

**EFFECT OF NONSOLVENT ADDITIVE ON DEVELOPMENT OF  
POLYETHERSULFONE (PES) MEMBRANE FOR O<sub>2</sub>/N<sub>2</sub> SEPARATION**

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*Special dedicated to my beloved family, supervisor, lecturers and to all my friends that prays for my success...*

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## ABSTRACT

The objectives of this study are to develop new dope formulation for producing asymmetric membrane for O<sub>2</sub>/N<sub>2</sub> separation by using three different types of nonsolvent additives (NSA). Polyethersulfone (PES) asymmetric flat sheet membrane was prepared by the dry/wet phase inversion process from casting solution containing polyethersulfone (PES) as polymer, 1-methyl-2-pyrrolidone (NMP) as solvent and three different types of NSA which are water, ethanol, and methanol. The casting solutions were casted using manually casting technique. Then, the membranes were coated with silicone polymer in order to improve the membrane surface. The membranes were tested using O<sub>2</sub> and N<sub>2</sub> gases permeation test system. The morphologies of the membranes were then examined by using scanning electron microscopy (SEM). Consequently, from the pure gas permeation test results, it was found that the optimum weight percent solution containing the best nonsolvent were 27.24% wt of PES, 64.72% wt of NMP and 7.54% wt of H<sub>2</sub>O. SEM results showed the different NSA used will produce different influence on gas separation characteristics and morphologies of the produced membranes. The newly developed PES membranes with new casting solution formulation that used H<sub>2</sub>O as NSA, resulted O<sub>2</sub>/N<sub>2</sub> selectivity of 3.22 and permeability of O<sub>2</sub> gas was 11.97 GPU and permeability of N<sub>2</sub> gas was 3.71 GPU. Addition of H<sub>2</sub>O as NSA resulted the lowest skin thickness compared to EtOH and MeOH which 781.5nm. Thicker of skin thickness of membranes means the chance of pinhole formation seems to be least which was contributed to high permeation of O<sub>2</sub> gas and low permeation of N<sub>2</sub> gas. Therefore, the PES membranes prepared from NMP/H<sub>2</sub>O proved to provide the best separation characteristics compared to those membranes produced from NMP/EtOH solvent and NMP/MeOH solvent system. As a conclusion, it should be emphasized that the membrane of the highest flux and highest selectivity could be obtained by proper adjustment of the skin layer thickness and the sub layer morphology which was done by proper choice of nonsolvent additive. Thus, choosing the best nonsolvent additive had successfully developed asymmetric PES membranes for O<sub>2</sub>/N<sub>2</sub> separation applications.

## ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan satu jenis formulasi berprestasi tinggi dan bebas kecacatan menggunakan membran asimetrik polyethersulfona (PES) bagi proses pemisahan  $O_2/N_2$ . Membran PES kepingan rata dihasilkan melalui hasil proses fasa balikan kering/basah yang mengandungi 1-methyl-2-pyrrolidona (NMP) digunakan sebagai pelarut, menggunakan tiga bahan tambah bukan pelarut (NSA) iaitu air suling ( $H_2O$ ), ethanol (EtOH), dan methanol (MeOH). Membran asimetrik kepingan rata dihasilkan menggunakan cara penuangan manual dan membrane disalut menggunakan silikon untuk meningkatkan prestasi permukaan membran dan kadar ketelapan membran diuji menggunakan mesin ujian kebolehtelapan gas tulen menggunakan mikroskop pengimpasan elektron (SEM). Keputusan kajian menunjukkan bahawa peratus berat optimum yang mengandungi NSA terbaik adalah 27.24%wt PES, 64.72%wt NMP dan 7.54%wt  $H_2O$ . Keputusan SEM menunjukkan bahawa NSA yang berbeza akan menghasilkan pengaruh yang berbeza pada ciri-ciri pemisahan gas dan struktur membran yang dihasilkan. Membran yang telah dihasilkan dengan formulasi yang baru yang menggunakan  $H_2O$  sebagai NSA menunjukkan kememilihan  $O_2/N_2$  dan fluks tekanan-ternormal ialah 3.224 dengan kadar ketelapan gas  $O_2$  adalah 11.97 GPU dan kadar ketelapan gas  $N_2$  adalah 3.71 GPU. Penambahan  $H_2O$  sebagai NSA menghasilkan ketebalan kulit terendah berbanding dengan EtOH dan MeOH iaitu bernilai 781.5nm. Semakin tebal kulit selaput bererti pembentukan lubang jarum yang terhasil adalah sedikit yang boleh disumbangkan untuk kualiti ketelapan  $O_2/N_2$  yang rendah. Oleh kerana itu, membran PES dihasilkan dari NMP/ $H_2O$  terbukti memberikan ciri-ciri pemisahan yang lebih baik berbanding dengan membran yang dihasilkan dari NMP/EtOH dan NMP/MeOH sistem pelarut. Kesimpulannya, membran fluks yang tertinggi dan kememilihan tertinggi boleh diperolehi dengan perubahan yang tepat dari ketebalan lapisan kulit dan lapisan struktur membran yang dilakukan oleh pilihan bahan tambah bukan pelarut yang tepat. Oleh itu, pemilihan NSA terbaik telah berjaya meningkatkan prestasi membran, menghasilkan membran bebas kecacatan dan menghasilkan kulit lapisan tipis untuk membran asimetrik untuk pemisahan  $O_2/N_2$ .



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## LIST OF SYMBOLS

$O_2$	:	Oxygen
$N_2$	:	Nitrogen
$^{\circ}C$	:	Celsius
$\alpha$	:	Selectivity
$d$	:	Kinetic diameter
$J_i$	:	Flux of the component i
$D_i$	:	Diffusion coefficient ( $cm^2/s$ )
$S_i$	:	Effective solubility coefficient ( $cm^3 (STP)/cm^3 \cdot cm.Hg$ )
$k_i$	:	Solubility constant
$P_i$	:	Partial pressure (cm Hg)
$\text{\AA}$	:	Amstrong
cP	:	Centrepoise
$T_g$	:	Glass transition temperature
$P$	:	Permeability coefficient of gas ( $cm^3 (STP)cm/cm^2 \cdot s \cdot cmHg$ )
$Q$	:	Volumetric flow rate of gas ( $cm^3/s$ ) at STP
$A$	:	Membrane structure area ( $cm^2$ )
$l$	:	Membrane thickness or skin layer thickness (cm)
$(P/l)$	:	Pressure-normalized flux ( $cm^3 (STP)/ cm^2 \cdot s \cdot cm Hg$ )
$P$	:	Pressure
$T$	:	Temperature
$\mu m$	:	Micrometer

**LIST OF ABBREVIATIONS**

NSA	:	Nonsolvent Additive
SEM	:	Scanning Electron Microscope
PES	:	Polyethersulfone
NMP	:	N-Methyl-Pyrrolidon
MW	:	Molecular Weight
GPU	:	Gas permeation unit
EtOH	:	Ethanol
H <sub>2</sub> O	:	Water
MeOH	:	Methanol
DA	:	Diffusivity selectivity A
DB	:	Diffusivity selectivity B
SA	:	Solubility selectivity A
SB	:	Solubility selectivity B
FTIR	:	Fourier Transform Infrared Spectroscopy



## CHAPTER 1

### INTRODUCTION

#### 1.1 RESEARCH BACKGROUND

According to Pinnau and Freeman, a membrane is a thin barrier that permits selective mass transport which can be fabricated from a wide variety of organic (e.g. polymers, liquid) or inorganic (e.g. carbons, zeolites etc) materials (Pinnau and Freeman, 2000). Currently, the vast majority of commercial membranes are made from polymers and the properties of the membrane are controlled by the material and membrane structure. Baker stated that a membrane is nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it and by referred to Mark, a synthetic membrane is a barrier which separates two phases and restricts the transport of various chemical species in a rather species manner which membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure; it may be solid or liquid; it may be neutral, may carry positive or negative charges, or may be bipolar (Baker,2000 and Mark,1990).

Polymeric materials are still the most widely used membranes for gas separation (Pabby *et al*, 2009). Asymmetric membranes are mostly produced by the method namely the dry and wet method (Li *et al*, 2008). Gas separation processes require a membrane with high permeability and high selectivity (Lin *et al*, 1996).

The addition of a suitable nonsolvent additive into the membrane casting solution accelerates the coagulation process from solution to gel when the casting solution was immersed in a coagulant which results membranes with thinner skin layer and more uniform structure (Dongliang *et al*, 1995). The different additives have

distinctive effects on dope viscosity but their individual effects on inherent viscosity are surprising similar (Na *et al*, 2009).

According to the previous researches, they observed that the membrane selectivity tends to decrease as the nodule size at the membrane surface become larger or the roughness of the membrane surface increases. He found that the membrane that contained 2-ethyl-1-hexanol as its additive had the highest permeance ratio, selectivity,  $\alpha$  O<sub>2</sub>/N<sub>2</sub> is 5.5 and the lowest mean diameter, 27.8nm which smaller nodules resulted in higher permeance ratio (Tan *et al*, 1999).

For TPX membranes, additives such as n-propanol, n-butanol, cyclohexanol, acetic acid and 1-methyl-2-pyrrolidone (NMP) can successfully increase the membrane porosity. In fact, not only the porosity but also the membrane morphology is influenced by the addition of nonsolvent (Juin *et al*, 1996). Besides, by adding nonsolvent, membrane formation mechanism changed from polymer crystallization to liquid-liquid phase separation. By increasing the nonsolvent concentration, interaction between polymer and mixture of solvent and nonsolvent became worse and cloud point temperature increased (Saeid *et al* 2008).

Norida found that by using water as nonsolvent additive, at evaporation rate 8 seconds and membrane is coated, the selectivity of O<sub>2</sub>/N<sub>2</sub> is low which 5.12 with high permeability of N<sub>2</sub> which 2.03 and O<sub>2</sub> which 10.32. Meanwhile, at evaporation rate is 20 seconds, when selectivity of O<sub>2</sub>/N<sub>2</sub> is high, which 11.79, the permeability of N<sub>2</sub> and O<sub>2</sub> will be low which 0.63 for N<sub>2</sub> and 7.30 for O<sub>2</sub>. By using ethanol as nonsolvent additive, membrane is coated and at evaporation rate is 8 seconds, O<sub>2</sub>/N<sub>2</sub> produce low selectivity which 4.42 while the permeability of N<sub>2</sub> and O<sub>2</sub> both high which 3.28 and 14.29 respectively. In contrast, at evaporation time is 20 seconds, the selectivity is high which 5.77 while the permeability of N<sub>2</sub> is 1.26 and permeability of O<sub>2</sub> is 7.26 (Norida, 2004).

So, this can conclude that addition of nonsolvent additive influence the permeability of O<sub>2</sub>/N<sub>2</sub> hence contribute to change the membrane selectivity.

## **1.2 PROBLEM STATEMENT**

One of the major problems confronting the use of membrane based separation processes in a wide range of applications is the lack of membranes with high flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good separation membrane. In this research the different types of nonsolvent additive (NSA) will be used to produce high selectivity and high permeability.

Previous research showed that by using different type of NSA will produce different permeability results and membrane morphology. Therefore, in this study, the aim is to get membrane with high permeability and selectivity by changing the membrane morphology in order to get defect free membrane.

## **1.3 OBJECTIVES OF THE RESEARCH**

Based on the problem statement described in the previous section, the following are the objectives of this research:

1. Developing new types solution formulation asymmetric polyethersulfone membrane for gas separation application.

## **1.4 SCOPES OF THE RESEARCH**

1. To develop different type of solution formulation by varying the different type of nonsolvent additives (NSA) for the development of high performance and polyethersulfone membrane.
2. Characterization of uncoated membrane and coated by using pure gases N<sub>2</sub> and O<sub>2</sub> as test gases to determine their performances.
3. Morphological studies of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).

## **1.5 RATIONALE AND SIGNIFICANCE**

Polyethersulfone (PES) has been chosen as the polymer membranes as it has good process ability, inexpensive production and low operating cost and modular design. In short, it offer low capital cost, low energy consumption, ease of operation and cost effectiveness. Besides, membrane with higher permeability leads to higher productivity and lower capital cost whereas membrane with higher selectivity leads to more efficient separations, higher recovery and lower power cost.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 MEMBRANE SEPARATION TECHNOLOGY

According to Freeman and Pinnau, separation of gases using polymer membranes is an important unit operation that competes effectively with well-established processes such as cryogenic distillation, absorption and pressure-swing adsorption. Commercially, the most widely practiced gas separations using membranes are the production of high purity nitrogen from air, recovery of hydrogen from mixtures with larger components such as nitrogen, methane, and carbon monoxide, and purification of natural gas by removal of carbon dioxide. In these separations, membranes with adequately high fluxes of the more permeable components (oxygen, hydrogen, and carbon dioxide, respectively) and sufficient selectivity have been developed for membranes to be competitive with other gas separation technologies. The membrane materials used in these separations are glassy polymers, which derive high selectivity in large measure from their ability to separate gases based on subtle differences in penetrant size. Such polymers are most permeable to the smallest components in a mixture and least permeable to the largest components (Freeman and Pinnau, 1999).

Membranes with higher selectivity are desirable because higher product purity can be achieved in a separation process. Typically, porous membranes are used in dialysis, ultrafiltration, and microfiltration applications. Optimum porous membranes have high porosity and a narrow pore size distribution. Membranes having a dense, selective layer are applied in reverse osmosis, pervaporation, and gas separation processes. Permeation through dense membranes occurs by a solution/diffusion

mechanism. Ideal dense membranes should have a very thin selective layer, because flux is inversely proportional to the membrane thickness. In addition, the thin separating layer should be molecularly dense, because even a very small area fraction of defects in the membrane can cause a significant decrease in selectivity (Pinnau and Freeman, 2000). Table 2.1 show the common polymer used for production of commercial membranes.

**Table 2.1:** Common Polymers Used for Production of Commercial Membranes (Pinnau and Freeman, 2000)

<b>Membrane Processes</b>	<b>Membrane Material</b>
Microfiltration	Cellulose regenerated, cellulose nitrate, cellulose acetate, polyamide, polysulfone, poly(ether sulfone), polycarbonate, poly(ether imide), poly(vinylidene fluoride), polytetrafluoroethylene, polypropylene, polyacrylonitrile
Ultrafiltration	Celulose regenerated, cellulose acetate, polyamide, polysilfone, poly(ether sulfone), polycarbonate, poly(ether imide), poly(vinylidene fluoride), polyacrylonitrile, poly(methyl methacrylate)
Nanofiltration	Polyamide
Dialysis	Cellulose regenerated, cellulose acetate, polyamide, polycarbonate, polyacrylonitrile, poly(methyl methacrylate)
Pervaporation	Poly(vinyl alcohol), polydimethylsiloxane
Gas Separation	Polysulfone, polycarbonate, poly(2,6-dimethyl-1,4-phenylene oxide), polyimide, polydimethylsiloxane

During the past few decades, membrane separation process has become one of the emerging technologies that underwent a rapid growth. It has drawn the attention of researchers in the separation technology field with its better performance compared to the conventional separation technology (Shin *et al*, 2008). The main membrane separation technologies include microfiltration, ultrafiltration, reverse osmosis and nanofiltration, electrodialysis, gas separation and pervaporation (Baker, 2004). Table 2.2 shows the summary of the established membrane separation technologies.

**Table 2.2:** Summary of the established membrane separation technologies (Baker, 2004)

<b>Process</b>	<b>Principle</b>	<b>Type of Membrane</b>	<b>Initial of Feed Phase</b>	<b>Driving Force</b>	<b>Industrial Applications</b>
Microfiltration	Separation of organic and polymeric compounds with micropore ranges of 0.1-10 $\mu$ m	Finely microporous 0.1-10 $\mu$ m	Liquid or gas	Pressure Difference 35-350kPa	Removal of suspended solids, bacteria in pharmaceutical, electronics industries
Ultrafiltration	Separation of water and microsolute from macromolecules and colloids	Finely microporous 1-100nm	Liquid	Pressure Difference 140-700kPa	Removal of colloidal material from wastewater, and food process streams
Reverse Osmosis	Passage of solvents through a dense membrane that is permeable to solvents but not solutes	Dense solution-diffusion	Liquid	Pressure Difference 700-7000kPa	Drinking water from sea, brackish or groundwater; production of ultra-pure water for electronics and pharmaceutical industries
Electrodialysis	Ions are transported through a membrane from one solution to another under the influence of an electrical potential	Electrically charged films	Liquid	Voltage difference 1-2V	De-ionized water from conductive spacers, recovery of organic acids from, heavy metal recovery
Gas Separation	Component of mixture of gaseous is removed through a pressure gradient	Dense solution-diffusion	Vapor or gas	Pressure difference 700-7000kPa	Removal of nitrogen from air, hydrogen from petrochemical/refinery vents, carbon dioxide from natural gas, propylene and VOCs from petrochemical vents
Pervaporation	Component of a mixture diffuses through, evaporates under a low pressure and is removed by a vacuum	Dense solution-diffusion	Liquid	Vapor pressure 7-70Kpa	Dehydration of solvents, separation of azeotropic mixtures

## 2.2 HISTORICAL BACKGROUND AND CURRENT STATUS OF THE TECHNOLOGY

Table 2.3 below represented the sequences of the history membrane process development.

