation rate can be calculated by using:

$$P_i = Q/A \cdot \Delta P = P_i/l$$

Where: Q= Gas Flowrate (cm<sup>3</sup>/s)

A= Area (cm<sup>2</sup>)

$\Delta P$ = Pressure in System (cm Hg)

$P_i$  = Permeability for Gas Component (cm<sup>3</sup>/s.cm<sup>2</sup>.cm Hg)

1 GPU = 1x10<sup>-6</sup> cm<sup>3</sup>/s.cm<sup>2</sup>.cm Hg

The selectivity can be calculated by using:

$$\text{Selectivity, } \alpha = P_i/P_j$$

Where:  $P_i$  = Permeability of one gas component

$P_j$  =Permeability of another gas component

### **3.9 Characterization**

#### **3.9.1 Scanning Electron Microscopy (SEM)**

The geometrical characteristics and the morphology of the developed asymmetric flat sheet membrane will be determined using scanning electron microscopy (SEM). Images of fiber surface, skin layer structure and cross sections of membrane prepared by using different solvents can be viewed clearly. The dried films will be broken in liquid nitrogen and will be sputtered with a thin layer of platinum using a sputtering apparatus. After that, the samples will be imaged and photographed by employing a scanning electron microscope.



### **3.9.2 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier Transform Infrared Spectroscopy (FTIR) is a very useful tool to detect the existence of the functional groups in a membrane. The FTIR results can display changes of the functional groups and elements in the membranes when they are heated from room temperature to high temperature, which is up to 250°C. In this study, this characterization technique is important to show us the effect of different solvent used in membrane to the membrane structure.

## CHAPTER 4

### RESULTS & DISCUSSIONS

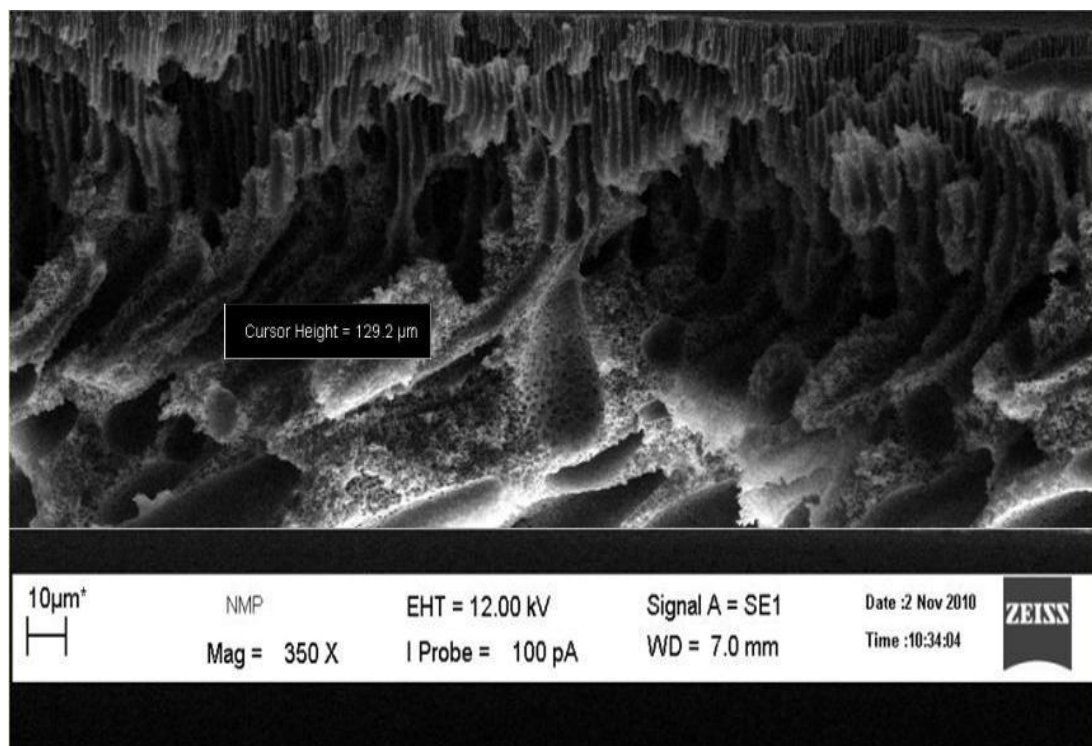
#### 4.1 Effect of Solvents on the Structure of Membrane

Generally, the higher the melting and boiling point of any material implies that the higher the viscosity will be. Based on Chemical Safety Data Sheet (CSDS), the boiling point of N-methyl-2-pyrrolidone (NMP) is greater than Dimethylacetamide (DMAc) and Dimethylformamide (DMF). Thus, the viscosity of the dope solution produced with N-methyl-2-pyrrolidone (NMP) solvent is higher. The solvents physical properties are tabulated in Table 4.1.

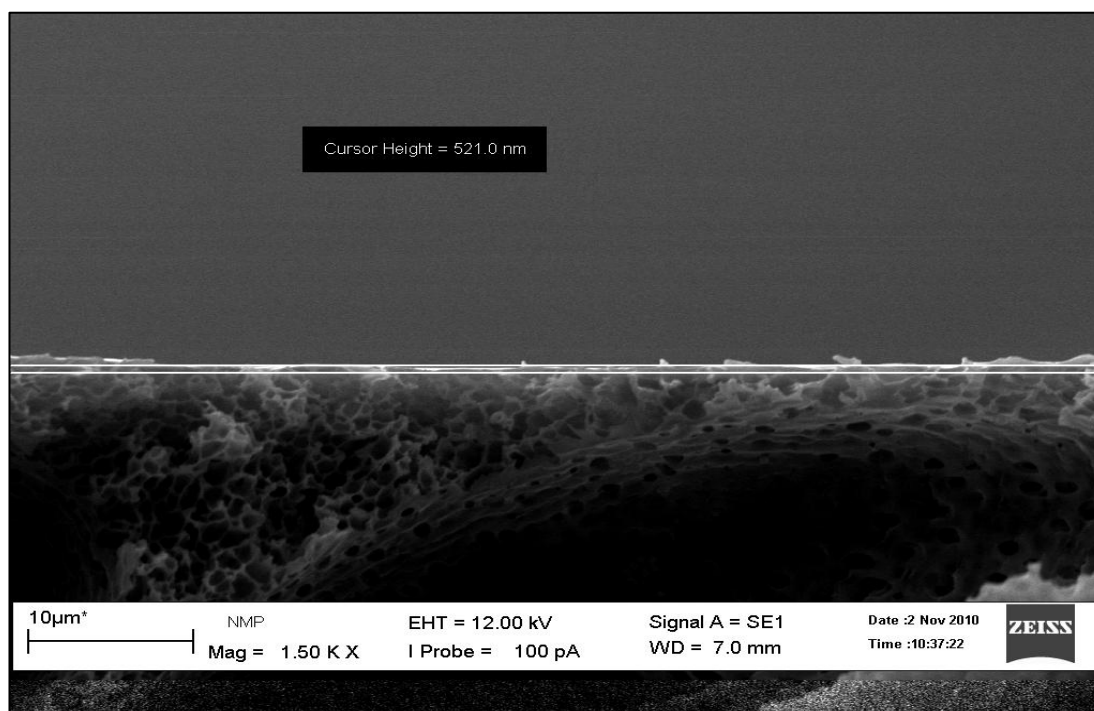
**Table 4.1:** Physical Properties of Various Solvents Used

Physical Properties	NMP	DMAc	DMF
Boiling Point	202-204°C	164-166°C	153°C
Melting Point	-24°C	-20°C	-61°C

