

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

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FOR CO<sub>2</sub>/CH<sub>4</sub> SEPARATION

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*To Mak and Abah : Che Noriah binti Salleh & Khaidzi bin Tuan Said.*

*“I will love you till the end of time”*

*To my beloved siblings: Nurul Aida, Ainiza, Ain Syahirah, Asma Izzah & Ain Afiqah.*

*“Thanks for your blessing”*

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## ABSTRACT

The objective of this study is to develop a high performance and defect free asymmetric polysulfone membrane for CO<sub>2</sub>/CH<sub>4</sub> separation and to investigate the effect of different type of solvents on the performance of the polysulfone membrane. The membrane were developed consist of 20% polysulfone (PSU) polymer, 77% solvent (NMP, DMAc, DMF) and 3% water (H<sub>2</sub>O) as non-solvent additive. Firstly, three type of casting solution had been developed by manipulating a different type of solvent which consist of N-methyl-2-pyrrolidone (NMP), N-N-Dimethylformamide (DMF) and N-Dimethylacetamide (DMAc). Formation of the asymmetric flat sheet membrane had been performed using casting block through a simple dry/wet phase inversion process. Water and methanol were used as solvent for solvent exchange process. On the next stage, pure CO<sub>2</sub> and CH<sub>4</sub> were used as test gases in the permeation test using pressure supply range between 1 to 4 bar. Consequently, the result showed that the asymmetric flat sheet membrane developed by using N-methyl-2-pyrrolidone (NMP) as a solvent achieved better performance in terms of permeability and selectivity of the membrane which is 7.34. The produced asymmetric polysulfone membranes were then carry out by characterized using Scanning Electron Microscopic (SEM) to investigate the structure and morphology of the membrane. Based on SEM images, it can observe that the membrane with N-methyl-2-pyrrolidone (NMP) as a solvent has the most porous structure. Finally, the membrane structure was further characterized the rheological induced molecular orientation in asymmetric membrane that observed by analyzing the wave length using Fourier Transform Infrared Spectroscopy (FTIR). As a conclusion, the polysulfone membrane prepared from PSU/NMP/H<sub>2</sub>O solvents system proved to give greatest separation characteristics compared to other membrane produced from PSU/DMAc/H<sub>2</sub>O and PSU/DMF/H<sub>2</sub>O solvent systems.

## ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan membrane asimetrik yang berprestasi tinggi dan bebas kecacatan polisulfone (PSU) membran asimetrik bagi proses pemisahan  $\text{CO}_2/\text{CH}_4$  dan mengkaji pengaruh pelbagai jenis pelarut untuk prestasi membran polisulfone (PSU) itu. Membran yang dihasilkan daripada 20% polimer polisulfone (PSU), 77% pelarut (NMP, DMAc, DMF) dan 3% air ( $\text{H}_2\text{O}$ ) sebagai bahan tambah bukan pelarut. Pada mulanya, tiga jenis larutan tuangan yang dihasilkan daripada pelarut yang dimanipulasikan yang terdiri dari N-methyl-2-pyrrolidona (NMP), NN-dimethylformamide (DMF) dan N-dimethylacetamida (DMAc). Pembentukan membrane asimetrik lembaran rata telah dilakukan dengan menggunakan blok rata melalui proses fasa kering/basah sederhana. Air dan methanol adalah digunakan sebagai pelarut untuk proses pertukaran pelarut. Seterusnya, gas carbon dioxide tulen dan methane tulen digunakan sebagai gas ujian dalam ujian ujikaji kebolehtelapan dengan tekanan yang disalurkan adalah berkisar antara 1 sampai 4 bar. Akibatnya, hasilnya menunjukkan bahawa membrane asimetrik lembaran rata yang dihasilkan dengan menggunakan N-methyl-2-pyrrolidona (NMP) sebagai pelarut mencapai prestasi yang terbaik dalam aspek ketelapan dan selektivitansi iaitu sebanyak 7.34. Kemudiannya, asimetrik membran polisulfona dianalisa menggunakan Mikroskop Elektron imbasan (SEM) untuk menyiasat struktur dan morfologi membran. Berdasarkan gambar SEM, didapati bahawa membran dengan yang menggunakan N-methyl-2-pyrrolidona (NMP) sebagai pelarut mempunyai struktur yang paling keropos. Akhirnya, struktur membran dianalisa bercirikan rheologi induksi molekul orientasi pada membran asimetrik yang diamati oleh menganalisis panjang gelombang dengan menggunakan Fourier Transform Infrared Spectroscopy (FTIR). Sebagai kesimpulan, membran polisulfon yang dihasilkan dari PSU/NMP/ $\text{H}_2\text{O}$  pelarut sistem terbukti memberikan ciri-ciri pemisahan terbesar berbanding dengan membran yang lain yang dihasilkan dari PSU/DMAc/ $\text{H}_2\text{O}$  dan PSU/DMF/ $\text{H}_2\text{O}$  sebagai pelarut.