**Table 2.3:** Historical Background and Current Status (Baker, 2000)

Year	Name of Scientist	Systematic Studies
1974	Abbe Nolet	<ul style="list-style-type: none"> <li>Coined the word 'osmosis' to describe permeation of water through a diaphragm.</li> </ul>
19 <sup>th</sup> –early 20 <sup>th</sup> centuries	-	<ul style="list-style-type: none"> <li>Membranes had no industrial or commercial uses but were used as laboratory tools to develop physical/chemical theories.</li> </ul>
1887	Traube and Preffer	<ul style="list-style-type: none"> <li>Explains the behaviour of either dilute solution.</li> </ul>
1907	Bechhold	<ul style="list-style-type: none"> <li>Devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test.</li> </ul>
-	Elford,Zsigmondy, Bachmann and Ferry	<ul style="list-style-type: none"> <li>Improved on Bechhold's technique.</li> </ul>
1930s	-	<ul style="list-style-type: none"> <li>Microporous collodion membranes were commercially available.</li> </ul>
1945	W.J.Kolf	<ul style="list-style-type: none"> <li>Had demonstrated the 1<sup>st</sup> successfully artificial kidney in The Netherland ( use of membranes in artificial organ )</li> <li>This development was complete by early 1960s.</li> </ul>
1950s	-	<ul style="list-style-type: none"> <li>The early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate.</li> <li>Membranes found their 1<sup>st</sup> significant application in the testing of drinking water at the end of World War 2.</li> </ul>
1960	-	<ul style="list-style-type: none"> <li>The elements of modern membrane science had been developed but membranes were used in only a few laboratory and small, specialized industrial applications.</li> <li>No significant membrane industry existed because too unreliable, slow, unselective and expensive.</li> </ul>



<b>Year</b>	<b>Name of Scientist</b>	<b>Systematic Studies</b>
Early 1960s	Loeb-Sourirajan	<ul style="list-style-type: none"> <li>• Making defect-free, high flux, anisotropic reverse osmosis membranes.</li> <li>• This membrane consist of an ultrathin, selective surface film on a much thicker but much more permeable microporous support which provide mechanical strength.</li> </ul>
1966	Alex Zaffaroni	<ul style="list-style-type: none"> <li>• Development of the membrane blood oxygenator for controlled drug delivery systems.</li> <li>• Widely used in pharmaceutical industry to improve the efficiency and safety of drug delivery.</li> </ul>
1980s	-	<ul style="list-style-type: none"> <li>• Microfiltration, ultrafiltration, reverse osmosis and electro dialysis were all established processes with large plants installed worldwide.</li> </ul>
	-	<ul style="list-style-type: none"> <li>• The emergence of industrial membrane gas separation processes.</li> <li>• 1<sup>st</sup> major development was the Monsanto Prism membrane for hydrogen separation.</li> </ul>
	Dow	<ul style="list-style-type: none"> <li>• Producing systems to separate nitrogen from air.</li> </ul>
	Cynara and Separex	<ul style="list-style-type: none"> <li>• Producing systems to separate carbon dioxide from natural gas.</li> </ul>
	GFT company ( a small German engineering company)	<ul style="list-style-type: none"> <li>• 1<sup>st</sup> commercial pervaporation systems for dehydration alcohol.</li> </ul>

Table 2.4 below lists the development of technically for some membrane processes.

**Table 2.4:** Development of (technical) membrane processes (Marcel, 1996)

<b>Membrane Process</b>	<b>Country</b>	<b>Year</b>	<b>Application</b>
Microfiltration†	Germany	1920	Laboratory use (bacterial filter)
Ultrafiltration†	Germany	1930	Laboratory use
Hemodialysis†	Netherlands	1950	Artificial kidney
Electrodialysis#	USA	1955	Desalination
Reverse Osmosis#	USA	1960	Sea water desalination
Ultrafiltration#	USA	1960	Concentration of macromolecules
Gas Separation#	USA	1979	Hydrogen recovery
Membrane Distillation†	Germany	1981	Concentration of aqueous solutions
Pervaporation#	Germany/Netherlands	1982	Dehydration of organic solvents

† Small scale

# Industrial scale

### 2.3 ADVANTAGES OF MEMBRANE TECHNOLOGY

Membrane separation processes are highly innovative process engineering operations. Certain types of materials are inherently difficult and expensive to be separated. Hence, membrane technology would be promising in the future and can offer an alternative to the conventional industrial separation methods. Recently, membrane separation processes are increasingly important and popular in industries and have become attractive alternatives to conventional methods such as absorption, distillation, extraction, leaching, crystallization and adsorption etc. They offer a number of significant advantages and attractions over competing technologies.

Membrane nowadays have gained wide acceptance and made significant inroads against competing technologies in many areas because of flexibility and performance reliability of membrane system, cost competitiveness, increasing demand and environmental awareness. Besides that, the advantages using polymer membranes are

good processability, inexpensive production and low operating cost (relatively low capital and running costs) and modular design (construction). In short, they offer low capital cost, low energy consumption, ease of operation and cost effectiveness.

## 2.4 SOLUTION-DIFFUSION MECHANISM

Solution-diffusion separation is based on both solubility and mobility factors. Diffusivity favors the smallest molecules while solubility selectivity favors the most condensable one (Norida, 2004). Diffusion, the basis of the solution-diffusion model, is the process by which matter is transported from one part of a system to another by a concentration gradient (Baker, 2000).

The diffusion can be defined as a relationship wherein the flux of a diffusing species is proportional to the concentration gradient by Fick's first law (Baker, 2000).

$$J_x = -D \frac{dC}{dx} \quad \text{-----} \rightarrow \quad \text{Equation 2.1}$$

where,

$J_x$  = the flux of the diffusing species ( $\text{g}/\text{cm}^2 \cdot \text{s}$ )

$dC/dx$  = the incremental change in concentration with distance

$D$  = diffusivity or diffusion coefficient = the proportionality constant ( $\text{cm}^2/\text{s}$ )

The solubility of a gas in a liquid is directly proportional to the gas pressure. This is a statement of Henry's Law, (Kotz *et al*, 2009).

$$S_g = K_H \cdot P_g \quad \text{-----} \rightarrow \quad \text{Equation 2.2}$$

where,  $S_g$  is the gas solubility,  $P_g$  is the partial pressure of the gaseous solute, and  $K_H$  is Henry's Law constant, Table 2.5 shows a constant characteristic of a solute and solvent.

**Table 2.5:** Henry's Law constant (25<sup>0</sup>C)

Gas	$K_H$ (mol/kg.bar)
N <sub>2</sub>	$6.0 \times 10^{-4}$
O <sub>2</sub>	$1.3 \times 10^{-4}$
CO <sub>2</sub>	0.034

Predicting membrane permeability can be divided into two parts because permeability is the product of the diffusion coefficient and the sorption coefficient (Baker, 2000).

$$P = D \cdot K \quad \text{-----} \rightarrow \quad \text{Equation 2.3}$$

where P is permeability, K is the sorption coefficient and D is diffusion coefficient.

James state that the equilibrium concentration (solubility), c, of a penetrant gas dissolved in a polymer can be related to the pressure, p, of the penetrant by the isothermal relation:

$$c = S(c) \cdot p \quad \text{-----} \rightarrow \quad \text{Equation 2.4}$$

where, S(c) [or S (p)] is a solubility coefficient (James, 2007).

According to Ismail and Lai, 2004, for the gas permeation measurement, gas permeation rate can be calculated by,

$$\left( \frac{P}{l} \right)_i = \frac{Q_i}{A \Delta p} \quad \text{-----} \rightarrow \quad \text{Equation 2.5}$$

where  $(P/l)_i$  is defined as pressure-normalized flux or permeability for gas *i*. The common unit of pressure-normalized gas flux is GPU (1GPU=1X10<sup>-6</sup> cm<sup>3</sup> (STP) cm/cm<sup>2</sup>.s.sm.Hg.  $Q_i$  is volumetric flow rate of gas *i*,  $\Delta p$  the pressure difference across

membrane,  $A$  the membrane effective surface area and  $l$  the membrane skin thickness. (Ismail and Lai, 2004). Selectivity (unitless) of asymmetric membrane can be determined by,

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{(P/l)_i}{(P/l)_j}. \quad \text{-----} \blacktriangleright \text{Equation 2.6}$$

Total gas flux through asymmetric polymeric membrane with defects is sum of permeation through polymeric material of skin layer and flux through defects. The former is exclusively predominated by solution-diffusion mechanism, while the latter occurs due to the combination of Knudsen diffusion, viscous diffusion and/or bulk diffusion (Marchese and Pagliero, 1994).

For simplicity in evaluation of skin structural parameters, following assumptions were made and stated as below (Ismail and Lai, 2004):

- a) Asymmetric membrane consists of a skin of uniform thickness supported on a porous sublayer. The skin represents the actual separating barrier, while the sublayer serves only as a mechanical support, with negligible effects on separation (with negligible substructure resistance).
- b) Contribution of gas flux permeating through dense skin is greater than 10% of slip flux in pore (defects).
- c) Gas permeation through asymmetric membrane is assumed a steady-state mode.
- d) Intrinsic permeability (and selectivity) is taken as being independent of pressure in experimental range of exploration (200-450cmHg).
- e) Downstream pressure is negligible if compared to upstream pressure.

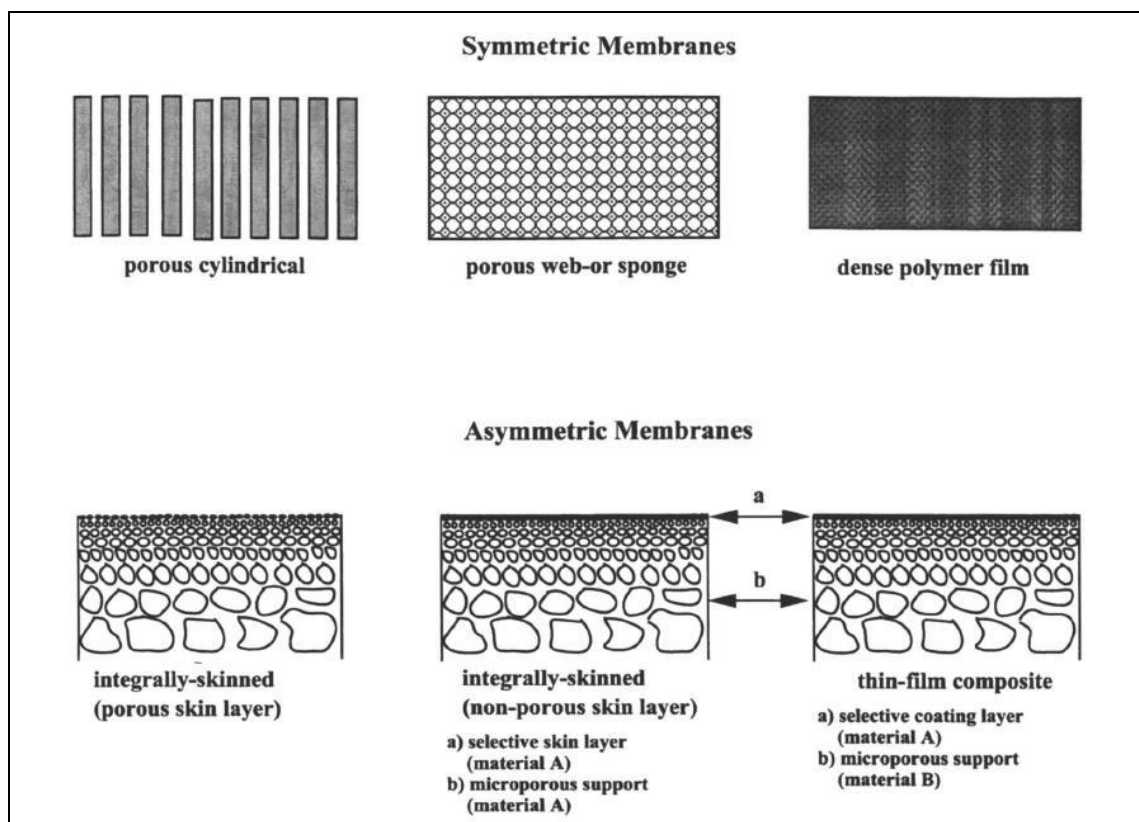
## 2.5 ASYMMETRIC MEMBRANE

Asymmetric membranes are mostly produced by dry/wet phase inversion method comprised of these steps (Li *et al*, 2008):

- a) Preparation of the polymer solution called dope.
- b) Molding (cast or spinning) of the dope.
- c) Coagulation of the dope by contact with nonsolvent of the polymer to form the asymmetric structure.
- d) Drying of the coagulated membrane.

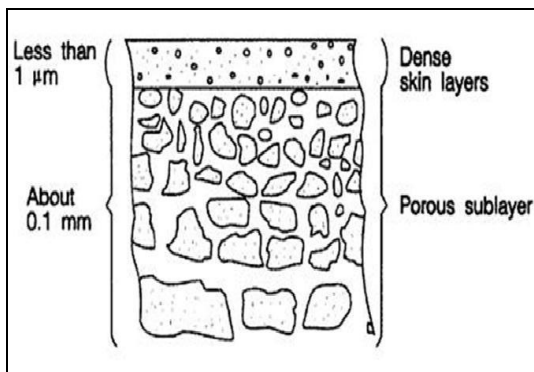
Membranes can be produced in flat sheet or tubular (hollow-fiber) geometry. Flat sheet membranes are packaged either in plate and frame or spiral wound modules, whereas tubular membranes are packaged in hollow fiber modules. Although hollow fiber modules have highest membrane packing density per module volume, spiral wound and plate and frame modules are also commonly used in large scale separation processes.

Membranes either have a symmetric (isotropic) or an asymmetric (anisotropic) structure. Symmetric membranes have a uniform structure throughout the entire membrane thickness, whereas asymmetric membranes have a gradient structure. The separation properties of symmetric are determined by their entire structure. On the other hand, the separation properties of asymmetric membrane are determined primarily by the densest region in the membrane. The most common symmetric and asymmetric membrane types are shown in Figure 2.1 (Pinnau and Freeman, 2000):



**Figure 2.1:** Schematic representation of symmetric and asymmetric structures.  
(Pinnau and Freeman, 2000)

Most membranes used in industries have an asymmetric structure. Asymmetric membrane consists of two layers. The first layer is the top one, very thin dense layer which also called as top skin layer. Top skin dense layer governs the performance (permeation properties) of the membrane. The second layer, the bottom one is the porous sublayer which only provides mechanical strength to the membrane. In the asymmetric membrane, when the material of the top layer and porous sublayer are the same, the membrane is called an integrally skinned asymmetric membrane (Knulbe *et al*, 2008). Figure 2.2 shows the cross sectional view on asymmetric membrane.



**Figure 2.2:** Cross sectional view on asymmetric membrane (Takeshi, 1994)

The attributes of an ideal gas separation membrane which are (Donald and Yuri, 1994):

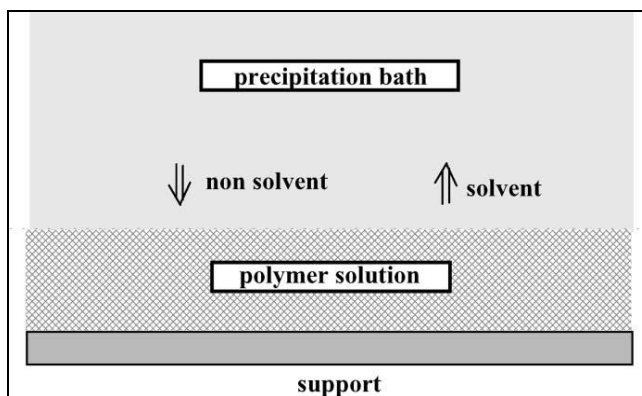
- a) The selective layer should be defect free so that gas transport takes place exclusively by solution diffusion, not by poorly selective flow through pores.
- b) The selective layer should be as thin as possible to maximize the fluxes.
- c) The supporting substructure should not contribute any resistance to gas transport.
- d) The substructure should provide sufficient mechanical strength to support the delicate selective layer in high pressure operation.

## 2.6 ASYMMETRIC MEMBRANE FORMATION

### 2.6.1 Phase Inversion

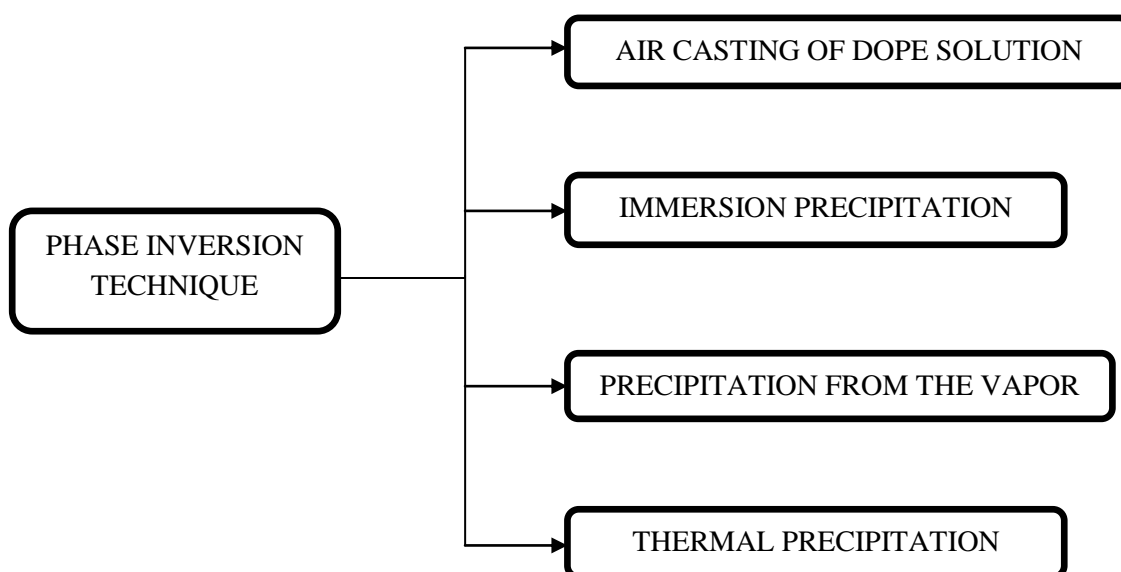
In phase separation by immersion precipitation technique, a polymer solution is immersed into a precipitation bath, which is non-solvent to the polymer. Figure 3 below illustrates the immersion precipitation technique. Mass transfer takes place (the solvent from the polymer solution diffuses into the precipitation bath, whereas the non-solvent diffuses into the polymer solution. Thus, solution composition is changed which takes to a demixing process (Christina *et al*, 2001). Figure 2.3 shows the schematic diagram of immersion precipitation technique.