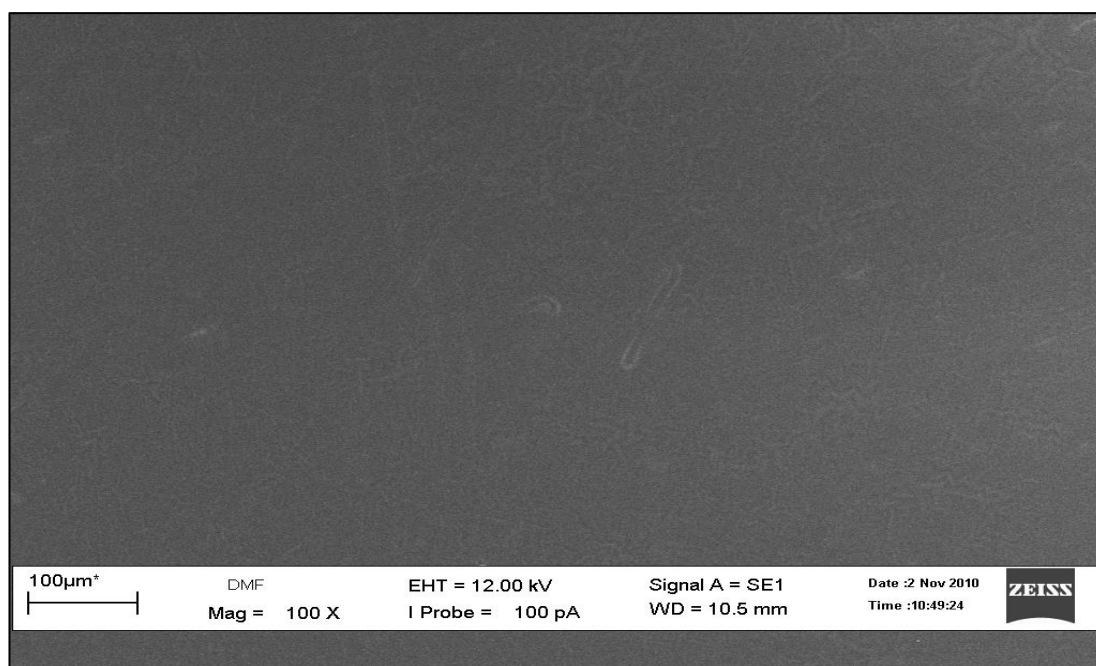
The viscosity and boiling point of the solvent will determine the interaction between solvent and non-solvent of the system. If interaction is good enough, an adequate performance and homogenous membrane can be produced. Figure 4.1 to 4.9 shows the Scanning Electron Microscope (SEM) of the Polyethersulfone asymmetric flat sheet membrane produced with different type of solvents.



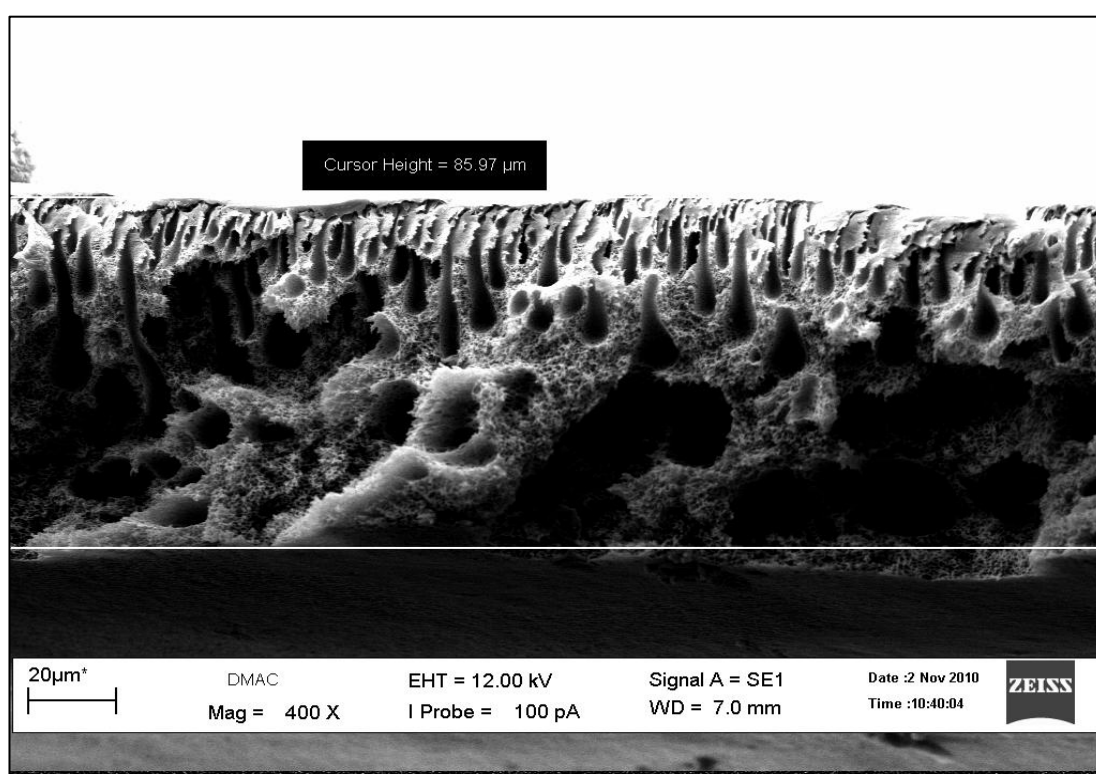
**Figure 4.1:** Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using NMP as Solvent at Magnification 350X



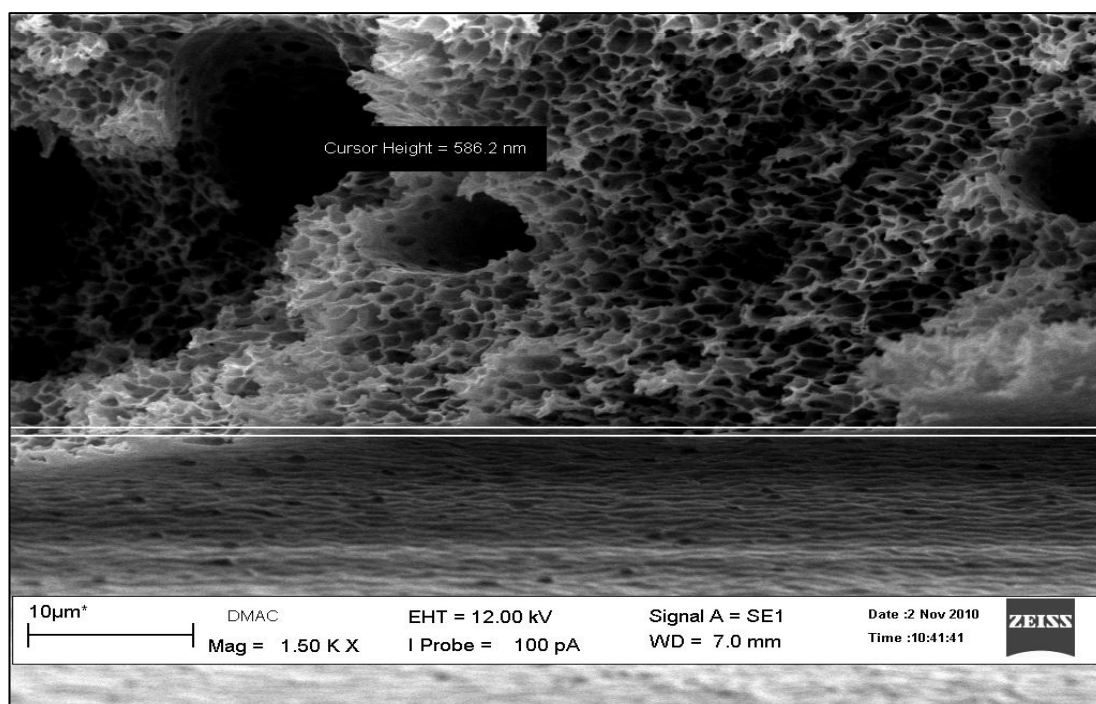
**Figure 4.2:** Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using NMP as Solvent at Magnification 1.50kX