**Figure 2.3:** Schematic diagram of immersion precipitation technique (Christina *et al*, 2001)

According to the previous researcher, membrane can be prepared by phase inversion and it can be categorized into four different techniques (Norida, 2004). Figure 2.4 shows the phase inversion techniques.

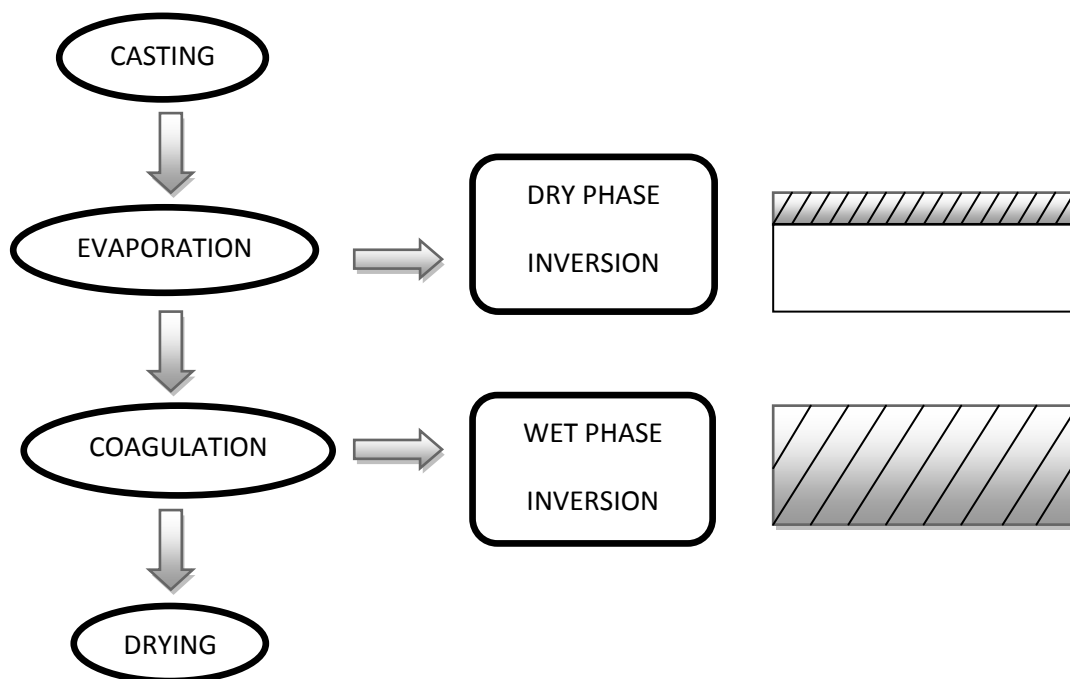


**Figure 2.4:** Phase Inversion Techniques

### 2.6.2 Dry/Wet Phase Inversion Process

In making asymmetric membranes by the wet or the dry/wet phase inversion process, the addition of a nonsolvent, usually an organic nonsolvent for the polymer, into the membrane casting solution is very important to obtain the optimal membrane structure and improve performance of the resulting membranes (Dongliang *et al*, 1995). If the solvent and nonsolvent components are removed solely by evaporation, membranes formation is defined as a dry phase inversion. If the entire phase separation process is the result of the solvent/nonsolvent exchange during the quench step, the structure formation process is often referred to as a wet phase inversion process (Arun *et al*, 2010).

Asymmetric membranes were made by a dry/wet phase inversion technique as illustrate in Figure 2.5 below:



**Figure 2.5:** Process Steps for the Preparation of Dry/Wet Phase Inversion Membrane, (Ingo *et al*, 1990)

### 2.6.3 Mechanism of Dry/Wet Phase Inversion

According to earlier studies, dry/wet phase inversion process is one of the most versatile methods to produce high performance asymmetric membranes for gas separation. Asymmetric membrane formation process involves formulation of a homogeneous multi-component solution that consists of a polymer, solvents (a less volatile solvent and more volatile solvent) and a nonsolvent. The solution is tailored to be close to thermodynamic instability limit and approaching phase transition boundary.

Membrane is cast at an appropriate shear; followed by a forced-convective evaporation for dry phase separation. A nascent skin layer is formed from a region with locally elevated polymer concentration due to a selective loss of highly volatile solvent from the outermost surface of freshly cast membrane. Underlying region beneath the nascent skin layer remains in a fluid state. The nascent membrane is then immersed in a coagulation bath for wet phase separation, where the bulk of the membrane structure is formed by counter-diffusion of solvents and nonsolvents and extraction of the remaining components occur (Ismail and Lai, 2004).

The dry/wet phase inversion processes often used in making asymmetric membranes for gas separation comprises of the exposure of the nascent membrane to air for a short duration (dry process) prior to entering a water bath for coagulation (wet process). The effect of the dry process on the dense skin layer formation of asymmetric membrane is important and also complicated. During this step, solvent and/or NSA evaporate from the surface layer of the nascent membrane, which results in increasing the local polymer concentration.

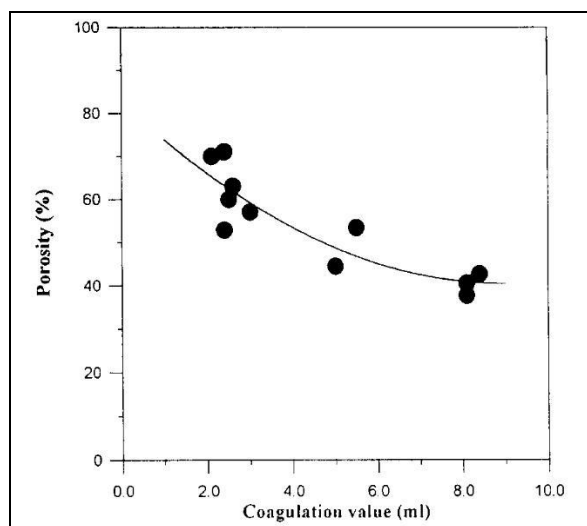
The rates of evaporation depend on their volatilities as well as temperature of the polymer solution and the atmosphere. If the boiling point of solvent is higher than that of the NSA, rapid vaporization of the NSA will increase the local solvent power. As a result, the solution composition of nascent membrane at the surface moves away from the point of phase separation. This tends to form membrane with dense and thick skin layer. Conversely, faster loss of solvent molecules from the membrane surface tends to form thin and porous skin layer. Besides, loss of the solvent and NSA, the solution in

the outermost region of the membrane absorbs moisture simultaneously and this will further hasten the process of phase separation ( Dongliang et al,1996).

## 2.7 EFFECT OF NONSOLVENT ADDITIVE ON THE STRUCTURE AND SEPARATION PERFORMANCE

The introduction of NSA in the polymer solution has been shown to play an important role in the development of membranes with improved separation characteristics. In formulating these polymer solutions, it was recognized that the solution composition could be controlled to close to the point of phase separation by adjusting the addition of NSA (Dongliang *et al*, 1996).

Changing the composition in the casting solution is a convenient method to obtain desired membrane structures. Adding nonsolvent in the casting solution can increase the porosity of membranes. Lower coagulation value indicates that the polymer solution is easier to phase separate, suggesting that the prepared membrane is more porous. Therefore, coagulation value is a good criterion for selecting suitable nonsolvent additives to elevate the membrane porosity. Figure 2.6 shows the relationship between membrane porosity and the coagulation value (Juin *et al*, 1996).



**Figure 2.6:** The relationship between the membrane porosity and the coagulation value (Juin *et al*, 1996).

When a NSA is added to a polymer-solvent solution, the interaction of the nonsolvent and solvent molecules leads to a reduction of the dissolving power of the solvent and this further enhances the polymer-polymer interaction. In this case, the polymer chains may have a smaller excluded volume because of a more tightly coiled conformation. The polymer aggregates are formed in the polymer solution. Thus, an initially homogeneous solution may become microscopically heterogeneous. If a sufficient amount of NSA is added, a polymer lean phase is responsible for the initiation of macrovoids.

The size of polymer aggregates depends on the interaction strengths of the solvent-NSA-polymer. Strong interaction of solvent-NSA and weak interaction of solvent-polymer and NSA-polymer tend to form large or even super polymer aggregates resulting in the formation of big cavities and finger-like structure. The kinetics of phase separation during the wet coagulation process plays a major role in the control of membrane morphology. The accelerate rate of phase separation due to the addition of NSA may restrict the rearrangement of polymer aggregates, resulting the formation of a membrane with small macrovoids. If the diffusion of the solvent molecules will further enhance the polymer-polymer interaction before the membrane is solidified. This is likely to intensively the formation of super aggregates with the creation of big macrovoids (Dongliang *et al*, 1996).

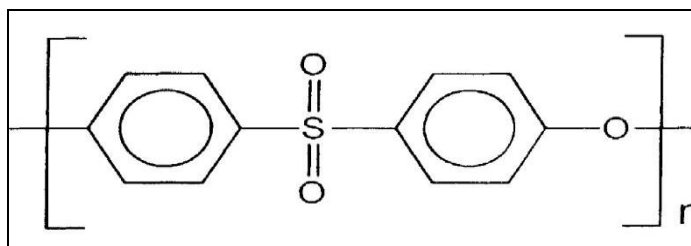
## CHAPTER 3

### METHODOLOGY

#### 3.1 MATERIALS

##### 3.1.1 Polyethersulfone (PES)

Polyethersulfone (PES) has excellent thermal and dimensional stability as well as good chemical resistance compared with polysulfone (PSf). PES has a higher degree of chain rigidity because its regular and polar backbone (Dongliang *et al*, 1996). PES is an excellent candidate for the preparation of gas separation membranes since it exhibits high chemical resistance, thermal and dimensional stability and high selectivity values. However, due to its higher high degree of chain rigidity, PES is less permeable than PSf and polyimide (PI) (Kapantaidakis and Koops, 2002). Figure 3.1 shows molecular structure of polyethersulfone:



**Figure 3.1:** Molecular structure of polyethersulfone (Kapantaidakis and Koops, 2002).

Table 3.1 below shows the physical, mechanical, electrical and thermal properties of polyethersulfone.

**Table 3.1:** Physical, mechanical, and thermal properties of polyethersulfone  
([www.polymerprocessing.com](http://www.polymerprocessing.com))

Parameter	Value
<b>Physical Properties</b>	
Molecular Weight (g/mol)	232.26
Density (g/cm <sup>3</sup> )	1.49
Viscosity Test (cm <sup>3</sup> /g)	52.3
<b>Mechanical Properties</b>	
Tensile Strength, Ultimate (MPa)	116
Tensile Strength, Yield (MPa)	106
Elongation at Break (%)	8.25
Elongation at Yield (%)	4.94
Modulus of elasticity (Gpa)	7.70
Compressive Yield Strength (MPa)	126
Compressive Modulus (Gpa)	1.78
<b>Thermal Properties</b>	
Thermal Conductivity (W/m.K)	0.22
Glass Transition Temperature (°C)	230

### 3.1.2 1-Methyl-2-Pyrrolidone (NMP)

1-Methyl-2-Pyrrolidone (NMP) also known as 4-Methylaminobutyric acid and a very weak base. NMP is a chemically stable and powerful polar solvent. NMP as solvent is allowed to evaporate for a certain period of time and then immersed into water (Marcel, 1996). Table 3.2 shows the physical and thermal properties of NMP.

**Table 3.2:** Physical and thermal properties of 1-Methyl-2-Pyrrolidone (NMP)  
([www.polymerprocessing.com](http://www.polymerprocessing.com))

Parameter	Value
<b>Physical Properties</b>	
Density (g/cm <sup>3</sup> )	1.03
Solubility in Water (%)	100
Viscosity (cP)	1.70
Molecular Weight (g/mol)	99.1
<b>Thermal Properties</b>	
Boiling Point (°C)	202
Flash Point (°C)	90

### 3.1.3 Properties of Nonsolvent Additives and Coagulation Bath

Three types of nonsolvent additives and two types of coagulation bath were used in this research:

Nonsolvent additives:

- a) Distilled water
- b) Ethanol
- c) Methanol

Coagulation bath:

- a) Tap water
- b) Methanol



Table 3.3 shows the properties of nonsolvent additives and coagulation bath.

**Table 3.3:** Properties of nonsolvent additives and coagulation bath

([www.polymerprocessing.com](http://www.polymerprocessing.com))

Parameter	Nonsolvent Additives			Coagulation Bath	
	Distilled Water	Ethanol	Methanol	Tab Water	Methanol
Molecular Weight (g/mol)	18.015	46.0684	32.04186	18.015	32.04
Density(g/cm <sup>3</sup> )	0.99325	0.7893	0.782	0.99325	0.7914
Viscosity(cP)	0.7977	1.074	0.521	0.7977	0.544
Melting Point( <sup>0</sup> C)	0	-114.14	-97	0	-97.53
Boiling Point( <sup>0</sup> C)	100	78.29	64.7	100	64.6

### 3.1.4 Physical and Thermal Properties of Test Gases

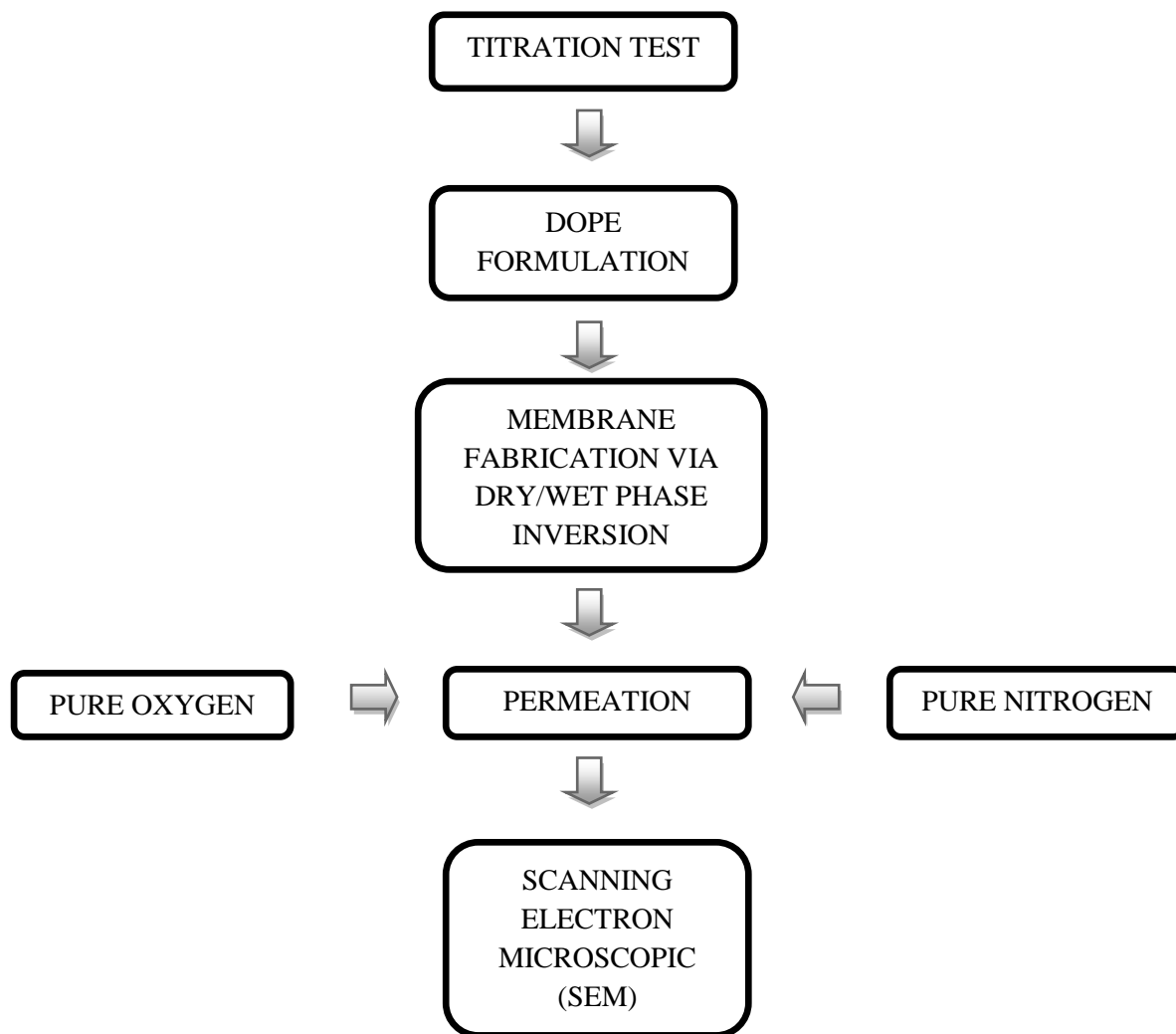
Pure gas oxygen and nitrogen were selected as test gases in this research. Table 3.4 shows the physical and thermal properties of these gases.

**Table 3.4:** Physical and thermal properties of gas oxygen and nitrogen (Norida, 2004 and [www.polymerprocessing.com](http://www.polymerprocessing.com))

Parameter	Value for O <sub>2</sub> Gas	Value for N <sub>2</sub> Gas
<b>Physical Properties</b>		
Molecular Weight (g/mol)	31.999	28.013
Density (g/cm <sup>3</sup> )	0.001308	0.001145
Molecular Speed (cm/s)	44400	47500
Gas Permeability Coefficient of PES Dense Film (P)	0.51	0.084
Permeability Coefficient of Silicone Rubber Dense Film (barrer)	649	354
Kinetic Diameter (m)	3.46E-10	3.64E-10
Intrinsic Selectivity (P <sub>O<sub>2</sub></sub> /P <sub>N<sub>2</sub></sub> )	6.1	
<b>Thermal Properties</b>		
Melting Point ( <sup>0</sup> C)	-218.79	-210
Boiling Point ( <sup>0</sup> C)	-182.95	-195.79

### 3.2 RESEARCH DESIGN

The workflow of this research is simplified in a flowchart as shown in Figure 3.2.