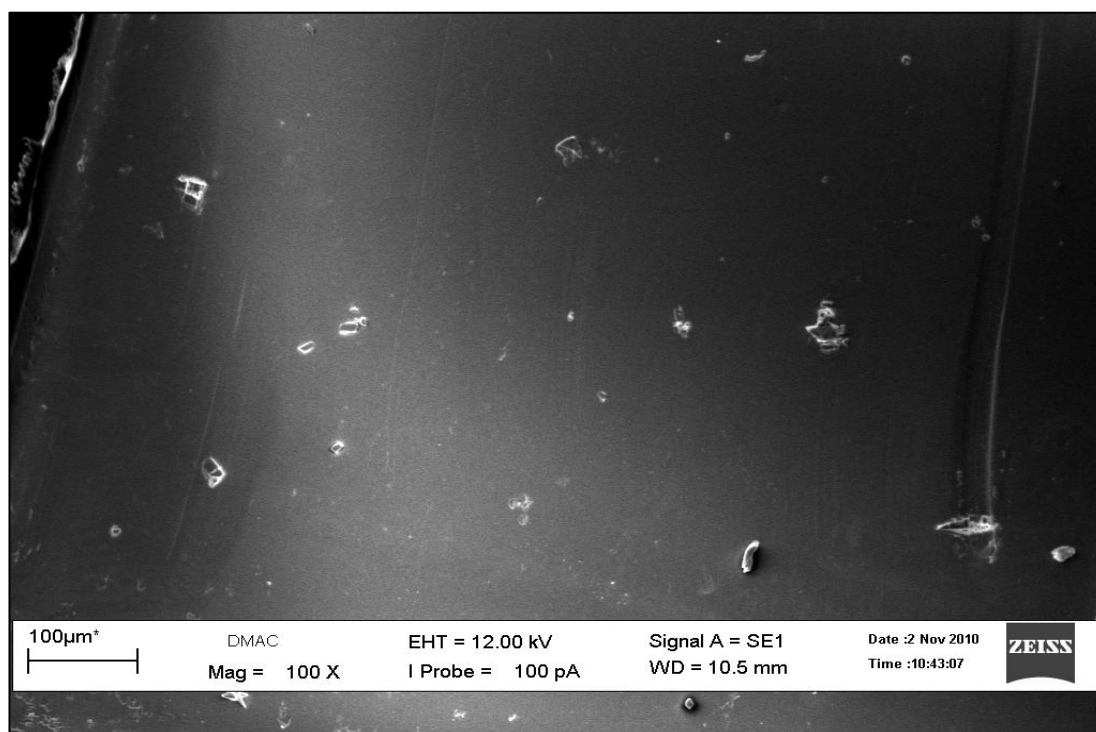
**Figure 4.3:** The Surface Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using NMP as Solvent at Magnification 100X



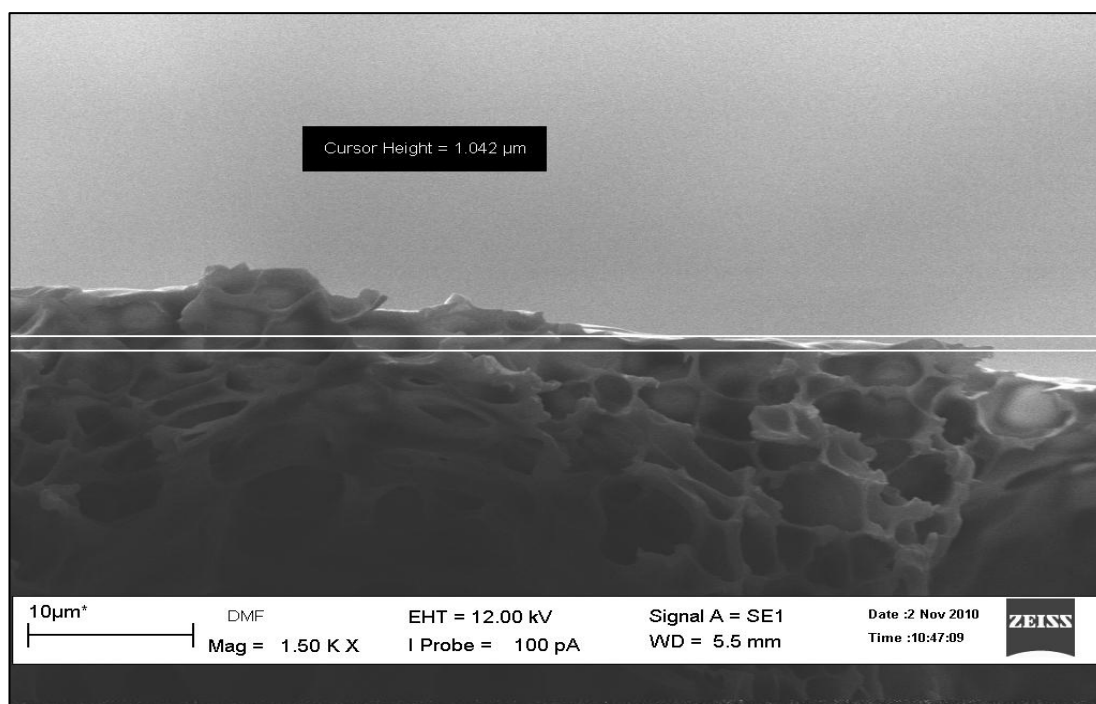
**Figure 4.4:** Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using DMAc as Solvent at Magnification 400X



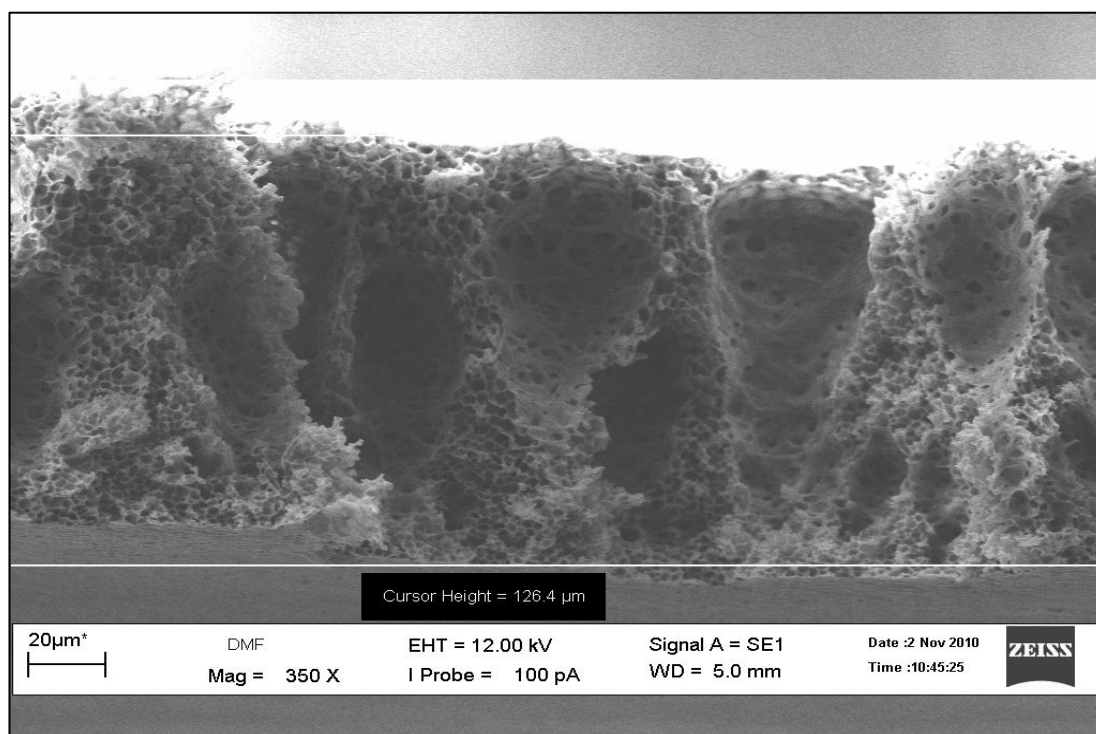
**Figure 4.5:** Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using DMAc as Solvent at Magnification 1.50kX