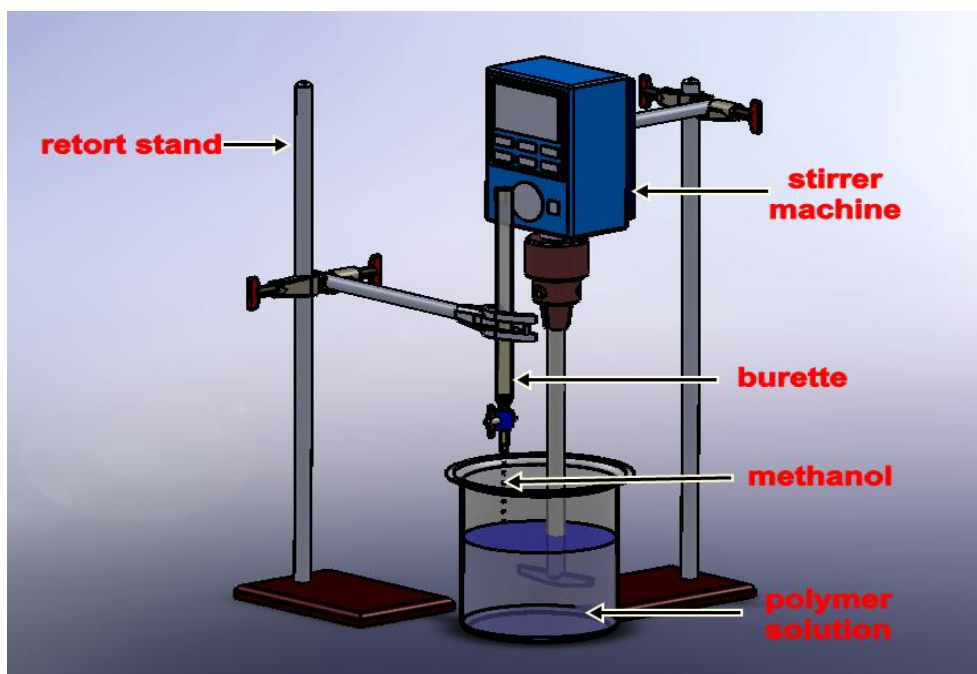


**Figure 3.2:** Research Design

### 3.3 TITRATION TEST

Titration test was used to measure the coagulation value of polymer solution or also known as cloud point. According to Boom *et al*, (1993), the cloud point curve that forms the border between the compositions that are completely stable and the line that represents compositions that can be at equilibrium with one another.

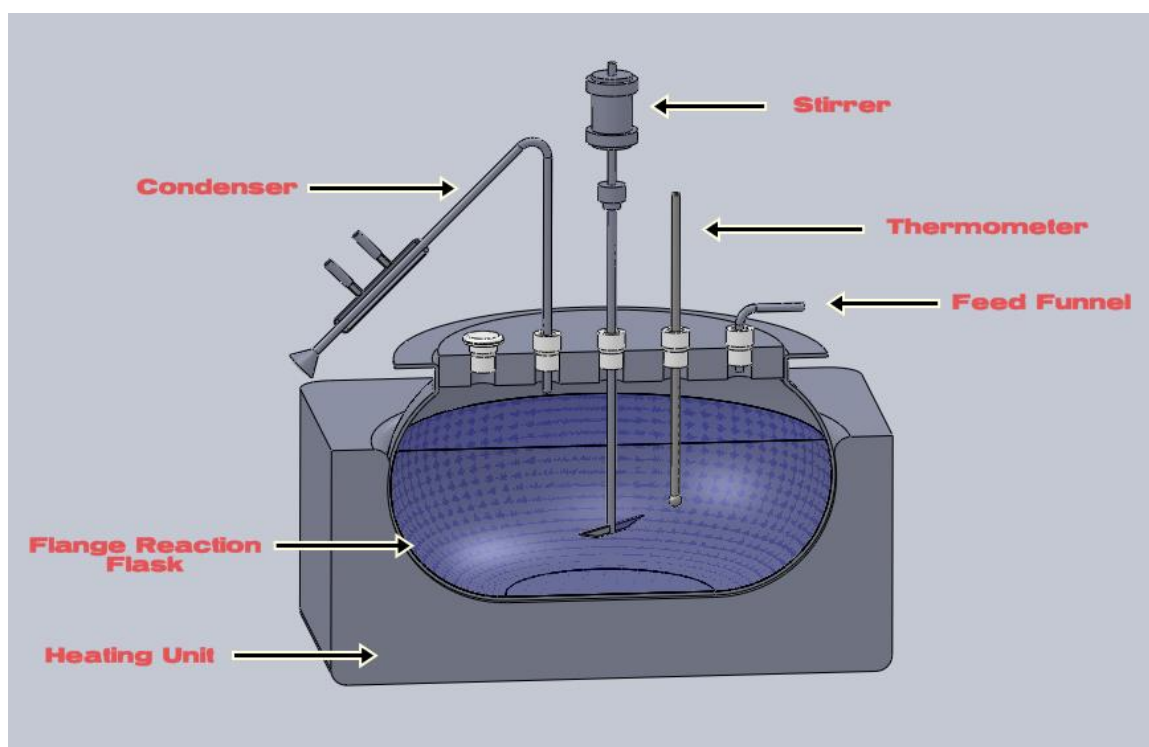
The polymer solution consists of polymer, solvent and nonsolvent additive. Polymer solution with 30wt% PES and 70wt% NMP and methanol as nonsolvent additive were prepared. The polymer solution (PES/NMP) was placed in closed beaker and was titrated with nonsolvent additive (methanol) at room temperature, 27<sup>0</sup>C. While the solution was being titrated, the solution also was stirred to make the polymer solution mixed completely until clear solution become cloudy. The quantity of coagulant added (methanol) which made the polymer solution turbid was obtained by getting the reading of the burette before and after the titration. The titration was repeated for three times and the average percentage of nonsolvent used was determined. Figure 3.3 below show the equipment for titration test.



**Figure 3.3:** Titration Test

### 3.4 PREPARATION OF DOPE FORMULATION

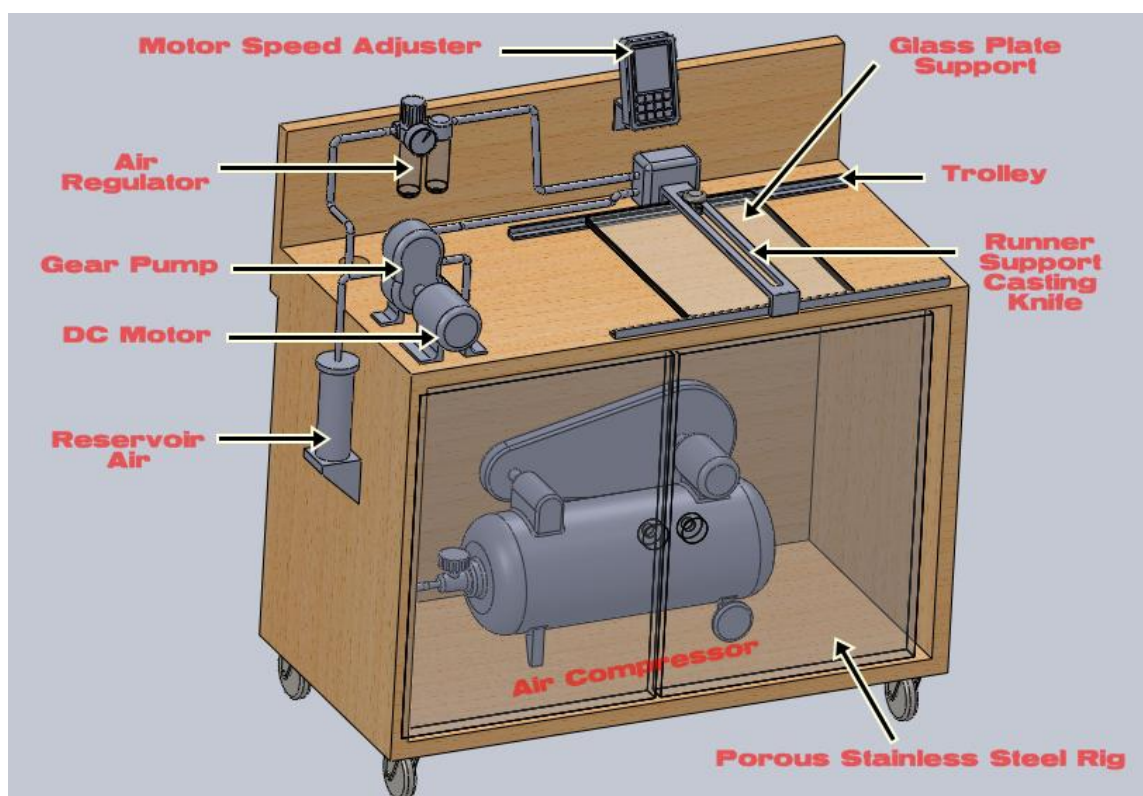
Figure 3.4 shows the apparatus to prepare dope formulation. Firstly, polyethersulfone was dried in a vacuum oven at temperature around  $150^{\circ}\text{C}$  for at least 4 hours to remove all absorbed water vapor. Then, the polymer was dissolved in 1-methyl-2-pyrrolidone (solvent) and distilled water/ethanol/methanol (nonsolvent additive). In order to ensure dissolution, the solution was heated at  $40^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  and stirred about 4 to 6 hours. Lastly, the homogeneity solution was kept in a storage bottle and also degassed using ultrasonic bath in order to remove micro bubbles in the solution.



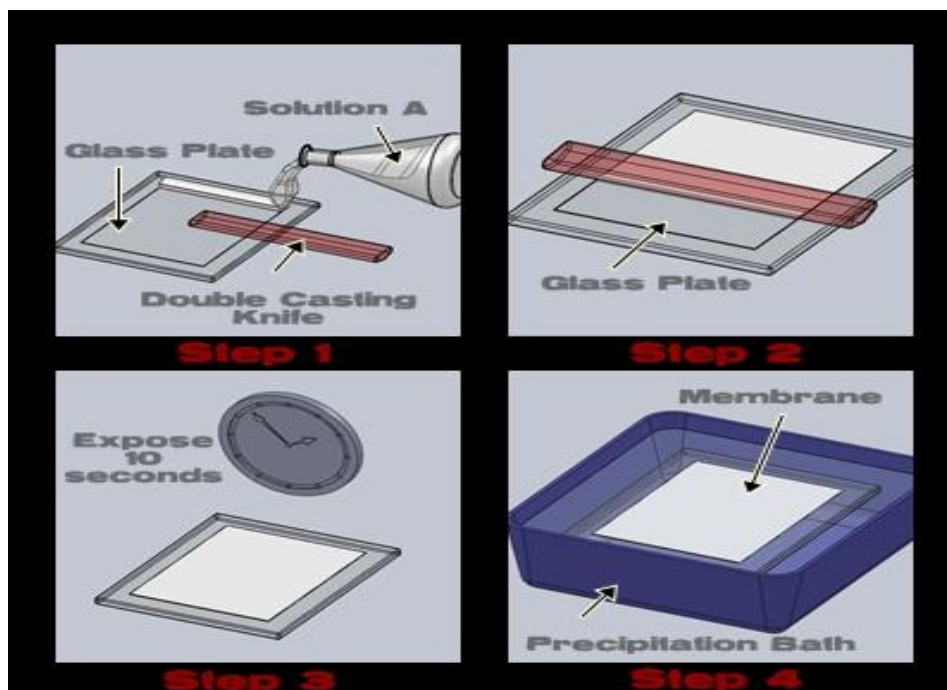
**Figure 3.4:** Apparatus to prepare dope formulation

### 3.5 MEMBRANE CASTING

There are two methods in order to cast the flat sheet membrane which by using pneumatically controlled flat sheet membrane casting machine and by manually casting of the polymer solution. This study was carried out using manually technique. Membrane has been casted manually on glass plate using casting knife. Therefore, the desired properties such as porous support with low transport resistance and thin dense skin may be achieved (Cristina *et al*, 2001). Figure 3.5 and Figure 3.6 show the way how to produce membrane.



**Figure 3.5:** Pneumatically controlled casting machine (1<sup>st</sup> method of membrane casting)

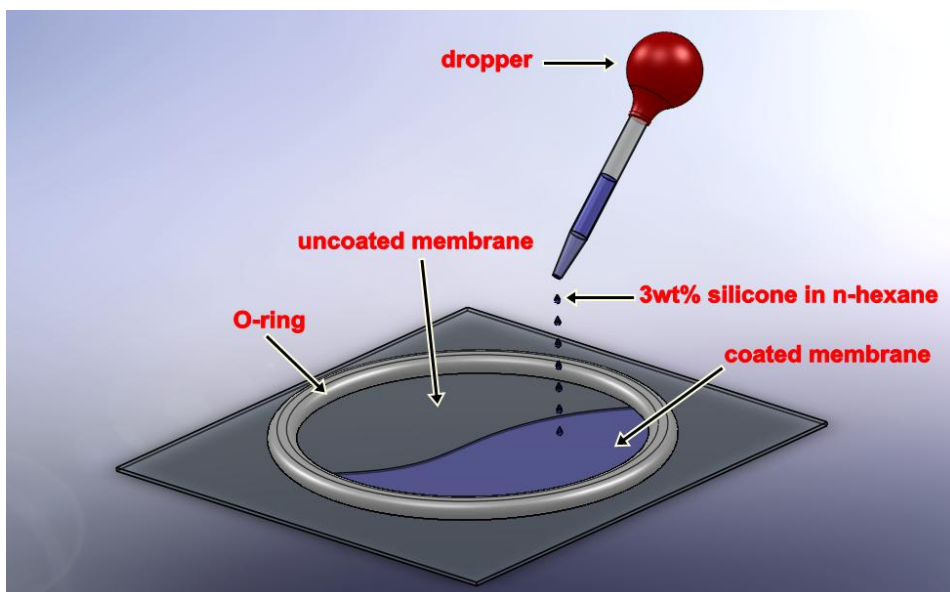


**Figure 3.6:** Membrane fabrication using dry/wet phase inversion (2<sup>nd</sup> method of membrane casting: manually)

### 3.6 MEMBRANE COATING

Defects on the membrane surface were healed by a coating technique (Kapantaidakis and Koops, 2002). Membranes must be coated with a thin layer of silicone rubber to repair the surface defects using the method developed by Henis and Tripody (Dongliang *et al*, 1996).

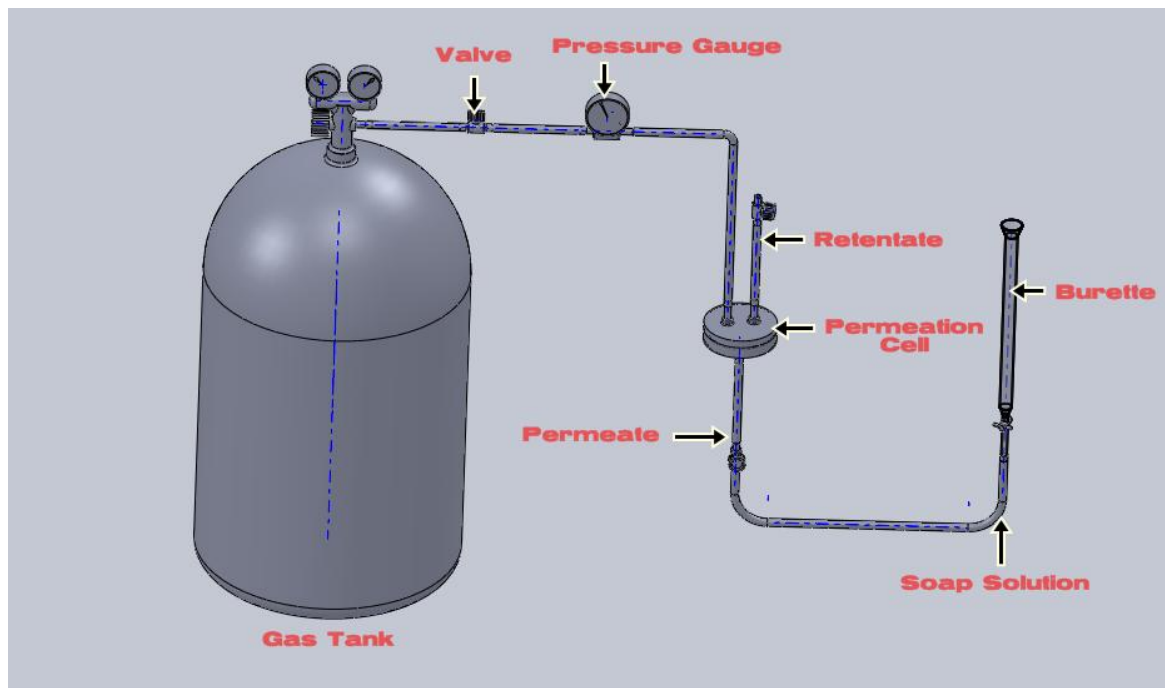
In this research, the membranes were cut into circular shape of 12.6 cm<sup>2</sup> in area. Next, surface layer of membrane was coated with silicone polymer (polydimethyl siloxane) (Sylgard-184, DowCorning) which the composition of the solution was prepared first (3wt% silicone in n-hexane). Then, the coating agent was dropped onto the skin layer of cut membrane until all the solution spread all over the membrane. The membrane was exposed to room temperature for 5 minutes until it dried. Then, the membrane was placed in oven at 40<sup>0</sup>C for 15 minutes. After that, the membrane was dried at room temperature for one day. Figure 3.7 below shows how the coating process done.



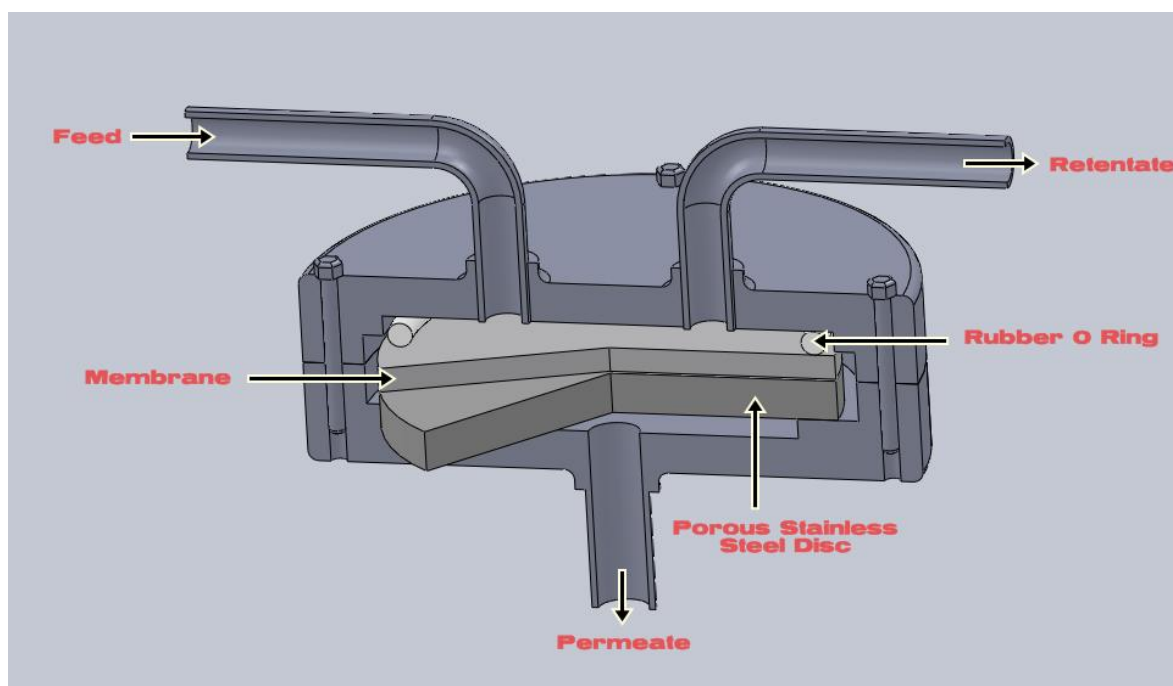
**Figure 3.7:** Membrane coating method

### **3.7 GAS PERMEATION TESTS**

Figure 3.8 and Figure 3.9 illustrate the gas permeation test system and cross sectional area of gas permeation cell setup respectively. This system was used to measure the permeability of tested gases by measuring the flow rate of the gas. The permeation test involved the use of gas permeation cell in which the membrane was placed on a porous stainless steel disc and tighten by rubber *O*-ring. Every gas permeation rate was measured by a constant pressure system using a soap bubble flow meter. The pressures applied were 1,2,3,4, and 5 bars.



**Figure 3.8:** Gas Permeation Test System



**Figure 3.9:** Cross Sectional Area of Permeation Cell



### **3.8 SCANNING ELECTRON MICROSCOPY (SEM)**

The morphologies of the resulting membranes were characterized by scanning electron microscopy (SEM). In order to leave undeformed structure on the membranes, a small piece of the tested membranes were cut and conditioned in liquid nitrogen. The samples were previously coated with platinum in a sputtering device (Biorad Polaron Division). Lastly, the morphologies were examined using SEM such as cross section, surface layer and the support of the membrane.

## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1 DOPE FORMULATION

Table 4.1 below shows the composition used to produce the membrane. The formulations were obtained by applied titration method.

**Table 4.1:** Polymer Composition

Solution	Polymer, Polyethersulfone (PES)	Solvent, N-Methyl Pyrrolidone (NMP)	Nonsolvent	
Batch 1	27.24% wt	64.72% wt	Water (H <sub>2</sub> O)	7.54% wt
Batch 2	22.44% wt	52.37% wt	Ethanol (EtOH)	25.19% wt
Batch 3	19.74% wt	46.05% wt	Methanol (MeOH)	34.21% wt

#### 4.2 THE EFFECTS OF UNCOATED MEMBRANE TO O<sub>2</sub>/N<sub>2</sub> PERFORMANCE

Uncoated membrane usually not very applicable in industries as its low performance compared to coated membrane. According to Kapantaidakis and Koops, 2002, uncoated membrane has the porous skin layer, loose substructure and high permeance value. The results for tested uncoated membranes were varied from pressure of 1 bar to 5 bars for three different polymer concentration as stated in Table 4.2.

**Table 4.2:** Results for tested uncoated membrane

Solution	Pressure (Bar)	Average Permeate Flow Rate Q ( x 10 <sup>3</sup> cm <sup>3</sup> /s)		Average Pressure-Normalized Flux (cm <sup>3</sup> (STP)/ cm <sup>2</sup> . s. cm Hg)x10 <sup>-6</sup> or GPU		Average Selectivity O <sub>2</sub> /N <sub>2</sub> (Unitless)
		O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	
<b>PES/NMP/H<sub>2</sub>O</b>	1	114.06	199.95	121.01	212.12	0.57
	2	464.93	493.50	246.62	261.77	0.94
	3	818.03	743.05	289.28	262.76	1.10
	4	1063.11	1004.96	281.96	266.54	1.06
	5	1128.92	1188.39	239.53	252.15	0.95
<b>PES/NMP/EtOH</b>	1	436.29	400.27	462.82	424.64	1.09
	2	747.56	731.70	396.54	388.13	1.02
	3	1031.68	946.92	364.83	334.86	1.09
	4	1217.03	1013.26	322.78	268.74	1.20
	5	1564.68	1346.83	331.99	285.77	1.16
<b>PES/NMP/MeOH</b>	1	114.59	85.08	121.57	90.26	1.35
	2	115.05	155.20	61.03	82.33	0.74
	3	250.34	282.39	88.53	99.86	0.89
	4	345.93	394.89	91.75	104.73	0.88
	5	547.21	497.33	116.11	105.52	1.10

As shown, significant differences exist for permeabilities and selectivities of O<sub>2</sub> and N<sub>2</sub> gases through asymmetric membrane from different pressures applied and different dope formulation. For overall observation results on uncoated membranes, the data obtained were unstable as the selectivity of the membrane were sometimes increased and decreased. The average permeate flow rate of membrane for O<sub>2</sub> gas seems to be more higher or faster than average permeate flow rate for N<sub>2</sub> gas. Thus, the permeability for O<sub>2</sub> gas through membrane relatively higher than permeability for N<sub>2</sub> gas. Meanwhile, sometimes, the selectivity results obtained reversely and not followed

the order which the permeability of N<sub>2</sub> gas is higher than permeability of O<sub>2</sub> gas. Uncoated membrane contains many macrovoids and defects which were caused by incomplete evaporation of the solvent (Pinnau and Freeman, 2000) that tends to give unstable average selectivity of O<sub>2</sub>/N<sub>2</sub> data.

From the experiment data, increasing pressure will increase the average permeate flow rate of the membrane which means the time needed for tested gas to permeate through membrane faster. Besides, if compared the selectivity for these three dope formulations, the highest selectivity obtained was 1.35 from PES/NMP/MeOH solution with average pressure normalized flux for O<sub>2</sub> was 121.57 GPU and N<sub>2</sub> was 90.26 GPU while the lowest selectivity obtained was 0.57 from PES/NMP/H<sub>2</sub>O solution with average pressure normalized flux or permeability for O<sub>2</sub> was 121.01 GPU and for N<sub>2</sub> was 212.12 GPU respectively. By comparing from PES/NMP/H<sub>2</sub>O, PES/NMP/EtOH, and PES/NMP/MeOH dope formulations, the highest average selectivity was at PES/NMP/EtOH solution as the range of its selectivity was between 1.02 – 1.20 while for PES/NMP/MeOH, the range selectivity was 0.74 – 1.35 and the worst selectivity was PES/NMP/H<sub>2</sub>O solution which the range of its selectivity was only 0.57 – 1.10.

#### **4.3 THE EFFECTS OF COATED MEMBRANE TO O<sub>2</sub>/N<sub>2</sub> PERFORMANCE**

Coating technique can heal defects on the membrane surface (Kapantaidakis and Koops, 2002) but, it is generally very difficult to produce defect-free asymmetric membranes which the difficulty in completely covering surface pores results from penetration of the coating solution into the porous support membrane structure. Because capillary forces in the porous membrane tend to pull the thin liquid polymer solution into the bulk support membrane, the coating layer can be disrupted easily (Pinnau and Freeman, 2000). Table 4.3 below showed the results for coated membrane with different dope formulations and the pressures were varied from 1 to 5 bars.

**Table 4.3:** Results for tested coated membrane

Solution	Pressure (Bar)	Average Permeate Flow Rate Q ( x 10 <sup>3</sup> cm <sup>3</sup> /s)		Average Pressure-Normalized Flux (cm <sup>3</sup> (STP)/ cm <sup>2</sup> . s. cm Hg)x10 <sup>-6</sup> or GPU		Average Selectivity O <sub>2</sub> /N <sub>2</sub> (Unitless)
		O <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	
<b>PES/NMP/H<sub>2</sub>O</b>	1	11.29	3.50	11.97	3.71	3.22
	2	15.96	5.83	8.47	3.09	2.74
	3	20.83	8.77	7.37	3.10	2.37
	4	26.05	9.89	6.91	2.62	2.63
	5	38.20	16.48	8.11	3.50	2.32
<b>PES/NMP/EtOH</b>	1	8.43	5.04	8.94	5.35	1.67
	2	17.90	13.54	9.49	7.18	1.32
	3	28.93	13.66	10.23	4.83	2.12
	4	45.93	23.58	12.18	6.26	1.95
	5	67.90	50.90	14.41	10.80	1.33
<b>PES/NMP/MeOH</b>	1	5.85	3.92	6.21	4.16	1.49
	2	8.82	8.03	4.68	4.26	1.10
	3	16.96	16.49	6.00	5.83	1.03
	4	28.77	24.40	7.63	6.47	1.18
	5	38.51	34.01	8.17	7.22	1.13

From the results observed above, the selectivity of dope formulation by using water as nonsolvent additive (NSA) was the highest compared to other used of nonsolvent additives. The results showed much more stable as the permeability of O<sub>2</sub> gas was higher than N<sub>2</sub> gas for every pressure tested. This means, the coating technique was done successfully and tend to make the membrane structure less defect compared to the uncoated membrane. The reason why the pressure-normalized flux or the

permeability of the membrane for tested O<sub>2</sub> gas was relatively higher than permeability of the membrane for tested N<sub>2</sub> gas was due to the kinetic diameter of each tested gases. The kinetic diameter for O<sub>2</sub> gas was smaller than N<sub>2</sub> gas which 3.46 Å while kinetic diameter for N<sub>2</sub> gas was 3.64 Å respectively (Å= x10<sup>-10</sup>). The pore size for O<sub>2</sub> gas was smaller than N<sub>2</sub> gas which the smaller kinetic diameter gases will easily dissolved through the porous membrane.

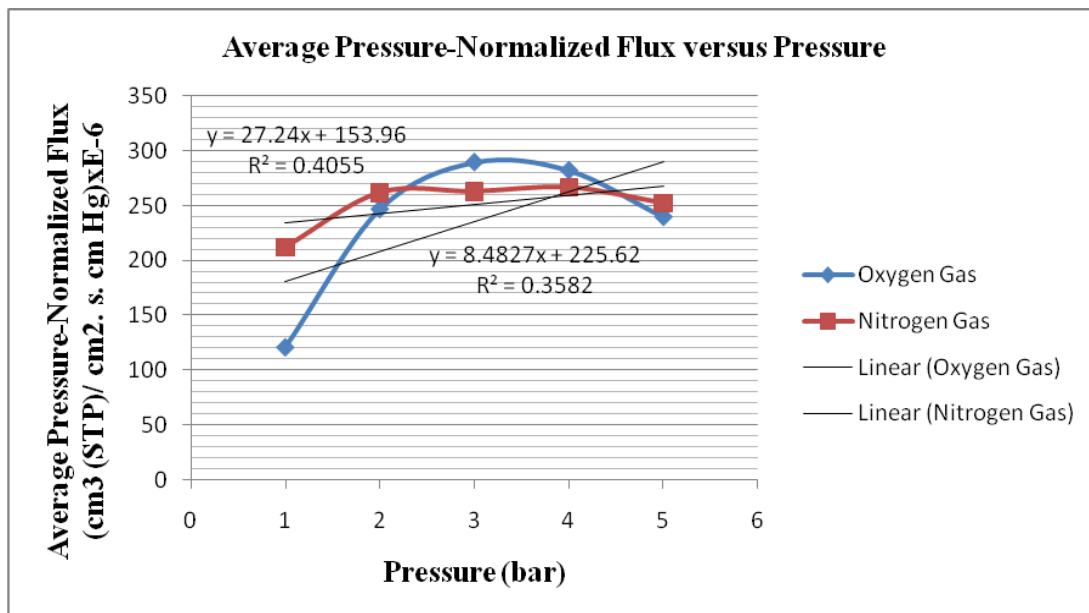
Besides, increased in pressure will increased mostly the average permeate flow rate. For example, at pressure 1 bar from dope formulation PES/NMP/H<sub>2</sub>O, the average permeate flow rate of O<sub>2</sub> gas was 11.29 x 10<sup>-3</sup> cm<sup>3</sup>/s and when the pressure was increased to be 5 bars, the average permeate flow rate of O<sub>2</sub> gas was 38.20 x 10<sup>-3</sup> cm<sup>3</sup>/s. While the results obtained for N<sub>2</sub> gas also the same which increased the pressure will increased the average permeate flow rate. The highest selectivity among these three dope formulations was PES/NMP/H<sub>2</sub>O at pressure applied 1 bar which the average selectivity O<sub>2</sub>/N<sub>2</sub> was 3.22 with average pressure-normalized flux for O<sub>2</sub> gas was 11.97 GPU and N<sub>2</sub> gas 3.71 GPU. In addition, the highest average selectivity was at PES/NMP/ H<sub>2</sub>O solution as the range of its selectivity was 2.32 – 3.22 from 1 – 5 bars. Next was PES/NMP/EtOH solution with average range of selectivity was from 1.32 – 1.67 and lastly, the PES/NMP/MeOH with average selectivity range was 1.03 – 1.50.

#### **4.4 PERFORMANCE OF UNCOATED AND COATED MEMBRANE FOR DOPE FORMULATION CONTAINING H<sub>2</sub>O AS NSA**

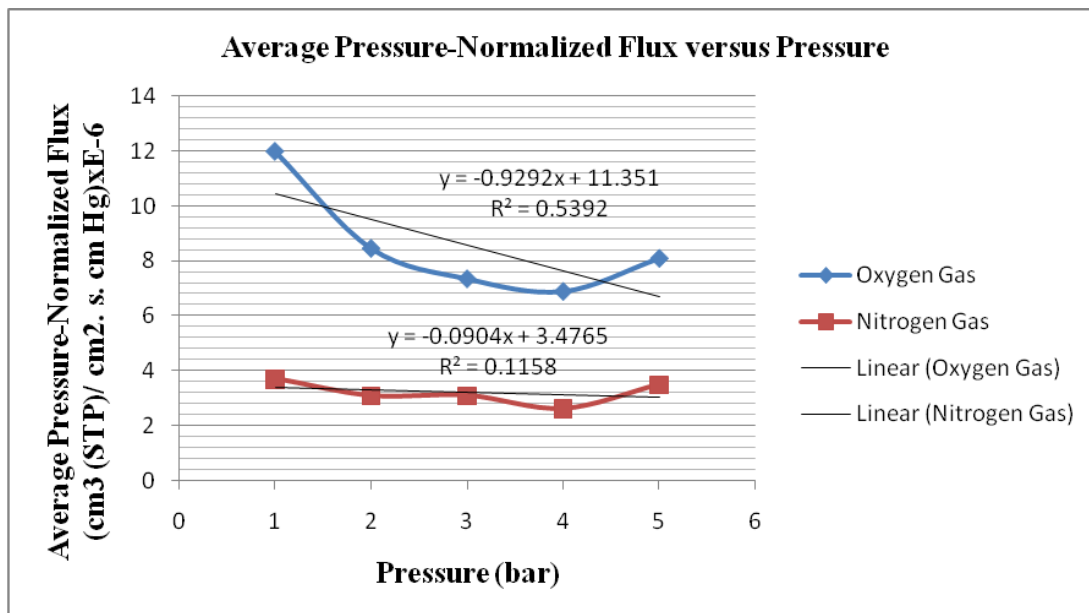
Figure 4.1 showed the average pressure-normalized flux against pressure for uncoated membrane. The trend of the graph was not very constant as the membrane used was uncoated which contained many defects. Figure 4.2 showed average pressure normalized against pressure. Negative slopes were achieved for both O<sub>2</sub> gas linear and N<sub>2</sub> gas linear as increased the pressure will reduce the average pressure-normalized flux.

The graph for uncoated and coated membrane was simplified as Figure 4.7 and Figure 4.8. Figure 4.7 showed the selectivity O<sub>2</sub>/N<sub>2</sub> against pressure and dope formulation for uncoated membrane. The selectivity O<sub>2</sub>/N<sub>2</sub> against pressure was not constant and low. The highest selectivity achieved was only 1.10 while the selectivity

O<sub>2</sub>/N<sub>2</sub> against pressure increased when the membrane was coated. The highest selectivity achieved was 3.22.