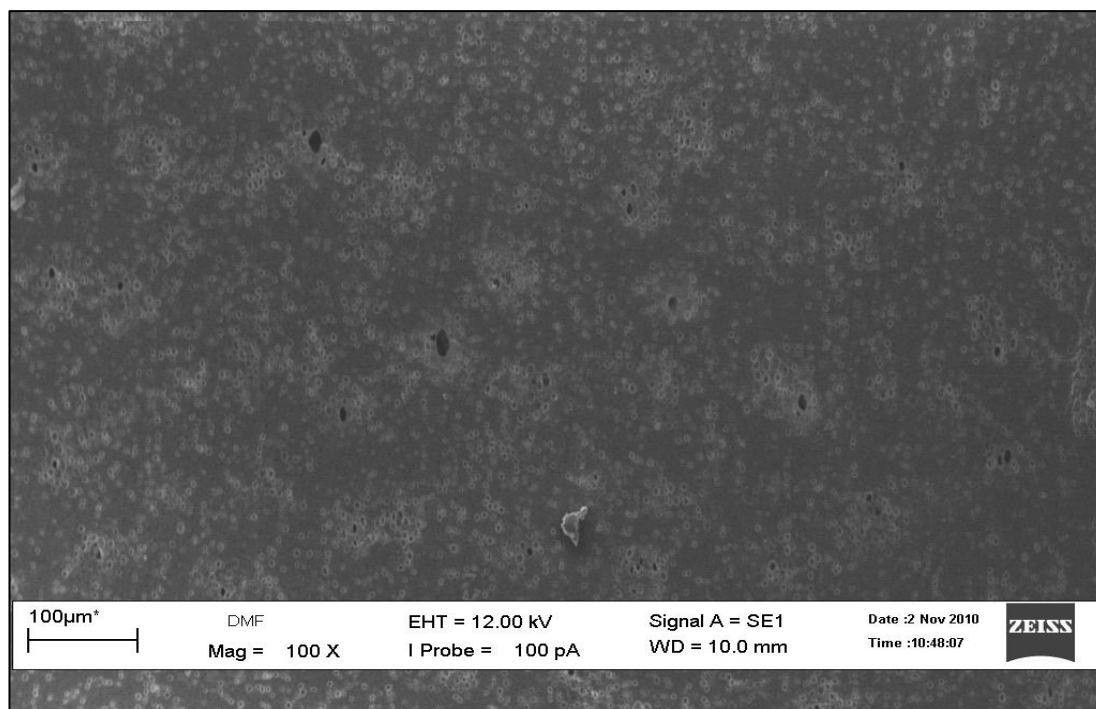
**Figure 4.6:** The Surface Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using DMAc as Solvent at Magnification 100X



**Figure 4.7:** The Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using DMF as Solvent at Magnification 1.50kX



**Figure 4.8:** The Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using DMF as Solvent at Magnification 350X



**Figure 4.9:** The Surface Structure of Polyethersulfone Asymmetric Flat Sheet Membrane using DMF as Solvent at Magnification 100X.

N-methyl-2-pyrrolidone (NMP) (Figure 4.1 to 4.3) displays the best structure as compared to Dimethylacetamide (DMAc) (Figure 4.4 to 4.6) and Dimethylformamide (DMF) (Figure 4.7 to 4.9). The finger-like structure with straight pore length is the most important criteria for causing a good separation. From observation, the membrane structure of N-methyl-2-pyrrolidone (NMP) based membrane fulfills the requirement to be a high performance asymmetric flat sheet membrane. It has specifications such as apparent skin layer and more open structure beneath the skin with asymmetric region. The porosity and thickness of the top layer, porosity of the sublayer and presence of finger-like can be determined too. The spongy structure at the top layer provided a good permeability and function as a support to the skin layer of the NMP membrane. The finger-like layer provided enough resistance to support the membrane upon any applied pressure. The thickness of spongy top layer and finger-like structure determined were 521nm and 129.2μm respectively.



Besides that, an asymmetric flat sheet membrane structure from top to bottom layer with homogeneous region can be seen clearly. This condition occurred due to the influence of the prepared dope solution viscosity. Since dope solution with N-methyl-2-pyrrolidone (NMP) as solvent have higher viscosity than others, straight pore from top to bottom layer was formed. Viscosity of the dope solution can also affect the pore size at the skin layer. Membrane with N-methyl-2-pyrrolidone (NMP) as solvent produce a small pores membrane.

Figure 4.4 to 4.6 shows the morphological structure of Dimethylacetamide (DMAc) solvent-membrane. It has a skin layer that determined the separation selectivity, spongy structure at top layer for diffusion and macrovoid at the bottom. This membrane might perform well based on the existence of the finger-like structure but it was not good enough to be a high performance membrane. This is because it possessed good separation ability but did not have good pressure resistance. The macrovoids could cause the membrane to rupture or leaking if high pressure is applied in the separation process. The slanting finger-like structure is produced due to the interaction between solvent and non-solvent of the prepared dope solution. The more slanting type structure formed means the lower the interaction between solvent and non-solvent of the membrane system before immersion in coagulant bath. This is because the evaporation rate of the solvent is higher than the permeation rate of the non-solvent into the membrane. This Dimethylacetamide (DMAc) solvent-membrane sponge layer thickness was  $85.97\mu\text{m}$  and the skin thickness was  $586.2\text{nm}$ . Thus, Dimethylacetamide (DMAc) turned up to be quite unsuitable solvent for the preparation of high performance Polyethersulfone (PES) asymmetric flat sheet membrane for gas separation.

Figure 4.7 to 4.9 shows the cross sectional area of membrane using Dimethylformamide (DMF) as solvent. Like Dimethylacetamide (DMAc), this membrane might still perform well since it was only influenced by the selectivity of skin layer. On the other hand, the top layer structure was not as good as Dimethylacetamide (DMAc) membrane. From observation, the membrane structure consists of skin layer that determine separation selectivity. As compared to DMAc and NMP, DMF has the lowest boiling point. The boiling point did influence the interaction between solvent and non-solvent in the membrane system and hence the



structure of the membrane. A membrane with no sponge type structure has a very low-pressure resistance. The skin layer of this Dimethylformamide (DMF) membrane is measured to be 1.042 $\mu\text{m}$ ; the spongy structure should exist to be a support to the skin layer. This Dimethylformamide (DMF) solvent-membrane thickness was measured to be 126.4 $\mu\text{m}$ . The membrane morphologies produced by those three different solvents proved that the interaction between solvent and non-solvent is the major factor that influences the structure of the produced membrane.

## 4.2 Effect of Solvents on the Membrane Performance for Gas Separation

In this study, the performance of the membrane produced is evaluated by conducting gas permeation test. The permeation rate can be calculated by using:

$$P_i = Q/A \cdot \Delta P = P_i/l$$

Where: Q= Gas Flowrate ( $\text{cm}^3/\text{s}$ )

A= Area ( $\text{cm}^2$ )

$\Delta P$ = Pressure in System (cm Hg)

$P_i$  = Permeability for Gas Component ( $\text{cm}^3/\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg}$ )

1 GPU =  $1 \times 10^{-6} \text{ cm}^3/\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg}$  (The calculated permeability should be converted in GPU unit).

The selectivity can be calculated by using:

$$\text{Selectivity, } \alpha = P_i/P_j$$

Where:  $P_i$  = Permeability of one gas component

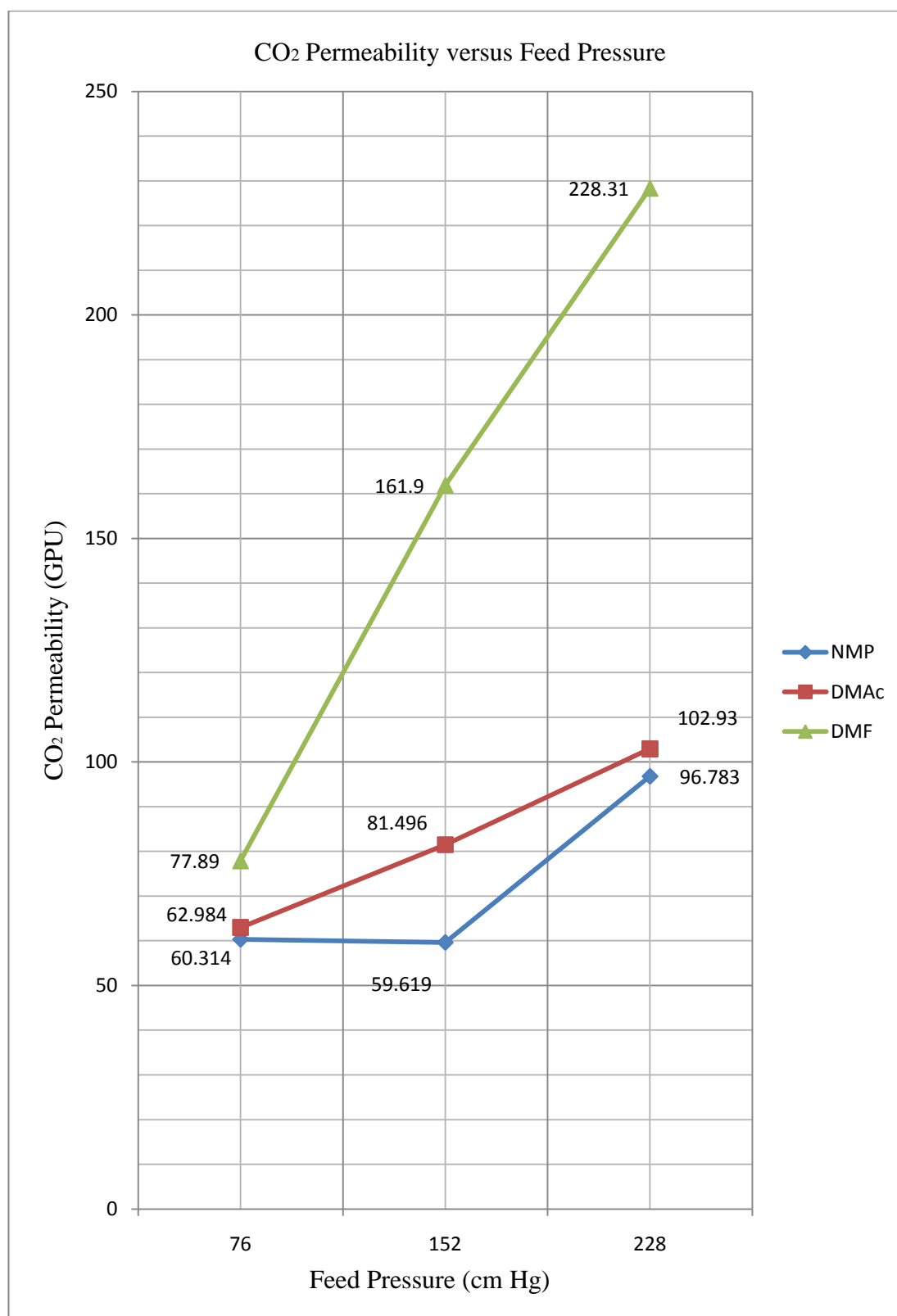
$P_j$  = Permeability of another gas component