**Figure 4.1:** Average Pressure-Normalized Flux versus Pressure for Uncoated Membrane

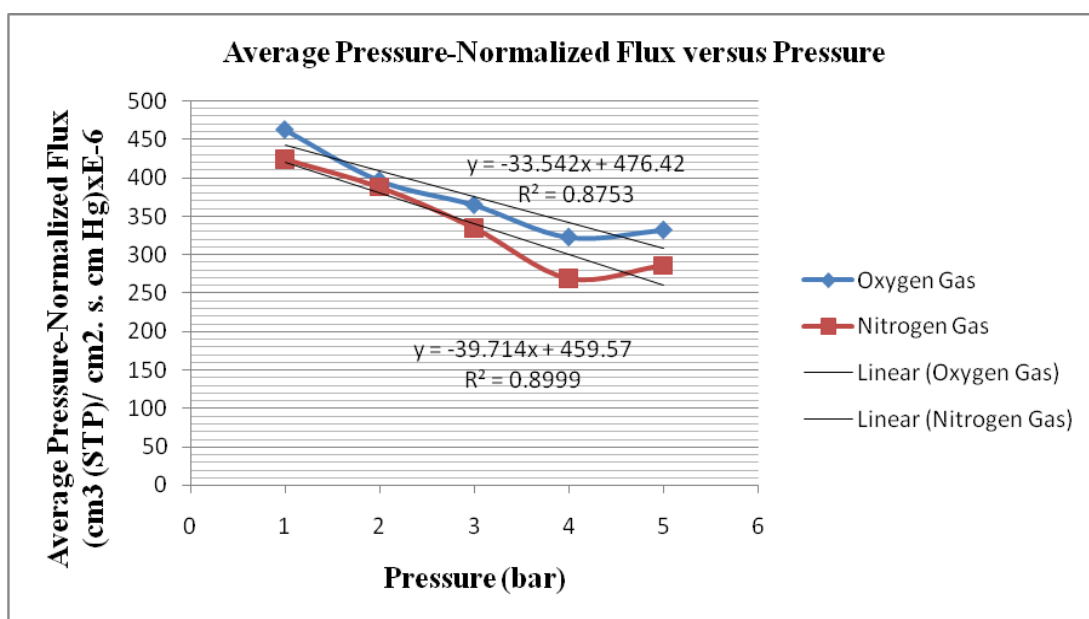


**Figure 4.2:** Average Pressure-Normalized Flux versus Pressure for Coated Membrane

#### 4.5 PERFORMANCE OF UNCOATED AND COATED MEMBRANE FOR DOPE FORMULATION CONTAINING EtOH AS NSA

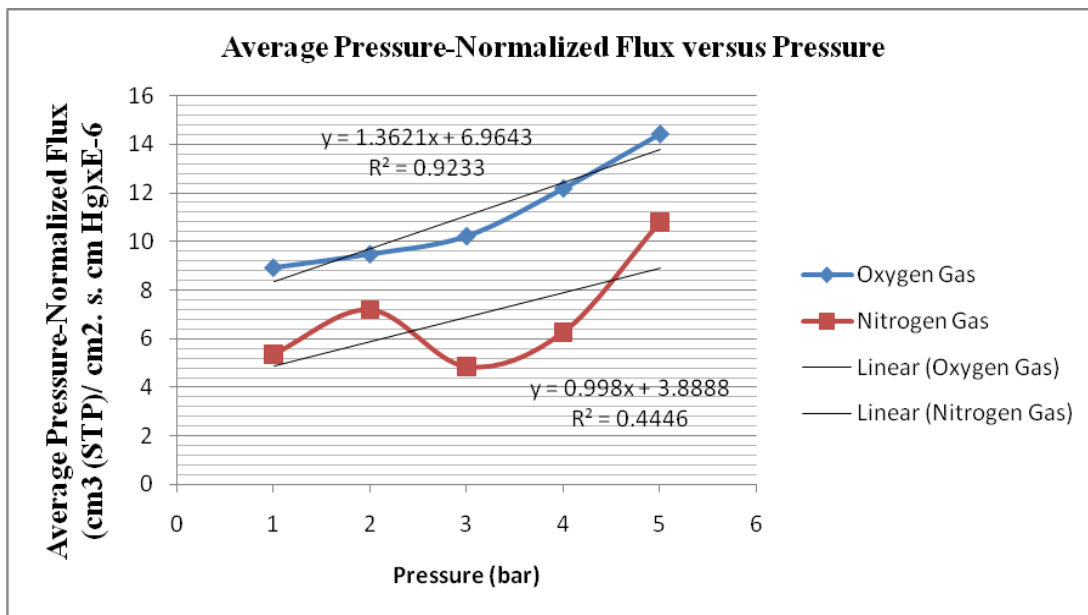
Figure 4.3 and Figure 4.4 showed the average pressure-normalized flux against pressure for uncoated and coated membrane. For uncoated membrane, increased in pressure resulted lower average pressure-normalized flux while for coated membrane, increased in pressure will increased the average pressure-normalized flux.

Summarized graph for uncoated and coated membrane were shown in Figure 4.7 and Figure 4.8. For uncoated membrane, dope formulation of PES/NMP/EtOH gave lower selectivity range from 1.01 to 1.20 for applied pressure from 1 to 5 bars while for coated membrane, this dope formulation selectivity increased a little bit which the range of the selectivity was from 1.32 to 2.12.



**Figure 4.3:** Average Pressure-Normalized Flux versus Pressure for Uncoated Membrane

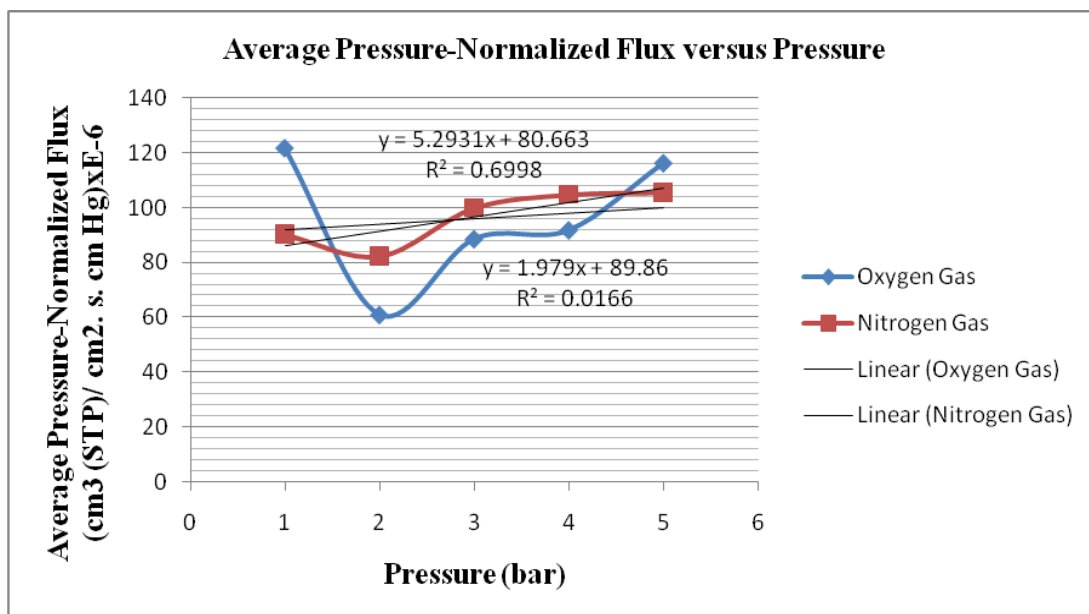




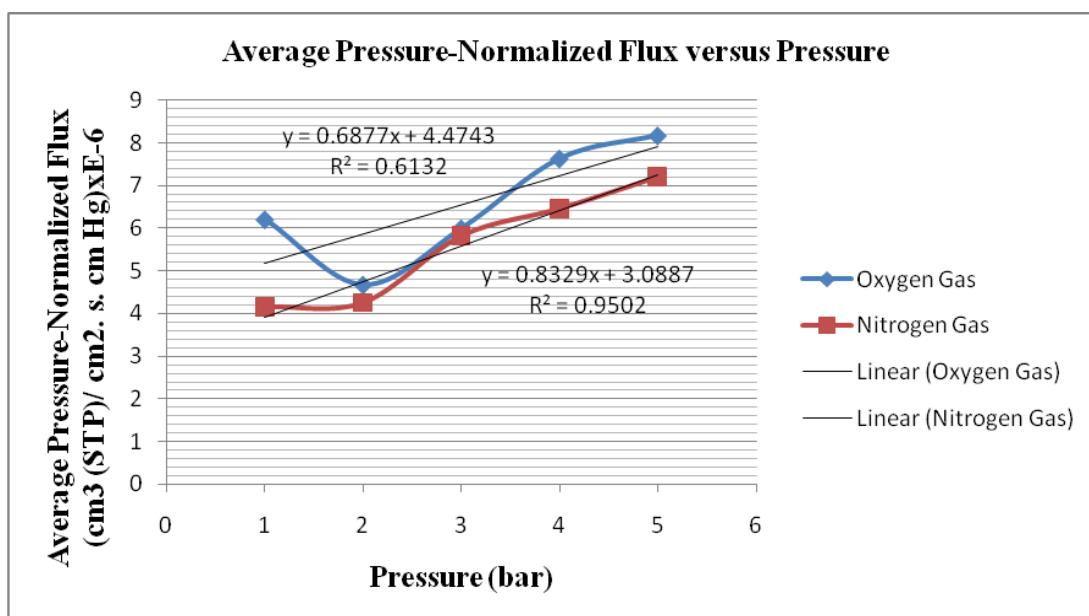
**Figure 4.4:** Average Pressure-Normalized Flux versus Pressure for Coated Membrane

#### 4.6 PERFORMANCE OF UNCOATED AND COATED MEMBRANE FOR DOPE FORMULATION CONTAINING MeOH AS NSA

The graphs on average pressure-normalized flux against pressure for uncoated and coated membrane were shown in Figure 4.5 and Figure 4.6. Both graphs showed positive linear slope as pressure increased, the average pressure-normalized flux increased. When the membrane was coated, the permeability of oxygen gas became higher than permeability of nitrogen gas. As conclusion, solution PES/NMP/MeOH gave the highest selectivity at pressure 1 bar for uncoated membrane which the value was 1.35 while for coated membrane, the highest selectivity was at 1 bar also with selectivity was 1.49.

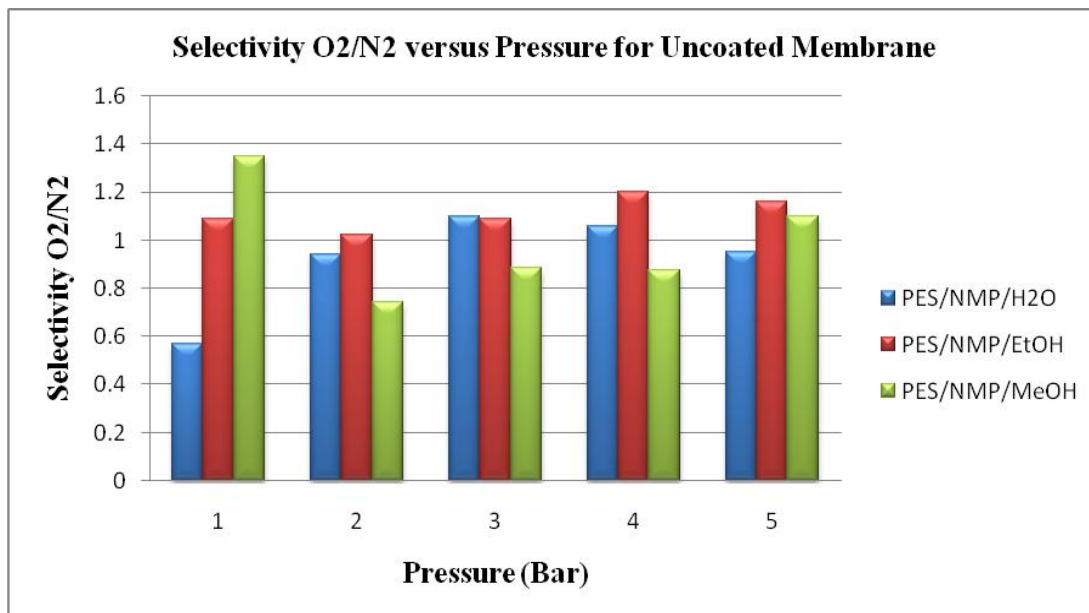


**Figure 4.5:** Average Pressure-Normalized Flux versus Pressure for Uncoated Membrane

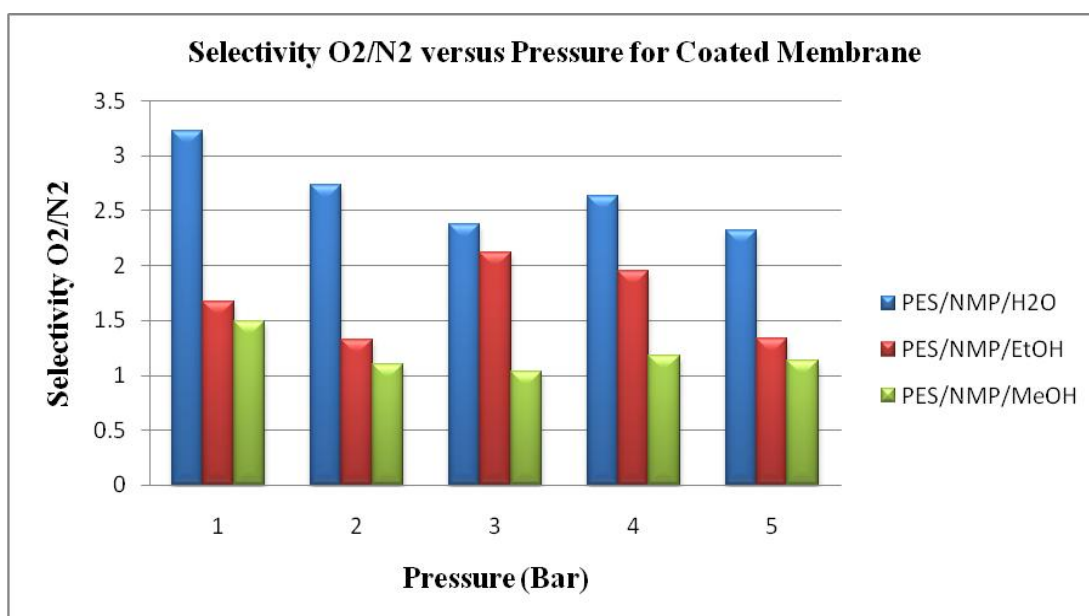


**Figure 4.6:** Average Pressure-Normalized Flux versus Pressure for Coated Membrane

#### 4.7 SUMMARIZED GRAPH OF UNCOATED AND COATED MEMBRANE (SELECTIVITY O<sub>2</sub>/N<sub>2</sub> AGAINST PRESSURE)



**Figure 4.7:** Selectivity O<sub>2</sub>/N<sub>2</sub> versus Pressure for Uncoated Membrane



**Figure 4.8:** Selectivity O<sub>2</sub>/N<sub>2</sub> versus Pressure and Dope Formulation for Coated Membrane

#### 4.8 EFFECT OF NONSOLVENT ADDITIVES ON THE MORPHOLOGY OF FABRICATED ASYMMETRIC UNCOATED AND COATED MEMBRANE USING SCANNING ELECTRON MICROSCOPIC (SEM)

Aroon *et al*, 2010 found that the distance between the dope composition (triangle given on the polymer-solvent/additive axis) and the bimodal line is exactly in the same order. Hence, the thinnest skin results from the casting dope formulation whose composition is closest to the bimodal line, thus leading to the highest flux.

Figure 4.9, Figure 4.11 and Figure 4.13 showed that the membrane without coating has a finger-like macrovoids. Probably, the finger-like macrovoid ends at the top surface of the skin layer, making the surface defective with pinholes. Figure 4.10 shows the sponge-like structures of the membrane prepared from the water containing dope. The chance of the pinhole formation seems to be least. Figure 4.12 showed that the sublayer has a nodular structure when ethanol was added which avoid the formation of pinhole at the membrane surface. Figure 4.14 showed that the formation of finger-like macrovoids still appeared although the membrane was coated. So, the worst nonsolvent additive to be added into dope solution seems to be methanol. Hence, the chance of the pinhole formation at the membrane surface is in the order as below:

**Table 4.4:** Membrane skin thickness for each nonsolvent additive

<b>Nonsolvent additive</b>	Methanol > Ethanol > Water
<b>Skin thickness</b>	3.419 $\mu$ m > 976.9 $\eta$ m > 781.5 $\eta$ m

The membrane skin thickness is obtained from SEM results. Reflecting the above order, the order of the selectivity is:

**Table 4.5:** Selectivity for different nonsolvent used in dope formulation

<b>Nonsolvent additive</b>	Methanol < Ethanol < Water
<b>Selectivity</b>	1.49 GPU < 2.12 GPU < 3.22 GPU

Regarding the permeability of O<sub>2</sub> gas and N<sub>2</sub> gas, the obtained data can be interpreted by assuming the effect of skin layer thickness and the pinhole formation. It is further assumed that the skin layer thickness has a strong effect on the O<sub>2</sub> gas permeability while the pinhole formation has a stronger effect on the N<sub>2</sub> gas permeability. Then, the order of permeability at 1 bar as table below:

**Table 4.6:** Permeability for oxygen gas at different nonsolvent additive used

<b>For Oxygen Gas, O<sub>2</sub></b>	<b>Nonsolvent additive</b>	Methanol < Ethanol < Water
	<b>Permeability</b>	6.21GPU < 8.94GPU < 11.97GPU

**Table 4.7:** Permeability for nitrogen gas at different nonsolvent used

<b>For Nitrogen Gas, N<sub>2</sub></b>	<b>Nonsolvent additive</b>	Ethanol > Methanol > Water
	<b>Permeability</b>	5.35GPU > 4.16GPU > 3.71GPU

So, this can be conclude that, water is the best nonsolvent additive compared to ethanol and methanol as the permeability of O<sub>2</sub> gas was the highest and the permeability for N<sub>2</sub> gas was the lowest which resulted the highest O<sub>2</sub>/N<sub>2</sub> selectivity (Water selectivity: 3.22). It was said before this that O<sub>2</sub> gas permeance is governed by the skin layer thickness and the N<sub>2</sub> gas permeation by the pinhole formation. Perhaps, N<sub>2</sub> gas molecules are too large to permeate through the skin layer and flows mainly through the pinhole. Hence, the pinhole formation governs the N<sub>2</sub> gas permeance. While O<sub>2</sub> gas molecules are small enough to go through the asymmetric membrane of the skin layer more than through the pinholes and therefore, the skin layer thickness governs the O<sub>2</sub> gas permeance. Besides it is known that kinetic diameter for O<sub>2</sub> gas is 3.46 Å and N<sub>2</sub> gas is 3.64 Å which totally showed that the pore size of O<sub>2</sub> gas molecule is smaller than pore size of N<sub>2</sub> gas molecule.

**Table 4.8:** Membrane support height for uncoated membrane using different nonsolvent additive

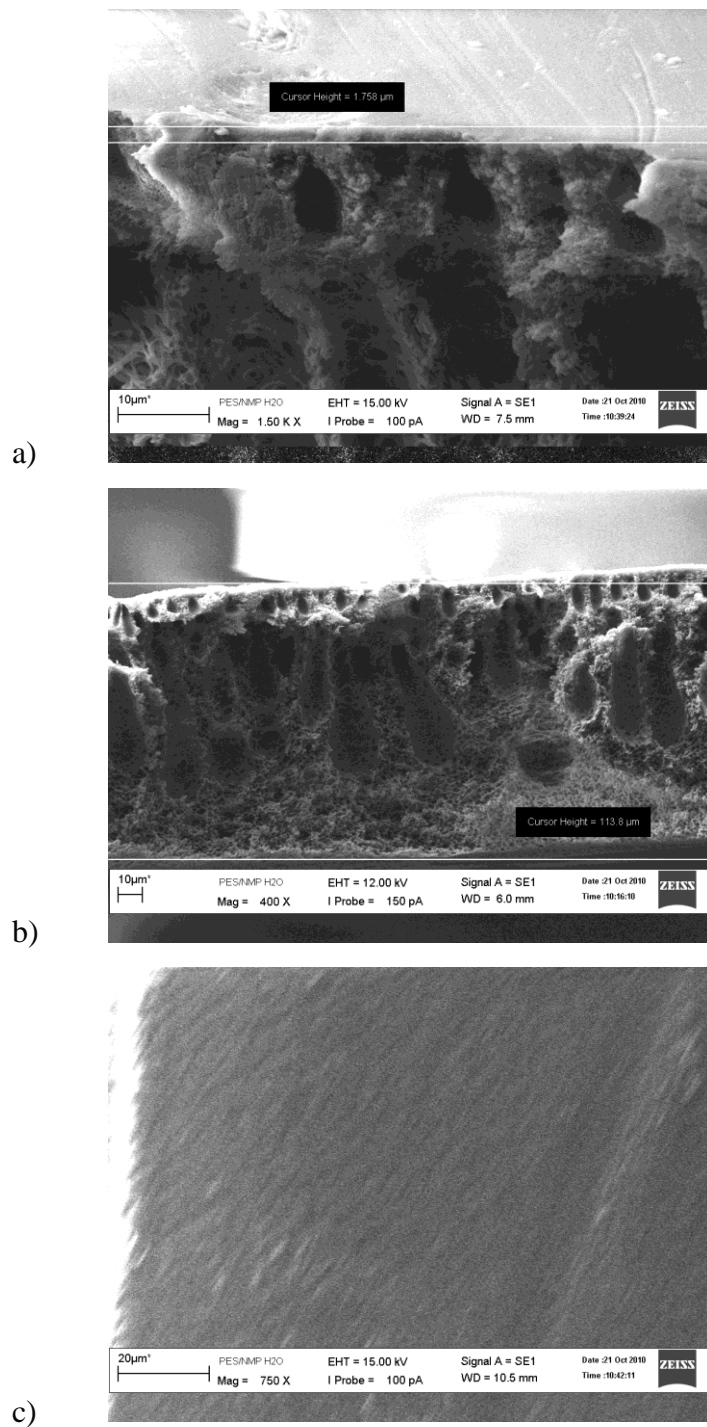
<b>Uncoated membrane</b>	<b>Nonsolvent additive</b>	Water > Methanol > Ethanol
	<b>Membrane support</b>	113.8 $\mu\text{m}$ > 101.4 $\mu\text{m}$ > 89.39 $\mu\text{m}$

**Table 4.9:** Membrane support height for coated membrane using different nonsolvent additive

<b>Coated membrane</b>	<b>Nonsolvent additive</b>	Methanol > Ethanol > Water
	<b>Membrane support</b>	114.3 $\mu\text{m}$ > 108.7 $\mu\text{m}$ > 102.1 $\mu\text{m}$

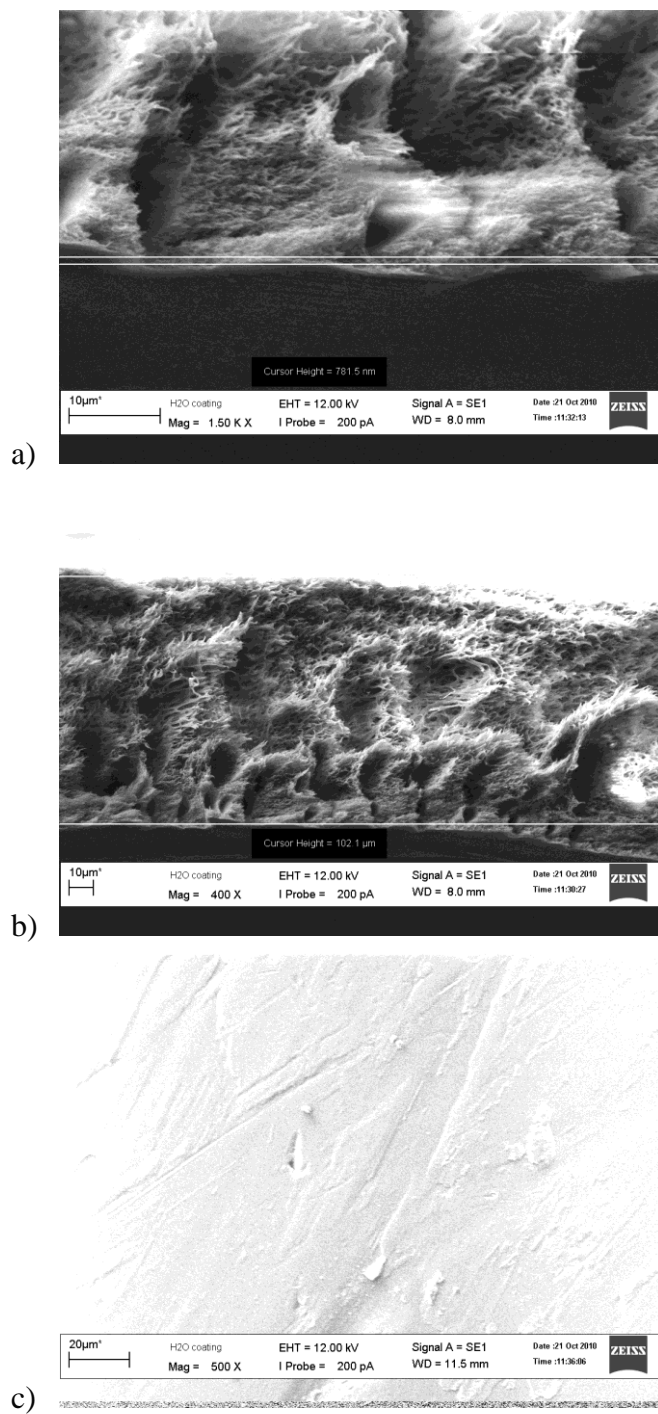
Membrane support for coated membrane showed the same order with the skin thickness of the membrane previously which the more lower its support height, the membrane could be less porous, less defect and contain small amount of macrovoids. It was proved when water support height is the lowest among others because water is the best nonsolvent additive as mentioned earlier.

Figures 4.9(c), 4.11(c), and 4.13(c) showed the surface of the uncoated membrane. Surface of uncoated membrane contained rough surface and there are many defects on the surface membrane. Figures 4.10(c), 4.12(c), and 4.14(c) showed the surface of coated membrane. Surface of coated membrane are smooth and the defect on the membrane surface can be healed.



**Figure 4.9:** Scanning Electron Microscopic PES/NMP/H<sub>2</sub>O solution (uncoated)

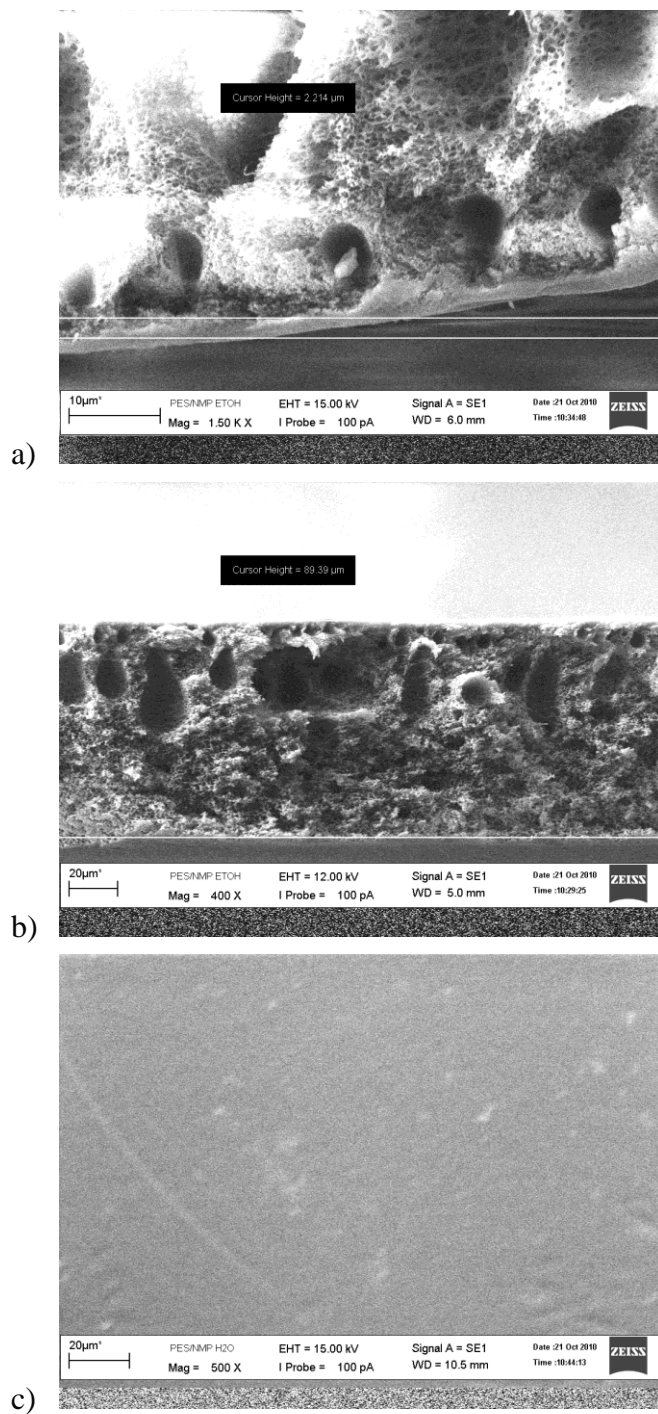
a) Skin measured b) Support measured c) Surface measured



**Figure 4.10:** Scanning Electron Microscopic PES/NMP/H<sub>2</sub>O solution (coated)

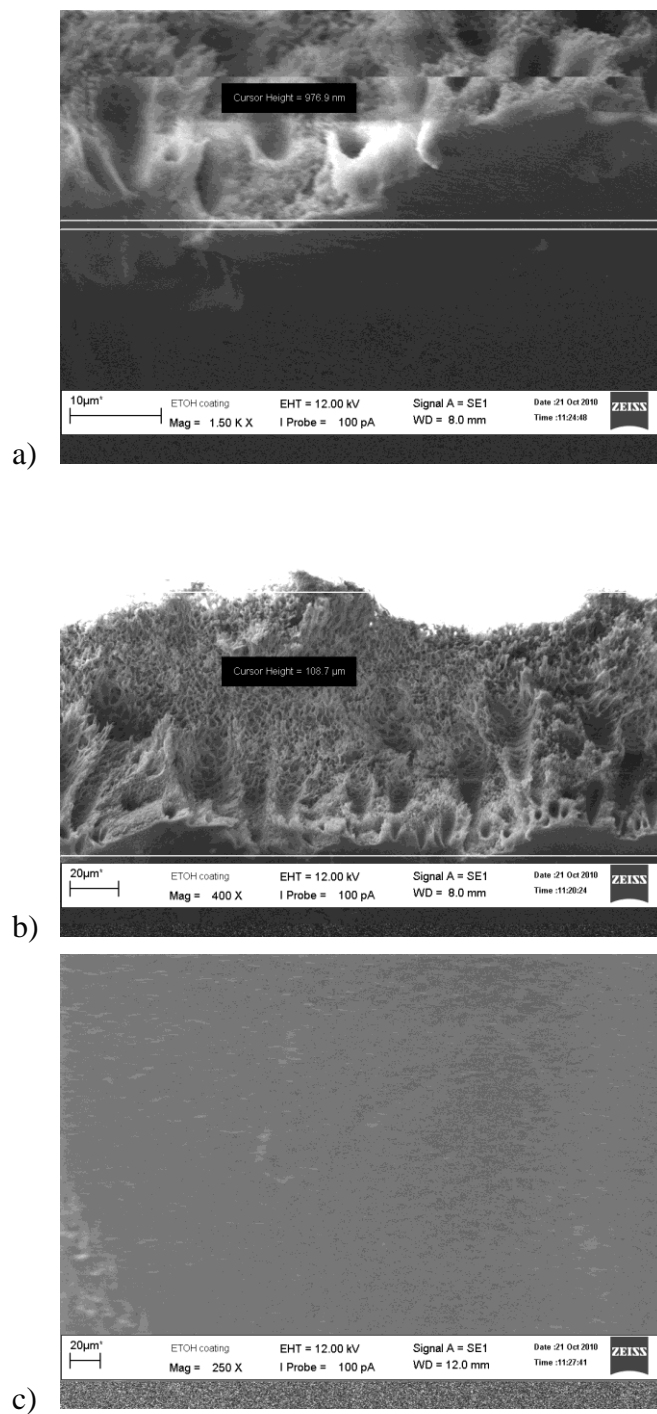
a) Skin measured b) Support measured c) Surface measured





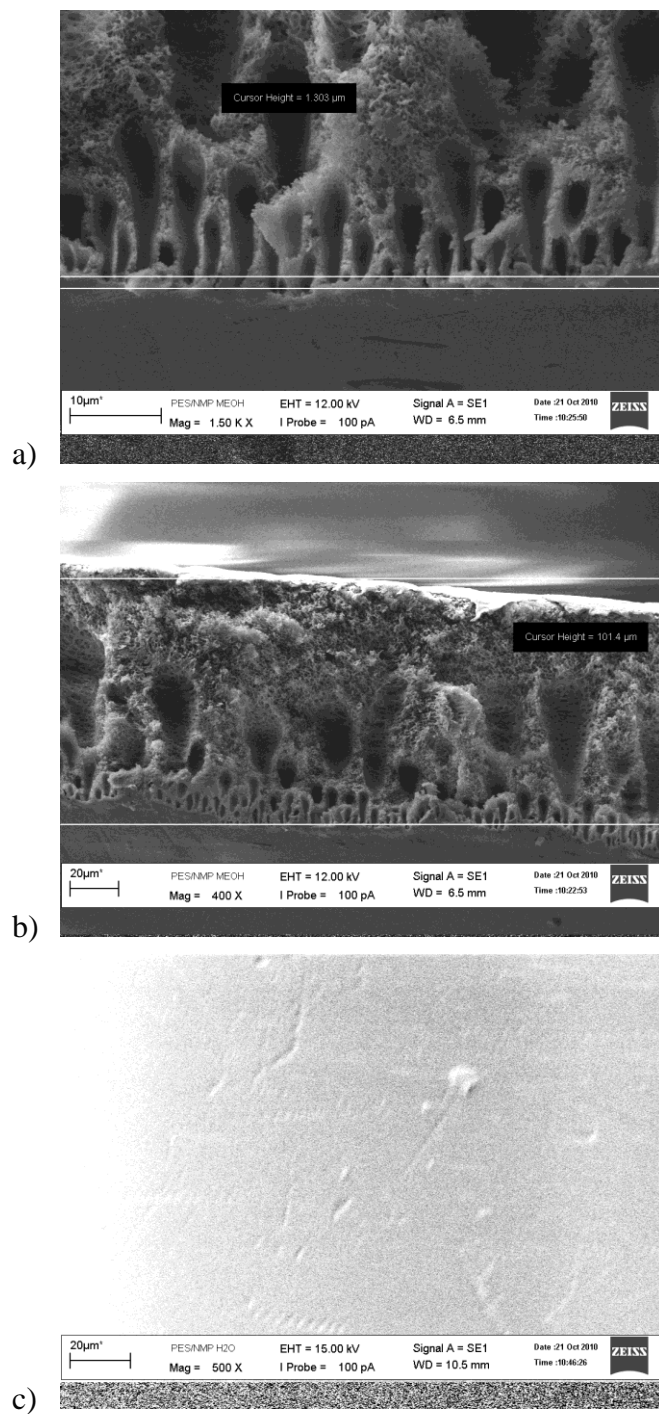
**Figure 4.11:** Scanning Electron Microscopic PES/NMP/EtOH solution (uncoated)