The permeation test were performed using a permeation cell with an effective permeation area of 24.63 $\text{cm}^2$ . Table 4.2 shows the tabulated calculation result of permeability and selectivity of each membrane produced using various solvents.

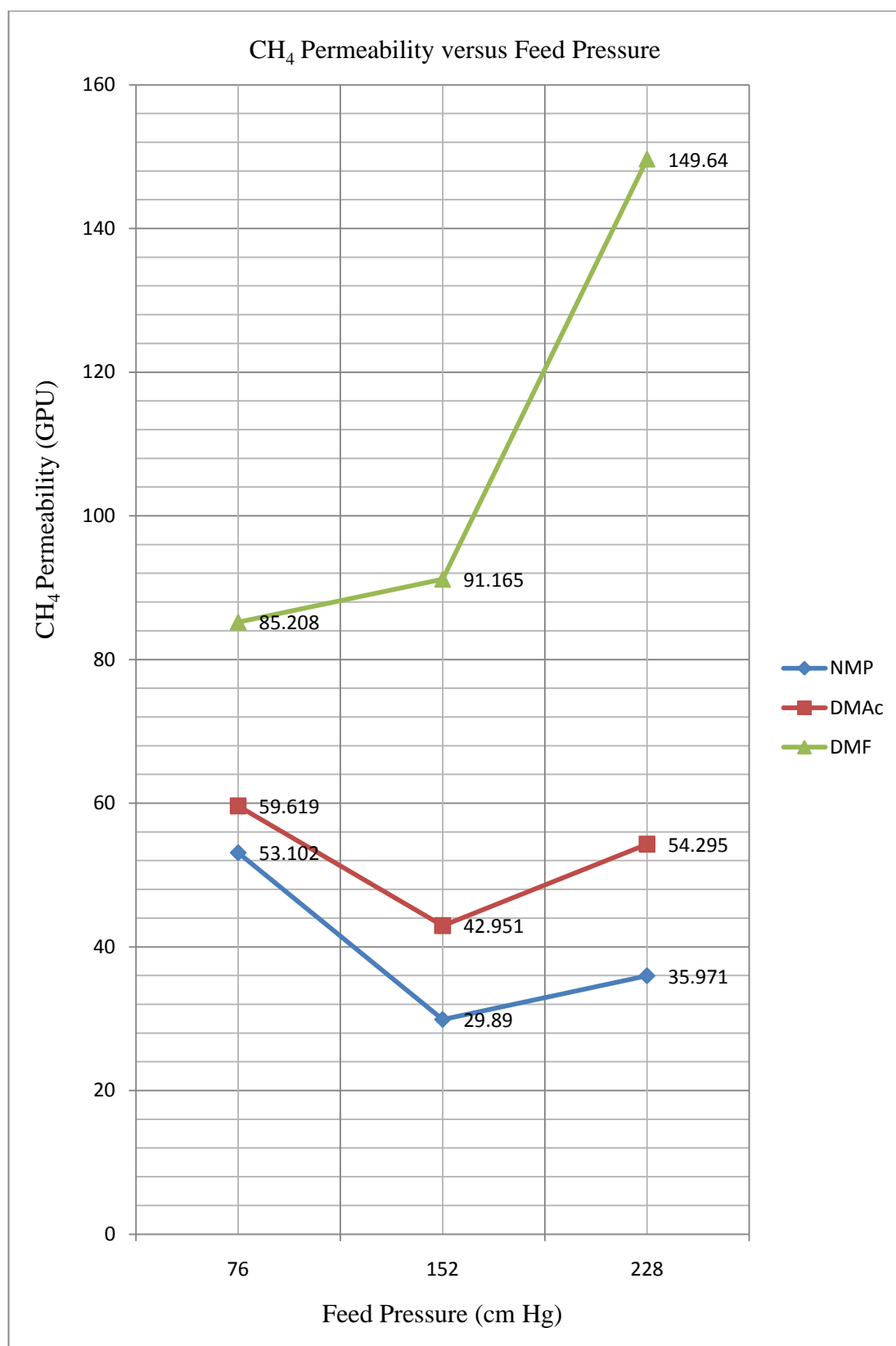
**Table 4.2:** Tabulated Calculation Result of Permeability and Selectivity of Membrane

Membrane Solvents	Pressure (cm Hg)	Permeability (GPU)		Selectivity $\alpha(\text{CO}_2/\text{CH}_4)$
		CO <sub>2</sub>	CH <sub>4</sub>	
NMP	76	60.314	53.102	1.1358
	152	59.619	29.890	1.9946
	228	96.783	35.971	2.6906
DMAc	76	62.984	59.619	1.0564
	152	81.496	42.951	1.8974
	228	102.93	54.295	1.8958
DMF	76	77.890	85.208	0.9141
	152	161.9	91.165	1.7759
	228	228.31	149.64	1.5257