a) Skin measured b) Support measured c) Surface measured



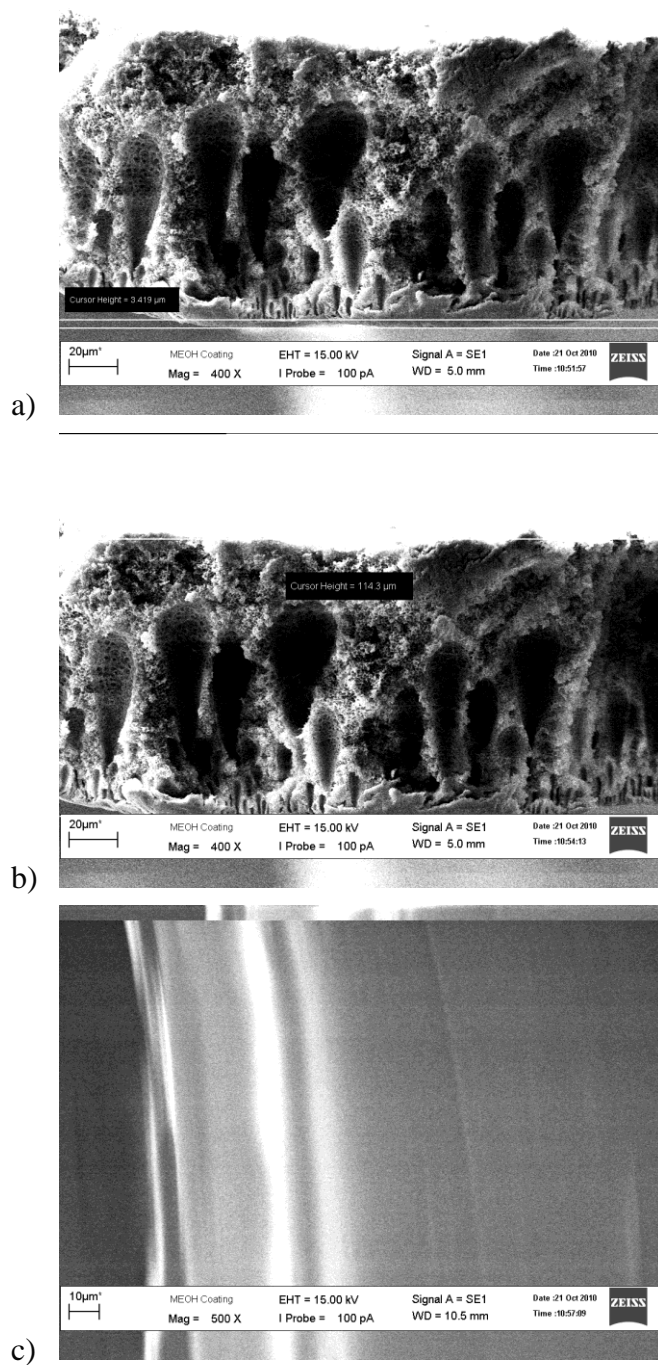
**Figure 4.12:** Scanning Electron Microscopic PES/NMP/EtOH solution (coated)

a) Skin measured b) Support measured c) Surface measured



**Figure 4.13:** Scanning Electron Microscopic PES/NMP/MeOH solution (uncoated)

a) Skin measured b) Support measured c) Surface measured



**Figure 4.14:** Scanning Electron Microscopic PES/NMP/MeOH solution (coated)

a) Skin measured b) Support measured c) Surface measured

#### 4.9 POLYMER-POLYMER INTERACTION

According to Wang *et al* 1996, the interaction of the nonsolvent and solvent molecules leads to a reduction of the dissolving power of the solvent and this further enhances the polymer-solvent solution. In this case, the polymer chains may have a smaller excluded volume because of a more tightly coiled conformation. The polymer aggregates are formed in the polymer solution. Thus, an initially homogeneous solution may become microscopically heterogeneous. If a sufficient amount of the NSA is added, a polymer lean phase may exist in the polymer solution. The polymer lean phase is responsible for the initiation of macrovoids.

Aroon *et al* 2010 stated that when a nonsolvent additive is used as a third component in the polymer-solvent solution, it can decrease the dissolving power of the solvent and thus increase polymer-polymer interaction. Therefore, adding a nonsolvent additive into a polymer solution increases the tendency of polymer chains to approach a more tightly coiled conformation.

It is well known that the properties of nonsolvent affect the morphology and performance of the membrane. Addition of NSA into a polymeric solution along with volatile solvent (NMP), can change liquid-liquid demixing behavior and as a result, can cause a change in the membrane morphology and performance. Besides, adding NSA to a polymeric solution can eliminate macrovoids formation during instantaneous demixing and change the morphology of the membranes from finger-like to sponge-like structure despite of instantaneous demixing.

Wang *et al* 1996 also found that the size of polymer aggregates depends on the interaction strengths of solvent-NSA-polymer. Strong interaction of solvent-NSA and weak interaction of solvent-polymer and NSA-polymer tend to form large or even super-polymer aggregates resulting in the formation of big cavities and finger-like structure. If the diffusion of the solvent molecules than that of the NSA, the rapid outflow of solvent molecules will further enhance the polymer-polymer interaction before the membrane is solidified.

Peng *et al* 2009 investigate that the dope containing 10wt% methanol is relatively closer to the cloud point than that containing 10wt% ethanol. However, the former results in many macrovoids which can be attributed to the viscosity effect on the macrovoid formation. The addition of 10wt% ethanol obviously increases the dope viscosity and enhances the polymer chain entanglement, so that the nonsolvent intrusion and convection, nonsolvent super saturation, as well as the mutual diffusion of solvent and nonsolvent during the coagulation which are critical factors for macrovoids formation are retarded. As opposed to ethanol, since methanol possesses very low viscosity itself, it would dilute the dope viscosity and chain-chain interaction and hence promote the macrovoid formation.

From this research, a similar rationale is applicable to explain the macrovoids formation on asymmetric membrane from dopes containing water. Water has similarly low viscosity, enhances the mutual solvent and nonsolvent exchange, and results in more macrovoids. Another reason may be effect of solubility parameter on the kinetics of the macrovoids formation. Since H<sub>2</sub>O/NMP (7.54/64.72wt%) and EtOH/NMP (25.19/ 52.37wt%) mixtures have good solubility parameters and hydrogen bonding to PES membrane, the mutual diffusion between H<sub>2</sub>O/NMP and EtOH/NMP and external coagulant would be hindered during the phase inversion and eventually the macrovoids were suppressed or prevented.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

In order to fabricate the ideal asymmetric membrane for gas separation, several requirements must be met which are the skin layer must be defect free, as thin as possible and the support of the membrane should provide sufficient mechanical strength. In this research, asymmetric polyethersulfone membrane had been produced which was obtained by manipulating the use of three different nonsolvent additives. Several conclusions had been made which are as follows:

- 1) Water was identified to be a good nonsolvent additive to the polymer solution compared to ethanol and methanol because only 7.54%wt amount of water is needed to bring the casting solution near to phase separation compared to ethanol 25.19%wt and methanol 34.21%wt which depend on polymer-polymer interaction between solvent-NSA, solvent-polymer and NSA-polymer. Increasing NSA in the casting solution will decrease the polymer concentration.
- 2) The selectivity of the membrane decreased as the roughness of the surface increased which was caused by the presence of polymer nodules at the surface of polymeric membrane. Increase in selectivity as nodules are packed more compactly and less of macrovoids appeared. Some defects were observed at the surface skin layer for uncoated membrane, however for coated membrane, the defects on the membrane surfaces were completely covered by the surface pores by using silicone rubber coating.

- 3) Asymmetric polyethersulfone membrane was successfully developed when water was used as nonsolvent additive in polymer solution. The permeability and selectivity of the membrane was 11.97GPU for O<sub>2</sub> gas and 3.2 respectively. Asymmetric polyethersulfone membrane was successfully developed when ethanol was used as nonsolvent additive in polymer solution. The permeability and selectivity of the membrane was 10.23GPU for O<sub>2</sub> gas and 2.1 respectively. Asymmetric polyethersulfone membrane was also successfully when methanol was used as nonsolvent additive in polymer solution. The permeability and selectivity of the membrane was 6.21GPU and 1.5 respectively.

For the conclusion, the optimum condition for fabrication the best performance of polyethersulfone flat sheet asymmetric membrane was from casting solution containing of 27.24%wt of polymer, 64.72%wt of solvent and 7.54%wt of nonsolvent additive for the coated membrane at pressure 1 bar, with permeability of O<sub>2</sub> and N<sub>2</sub> gases were 11.97GPU and 3.71GPU respectively. The selectivity of this membrane was 3.2. The choice of an appropriate nonsolvent additive and the right polymer formulation is very important for the formation of ideal asymmetric membranes having high gas permeabilities and selectivities.

## **5.2 RECOMMENDATIONS**

In order to improve for future work of gas separation using membrane, several recommendations were made based on results and conclusions obtained from this research.

- 1) This research was using pure gas as test gas. It is recommended to use mixture of gas for future research.
- 2) Effect of shear rate and evaporation time can be investigated in order to produce high performance of ideal asymmetric membrane.
- 3) Different type of compositions, coagulation medium, drying method can be considered to optimize membrane formation process.
- 4) The prepared membrane also can be characterized using FTIR in order to determine functional group of the membrane.



- 5) Improvement of membrane formation where casting manually can be replaced by using pneumatically controlled casting machine which is more systematic.

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## **APPENDICES**

Dope Formulation: 27.74%PES 64.72%NMP 7.54%WATER

Gas applied: Oxygen and Nitrogen

Volume changes:

10

cm<sup>3</sup>

Description: Uncoated

Pressure applied: 1,2,3,4,5 bar

Membrane area:

12.568

cm<sup>2</sup>

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
Gas Applied	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	258.42	111.9	53.26	40.3	20	22.8	16	16.96	12	12.94
Membrane 2	52.76	24.56	11.02	11.48	8.02	8.54	6	6.26	6.1	5.88
Membrane 3	87.76	96.8	33.38	27.68	14.14	16.14	11.14	12.08	10.94	9.16
Average Flowrate,Q	0.11406	0.199946	0.464927	0.493497	0.818032	0.743045	1.063111	1.00496	1.128918	1.188394
Q(10 <sup>3</sup> )	114.0605	199.9458	464.9266	493.4969	818.0321	743.0451	1063.111	1004.96	1128.918	1188.394
Permeability (GPU)	121.0062	212.1216	246.6192	261.7743	289.2822	262.7644	281.9624	266.5395	239.5328	252.1523
Selectivity	0.570456834		0.942106358		1.100918504		1.05786345		0.949953036	

Gas applied: Oxygen and Nitrogen

Volume changes:

2

cm<sup>3</sup>

Description: Coated

Pressure applied: 1,2,3,4,5 bar

Membrane area:

12.568

cm<sup>2</sup>

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
Gas Applied	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	151.4	455.42	107.26	311.6	95.74	232.02	73.38	227.14	44.02	127.46
Membrane 2	208.38	845.18	149.28	359.88	95.62	230.78	87.78	185.2	59.12	111.6
Membrane 3	181.02	534.36	126.28	362.72	96.7	221.54	71.14	198.82	56.6	126.4
Average Flowrate	0.011285	0.0035	0.015961	0.00583	0.02083	0.008771	0.026051	0.009888	0.0382	0.016478
Q(10 <sup>3</sup> )	11.28546	3.500235	15.96058	5.829929	20.82952	8.771308	26.05107	9.887876	38.19969	16.47838
Permeability (GPU)	11.9727	3.713383	8.466253	3.092473	7.365981	3.101813	6.909364	2.622501	8.105176	3.496367
Selectivity	3.224201679		2.737697109		2.374733622		2.634647183		2.318170992	

Dope Formulation: 22.44%PES 52.37%NMP 25.19%ETHANOL

Gas applied: Oxygen and Nitrogen

Volume changes:

10

cm<sup>3</sup>

Description: Uncoated

Pressure applied: 1,2,3,4,5 bar

Membrane area:

12.568

cm<sup>2</sup>

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
Gas Applied	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	32.8	40.2	15.4	20.56	15.32	16.4	8.42	15.06	6.92	14.48
Membrane 2	39.68	51.12	25.74	19.96	8.28	14.06	8.22	13.02	6.32	6.22
Membrane 3	13.3	13.22	8.3	8.28	8.1	6.58	8.02	6.22	6	5.74
Average Flowrate	0.436258	0.400268	0.747557	0.731704	1.03168	0.946917	1.217025	1.013259	1.564677	1.346828
Q(10 <sup>3</sup> )	436.258	400.268	747.5568	731.7043	1031.68	946.9168	1217.025	1013.259	1564.677	1346.828
Permeability (GPU)	462.8241	424.6425	396.5398	388.1308	364.8347	334.8599	322.7842	268.7404	331.9918	285.7688
Selectivity	1.089914633		1.021665183		1.089514512		1.201100106		1.161749589	

Gas applied: Oxygen and Nitrogen

Volume changes:

2

cm<sup>3</sup>

Description: Coated

Pressure applied: 1,2,3,4,5 bar

Membrane area:

12.568

cm<sup>2</sup>

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
Gas Applied	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	267.18	474.9	152.44	262.94	96.5	155	42.6	105.12	26.58	48.88
Membrane 2	298	425.58	112.3	133.2	66.8	162.34	53.4	89.62	36.04	39.44
Membrane 3	180.41	321.94	87.88	111.18	55.36	126.97	37.47	68	27.41	32.74
Average Flowrate	0.008428	0.005041	0.017896	0.013537	0.028931	0.013658	0.045926	0.023585	0.067902	0.050905
Q(10 <sup>3</sup> )	8.42762	5.041073	17.89589	13.53672	28.93089	13.65827	45.92586	23.5847	67.9015	50.90461
Permeability (GPU)	8.940823	5.348051	9.492832	7.180522	10.23088	4.829997	12.18063	6.255224	14.40728	10.80089
Selectivity	1.671790816		1.322025372		2.118196412		1.947273721		1.333896994	



Dope Formulation: 19.74%PES 46.05%NMP 34.21%METHANOL

Gas applied: Oxygen and Nitrogen

Volume changes:

10

cm<sup>3</sup>

Description: Uncoated

Pressure applied: 1,2,3,4,5 bar

Membrane area:

12.568

cm<sup>2</sup>

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
Gas Applied	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	88.8	99.26	78.42	50.9	43.78	30.48	21.28	23.54	19.86	20.34
Membrane 2	82.34	150.76	107.78	64.2	36.5	38.76	42.2	25.34	19.46	19.62
Membrane 3	91.14	113.42	80.1	88.2	40.22	38.3	30.22	27.38	16.02	20.38
Average Flowrate	0.114594	0.085081	0.115048	0.155202	0.25034	0.282393	0.345933	0.394891	0.547206	0.497334
Q(10 <sup>3</sup> )	114.5939	85.08133	115.048	155.2019	250.34	282.3928	345.9328	394.8906	547.2063	497.3344
Permeability (GPU)	121.5721	90.26239	61.02695	82.32647	88.52818	99.86309	91.74962	104.7344	116.1057	105.524
Selectivity	1.346874376		0.741279836		0.886495464		0.876021708		1.100278469	

Gas applied: Oxygen and Nitrogen

Volume changes:

2

cm<sup>3</sup>

Description: Coated

Pressure applied: 1,2,3,4,5 bar

Membrane area:

12.568

cm<sup>2</sup>

	P(bar)= 1		P(bar)= 2		P(bar)= 3		P(bar)= 4		P(bar)= 5	
	Time(s)		Time(s)		Time(s)		Time(s)		Time(s)	
Gas Applied	O2	N2	O2	N2	O2	N2	O2	N2	O2	N2
Membrane 1	302.68	424.8	182.32	186.08	85.62	82.76	53.58	63.52	40.54	43.9
Membrane 2	401.2	571.02	311.14	370.8	180.8	194.96	105.34	117.58	88.5	83.19
Membrane 3	335.5	563.74	220.6	251.58	121.42	133	66.68	80.94	45.88	61.66
Average Flowrate	0.005851	0.003919	0.008821	0.008031	0.016964	0.016487	0.028769	0.024402	0.038508	0.034012
Q(10 <sup>3</sup> )	5.851312	3.919446	8.821294	8.030522	16.96424	16.48746	28.76917	24.40183	38.50828	34.01179
Permeability (GPU)	6.20763	4.158122	4.679235	4.259772	5.999095	5.830489	7.630269	6.471948	8.170651	7.216591
Selectivity	1.492892675		1.098470772		1.028918016		1.178975605		1.13220379	

### Calculation Steps:

Dope Formulation of 27.74% PES, 64.72% NMP, and 7.54% H<sub>2</sub>O with coated membrane at pressure 1 bar.

#### 1) Pressure Normalized Flux or Permeability of Gas i,

$$(P/l)_i = Q_i / A\Delta P$$

$$\text{Unit} = \text{GPU} @ 1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{HG}$$

$$Q_i = \text{Volumetric Flow Rate for Gas } i$$

$$\Delta P = \text{Pressure Difference Across Membrane}$$

$$A = \text{Membrane Surface Area}$$

$$l = \text{Membrane Skin Thickness}$$

$$\begin{aligned} (P/l) \text{ oxygen gas} &= (0.011285 \text{ cm}^2/\text{s}) \times (1/12.568 \text{ cm}^2) \times [(1 \text{ bar}/75 \\ &\text{Hg})/1 \text{ bar}] \\ &= (0.000011972 \text{ cm}/\text{s} \cdot \text{Hg}) \times (\text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{Hg} / 1 \times 10^{-6} \text{ cm}^3 \cdot \text{cm}) \\ &\times 1 \text{ GPU} \\ &= 11.9722 \text{ GPU} \end{aligned}$$

$$\begin{aligned} (P/l) \text{ nitrogen gas} &= (0.0035 \text{ cm}^2/\text{s}) \times (1/12.568 \text{ cm}^2) \times [(1 \text{ bar}/75 \text{ Hg})/1 \text{ bar}] \\ &= (0.000003713 \text{ cm}/\text{s} \cdot \text{Hg}) \times (\text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{Hg} / 1 \times 10^{-6} \text{ cm}^3 \cdot \text{cm}) \\ &\times 1 \text{ GPU} \\ &= 3.7131 \text{ GPU} \end{aligned}$$

#### 2) Selectivity of the membrane, $\alpha_{ij}$

$$\begin{aligned} \alpha_{ij} &= P_i/P_j \\ &= (P/l)_i / (P/l)_j \\ &= (P/l) \text{ oxygen gas} / (P/l) \text{ nitrogen gas} \\ &= 11.9722 \text{ GPU} / 3.7131 \text{ GPU} \\ &= 3.2 \text{ (unitless)} \end{aligned}$$