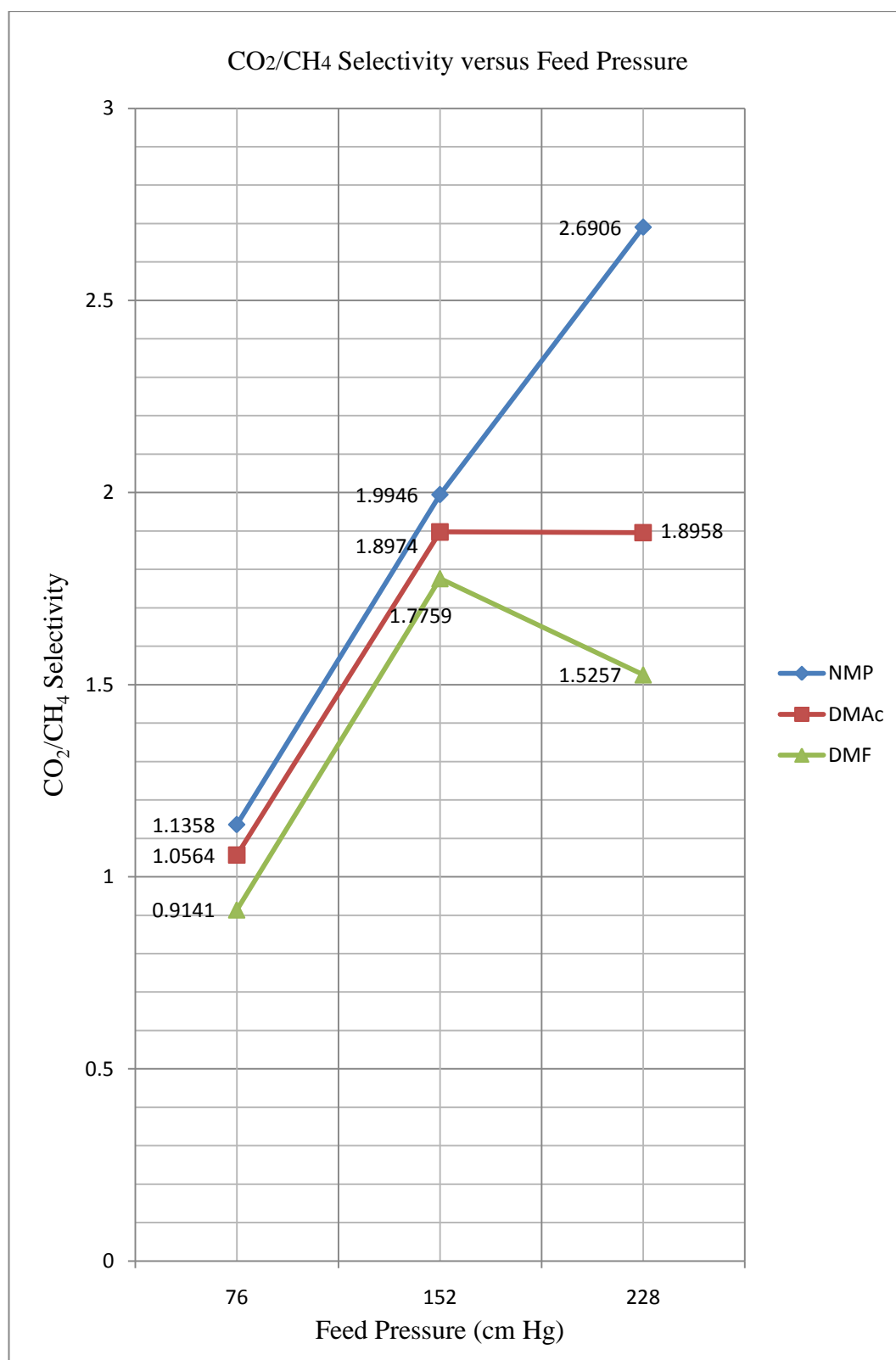
The gas separation characteristic is determined by plotting the permeance of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity of each membrane produced from different solvents against the feed pressure. The permeance of CO<sub>2</sub> and CH<sub>4</sub> of various solvent-membranes are presented in Figure 4.10 and 4.11 respectively while the CO<sub>2</sub>/CH<sub>4</sub> selectivity is presented in Figure 4.12.



**Figure 4.10:** CO<sub>2</sub> Permeance of Membranes Prepared using various Solvents against Feed Pressure



**Figure 4.11:** CH<sub>4</sub> Permeance of Membranes Prepared using various Solvents against Feed Pressure



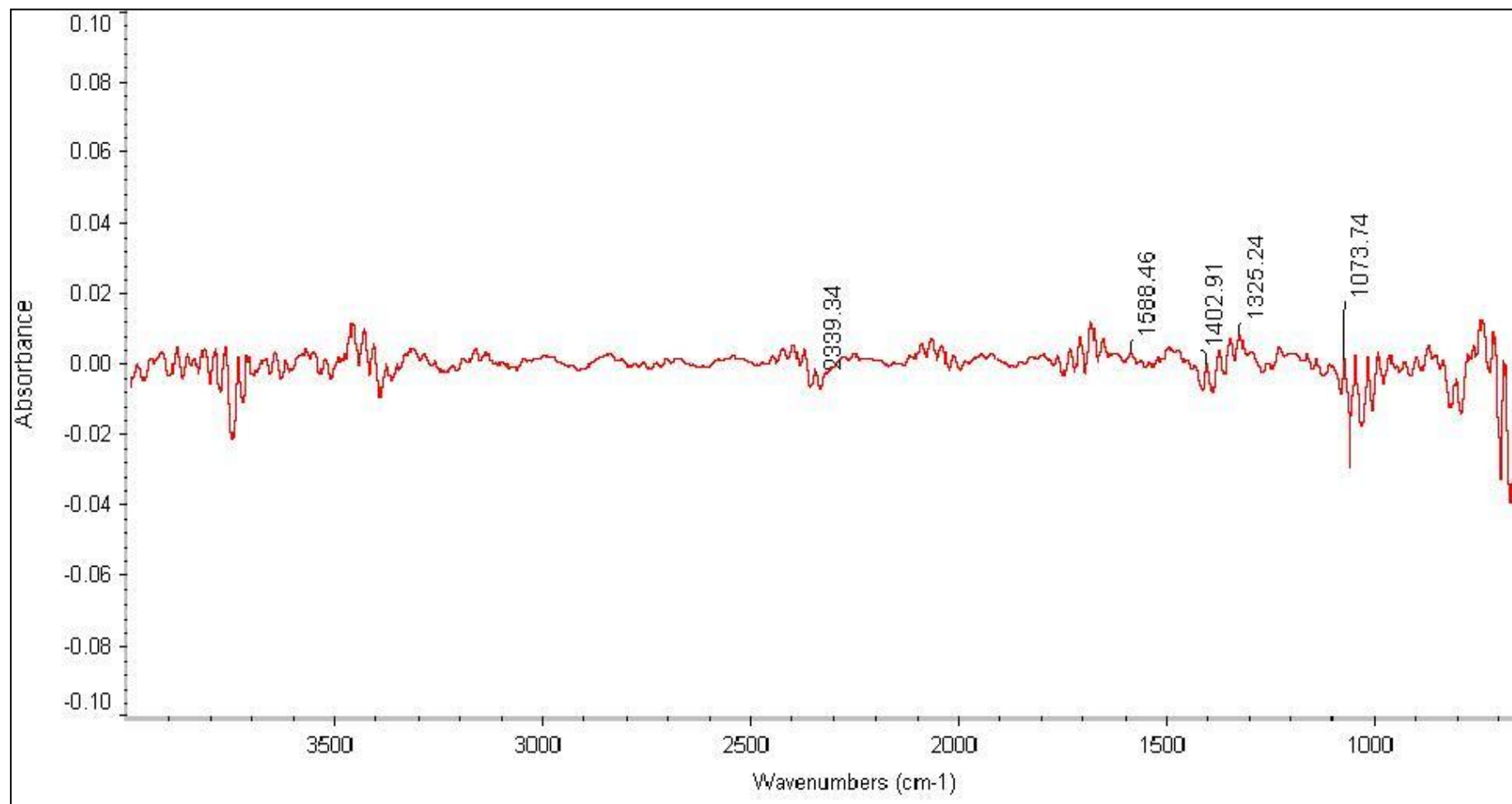
**Figure 4.12:** Graph of CO<sub>2</sub>/CH<sub>4</sub> Selectivity of Membranes Prepared using various Solvents against Feed Pressure

According to Figure 4.10, 4.11 and 4.12,  $\text{CO}_2$  and  $\text{CH}_4$  permeance values increase in the order of dimethylformamide (DMF) < dimethylacetamide (DMAc) < N-methyl-2-pyrrolidone (NMP) solvent system. The significant differences of gas permeance among membrane prepared from various solvent types could be explained by referring to their morphologies as discussed before. Permeating through the membrane, these gases can be broadly classified into two groups based on relative permeabilities which are fast gas penetrants ( $\text{CO}_2$ ) and slow gas penetrants ( $\text{CH}_4$ ). Here,  $\text{CO}_2$  is the fast gas component, permeating at a greater rate through the membrane and becoming enriched in permeate (or downstream) while  $\text{CH}_4$  becomes enriched in the residue (or retentate) stream.

The permeances of both the gases are much higher for the dimethylformamide (DMF) solvent-membrane compared to dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) solvent-membrane. The increasing permeance rate of the dimethylformamide (DMF) solvent-membrane indicates the possibility of membrane defects or pinholes even though the membrane already been coated before conducting the gas permeation test. Another factor that can lead to this is the pore size of the dimethylformamide (DMF) solvent-membrane. As discussed before, dimethylformamide (DMF) solvent-membrane produced big pore size compare to dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) solvent-membrane. This big pore size allows the gases to permeate easily through the membrane which in consequence, it shows that the membrane have lower selectivity. N-methyl-2-pyrrolidone (NMP) solvent-membrane which has small pore size gives lower permeance rate of both of the gases ( $\text{CO}_2$  and  $\text{CH}_4$ ). This is because; the gases hardly slip through the small pore size membrane which give the membrane high selectivity values. From the research, it shows that best solvent to produced high performance Polyethersulfone asymmetric flat sheet membrane is N-methyl-2-pyrrolidone (NMP).

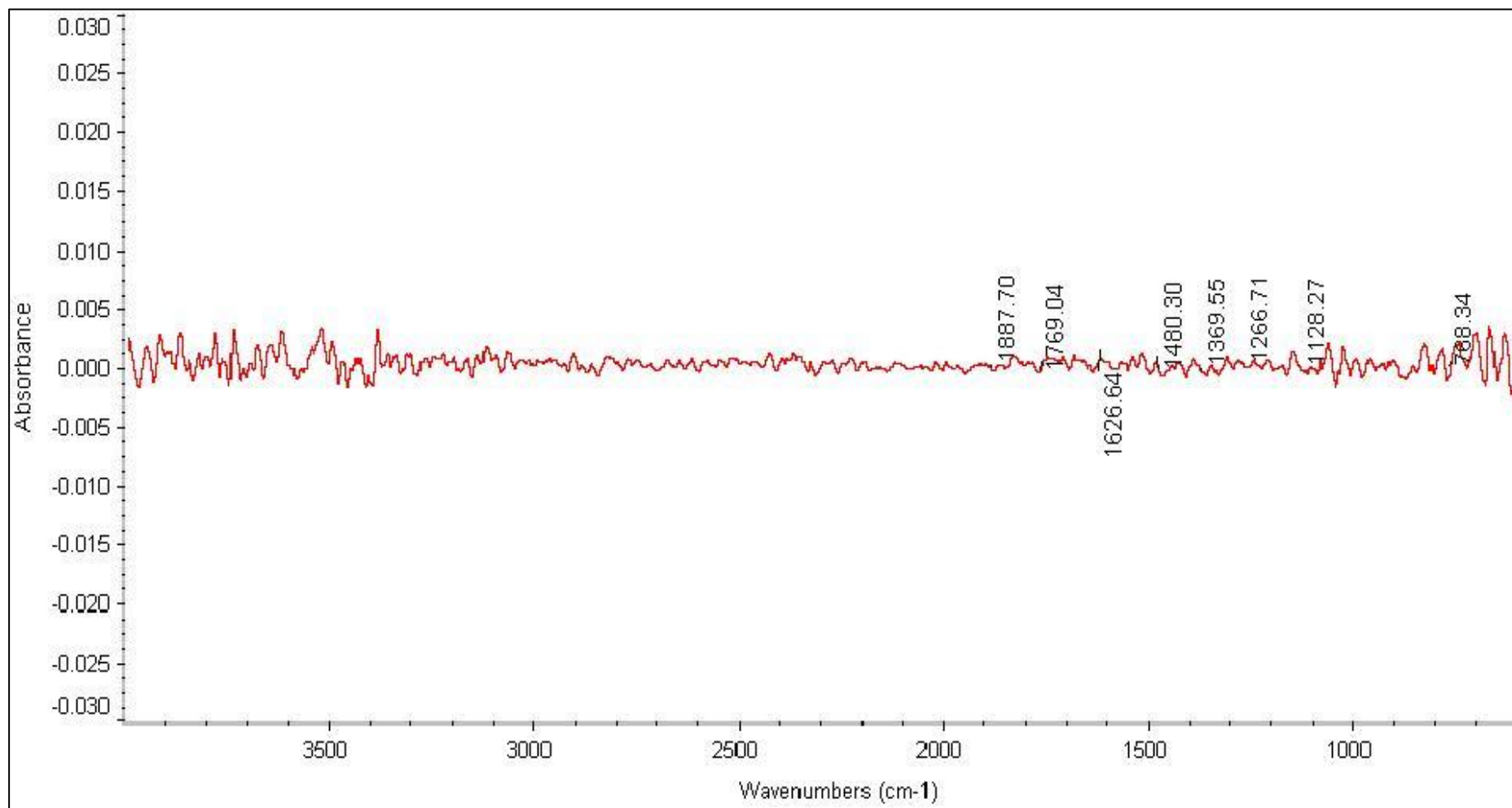
### 4.3 Effect of Solvents on the FTIR Analysis of Membrane

FTIR analysis, is a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, which in this research, the medium is membrane produced using various solvents type. It is used in failure analysis to identify unknown materials present in a specimen. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the membrane is subjected to a modulated infrared (IR) beam. The membrane's transmittance and reflectance of the infrared rays at different frequencies is translated into an infrared (IR) absorption plot consisting of reverse peaks. Figure 4.13 shows the FTIR absorbance peak for N-methyl-2-pyrrolidone (NMP) solvent-membrane; Figure 4.14 shows the FTIR absorbance peak for dimethylacetamide (DMAc) and Figure 4.15 shows the FTIR absorbance peak for dimethylformamide (DMF).

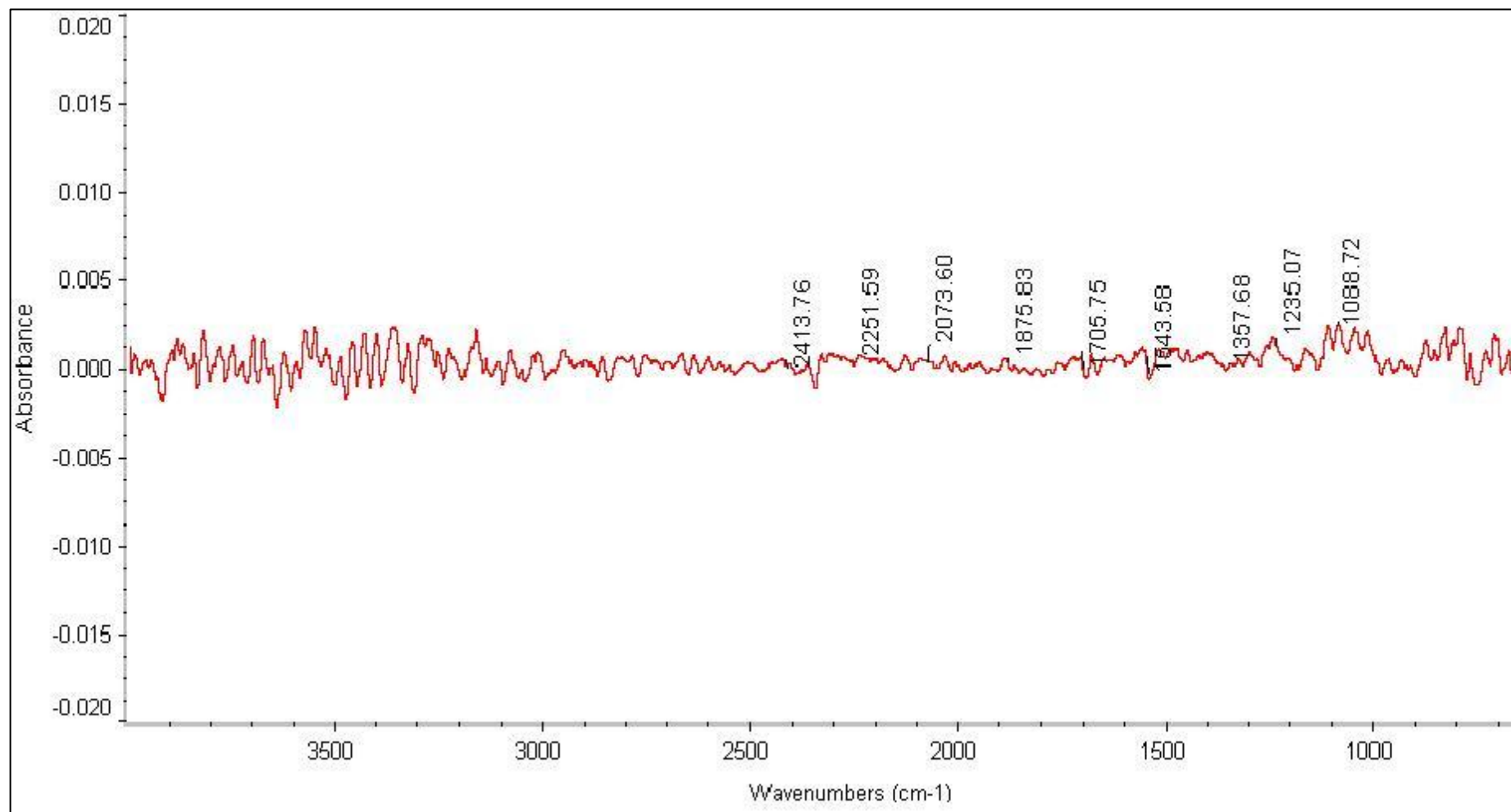


**Figure 4.13:** FTIR Absorbance Peak for N-methyl-2-pyrrolidone Solvent-Membrane





**Figure 4.14:** FTIR Absorbance Peak for Dimethylacetamide Solvent-Membrane



**Figure 4.15:** FTIR Absorbance Peak for Dimethylformamide Solvent-Membrane

The three figures is a comparison of FTIR analysis for asymmetric flat sheet membrane that produced using various solvents. The spectrum reveals the occurrence of interaction between the characteristic groups of Polyethersulfone and the solvents. The interactions were indicated by frequency shifts involving several characteristic groups and absorption intensity changes. The characteristic IR absorption bands for Polyethersulfone at  $1578\text{ cm}^{-1}$  is correspond to the C-H bond in the aromatic system. This area of aliphatic (C-H) stretch is very sensitive to structural effects. The region between  $500\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  is the fingerprint region and indicative of aromatic functional groups. Aromatic bands at  $1578\text{ cm}^{-1}$  and  $1486\text{ cm}^{-1}$  are characteristic for Polyethersulfone. Due to the contribution of the two possible resonance structure of an amide, the bond order of the carbonyl C=O bond is reduced, while that of the C-N bond is increased. Thus the infrared spectrum of N-methyl-2-pyrrolidone (NMP), Dimethylacetamide (DMAc) and Dimethylformamide (DMF) shows a lower C=O stretching frequency at  $1675\text{ cm}^{-1}$  than an unsubstitute C=O bond since it comes from the same group which is amide.

## CHAPTER 5

### CONCLUSIONS & RECOMMENDATIONS

#### 5.1 Conclusion

The use of synthetic membrane in gas separation continues to gain increasing importance in the field of membrane separation process. After conducting this research, it can be concluded that many effort has to come in the coming years to make sure that performance of the Polyethersulfone asymmetric flat sheet membrane for gas separation can be improved. The difference in solvent type for dope solution formulation really can affect the performance of the membrane. Interaction between solvent and non-solvent was discovered to be the main parameter to determine the best membrane structure and thus, membrane performance. Good interaction between these two materials can provide the best rate of evaporation of solvent and equal to the best rate of permeation of non-solvent. The viscosity of dope solution really influences the resulting pore size. The higher the viscosity of the dope solution produced, the smaller pore size will be.

The membrane using N-methyl-2-pyrrolidone (NMP) as solvent gave the best morphology compared to Dimethylacetamide (DMAc) and Dimethylformamide (DMF). The best structure with selective skin, sponge type at top layer, finger-like structure with asymmetric region provides good selectivity and membrane resistance. Dimethylacetamide (DMAc) and Dimethylformamide (DMF) solvent-membrane has less favourable structure due to their physical properties. Thus, when conducting gas permeation test, the N-methyl-2-pyrrolidone (NMP) solvent-membrane with the smallest pore size was found to have the highest selectivity of CO<sub>2</sub>/CH<sub>4</sub> followed by Dimethylacetamide (DMAc) and Dimethylformamide (DMF) since boiling point took the major influence in shaping the membrane structure.

Research and development on membrane for gas separation has to be increase and was supported by better resources. The study on this related topic also has to be emphasized in improving the emerging technologies such as membrane for gas separation especially for acid gas removal. In the future, may this study contribute to development of membrane as large scale for gas separation process a reality.

## **5.2 Recommendation**

Based on the study conducted, some recommendations are given for future work.

- 1) Asymmetric membrane should be prepared with a variety of polymer, solvent and coagulation medium in order to generalize membrane formation process.
- 2) Polyethersulfone asymmetric flat sheet membrane should be coated to ensure that any surface pinholes or defect on the membrane surface could be filled.
- 3) Onsite testing should be conducted to determine other effects such as operating temperature and pressure, humidity and aging on membrane properties in order to justify applicability of asymmetric membrane in actual application.
- 4) The conventional casting method must be replace with pneumatic control to ensure that the shear rate and shear stress while casting the membrane can be constant.
- 5) Comprehensive studies on other fabrication parameters of asymmetric membrane such as evaporation temperature, coagulation temperature and drying method must be carried out to further optimize membrane formation process.

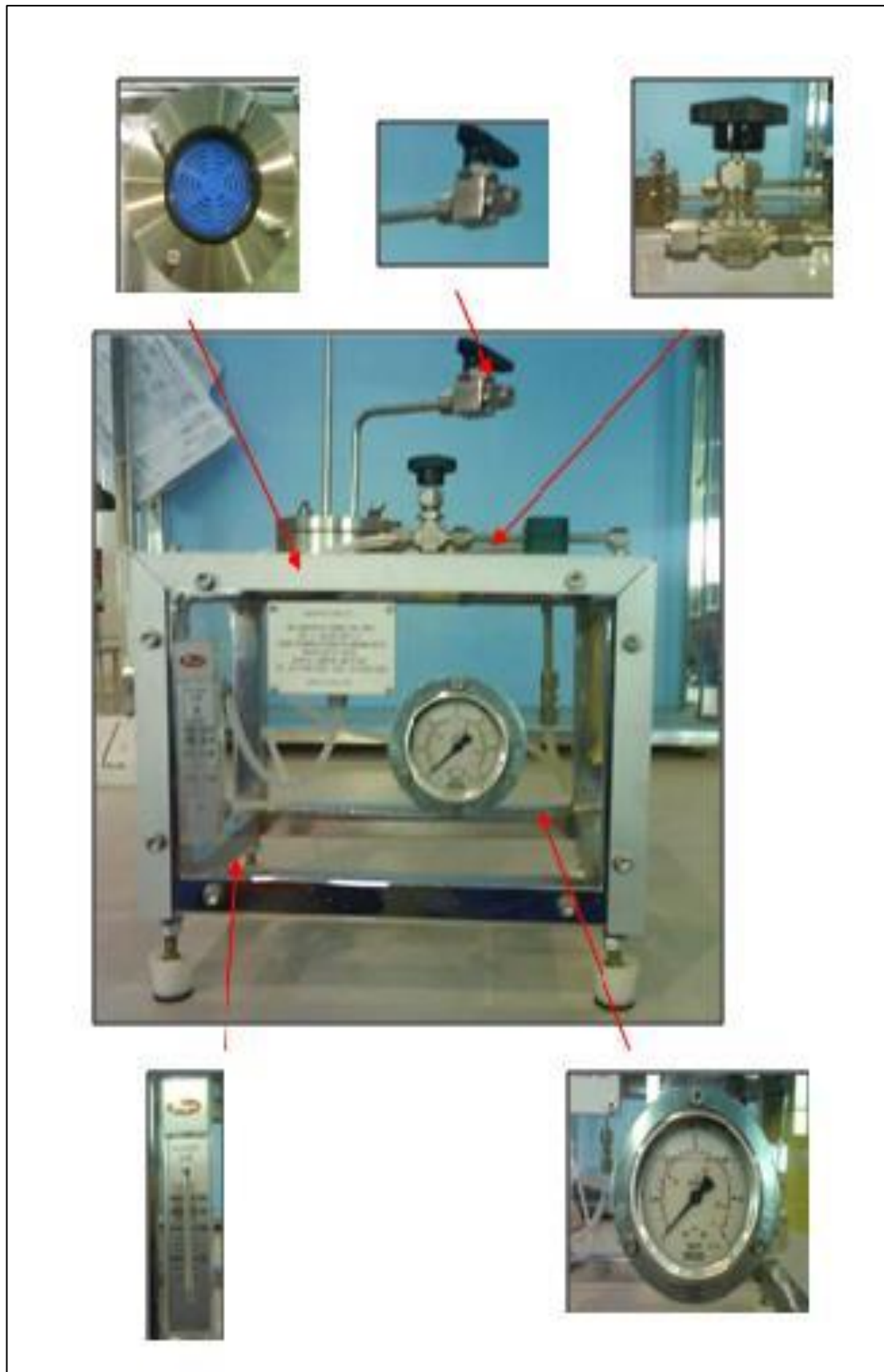
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Appendix A (Permeation Cell)



Appendix B (Dope Solution)



Appendix C (Membranes)





Appendix D (Membrane for Gas Permeation Test)



Appendix E (Polyethersulfone)