## TABLE OF CONTENTS

	<b>Page</b>
<b>SUPERVISOR’S DECLARATION</b>	iii
<b>STUDENT’S DECLARATION</b>	iv
<b>ACKNOWLEDGEMENT</b>	vi
<b>ABSTRACT</b>	vii
<b>ABSTRAK</b>	viii
<b>TABLE OF CONTENTS</b>	ix
<b>LIST OF TABLES</b>	xii
<b>LIST OF FIGURES</b>	xiii
<b>LIST OF SYMBOLS</b>	xvi
<b>LIST OF ABBREVIATIONS</b>	xvii
<b>CHAPTER 1            INTRODUCTION</b>	
1.1    Research Background	1
1.2    Problem Statement	3
1.3    Research Objective	3
1.4    Scope of Research	4
1.5    Rational & Significant of Study	4
<b>CHAPTER 2            LITERATURE REVIEW</b>	
2.1    Membrane Definition	5
2.2    Membrane Technology Review	6
2.2.1    Historical Development of Membrane	6
2.2.2    Membrane Process	7
2.3    Membrane Application	9
2.4    Membrane Separation Process	10
2.5    Membrane Principles	12
2.5.1    Asymmetric Membranes	12
2.6    Phase Inversion in Membrane Gas Separation	15
2.7    Membrane Modules	16

2.7.1	Flat Sheet Plate and Frame Module	17
2.7.2	Spiral Wound Module	17
2.7.3	Tubular Module	18
2.7.4	Hollow Fiber Module	19
2.8	Membrane in Gas Separation	20
2.8.1	Polymeric Membrane	21
2.8.2	Inorganic Membrane	22
2.8.3	Mixed Matrix Membrane	23

### **CHAPTER 3            METHODOLOGY**

3.1	Research Design	26
3.2	Material Selection	27
3.2.1	Polysulfone	27
3.2.2	N-Methy-2-Pyrrolidone	28
3.2.3	N,N-Dimethylformamide	29
3.2.4	N,N-Dimethylacetamide	30
3.2.5	Methane and Carbon Dioxide Gases	31
3.2.6	Nonsolvent Additives (NSA)	32
3.2.7	Coagulation Medium	32
3.2.8	Liquid Nitrogen (N <sub>2</sub> )	32
3.3	Preparation of Casting Solution (Dope)	33
3.4	Membrane Casting	34
3.5	Gas Permeation Tests	35
3.6	Membrane Characterization Methods	37
3.6.1	Scanning Electron Microscopic (SEM)	37
3.6.2	Fourier Transform Infrared (FTIR)	38

### **CHAPTER 4            RESULTS AND DISCUSSION**

4.1	Effect of Solvent on Gas Separation Membrane Separation	39
4.1.1	Composition of Dope Solution	39
4.1.2	Performance of Asymmetric Polysulfone Membrane	40
4.1.3	Performance of Asymmetric Polysulfone Membrane in Different Pressure	44
4.2	Effect of Solvent on Morphology of Asymmetric Membrane	55
4.3	Measurement on Chemical Structure in Polysulfone Asymmetric Membrane	60

**CHAPTER 5            CONCLUSION AND RECOMMENDATION**

5.1	Conclusions	63
5.2	Recommendations	64
<b>REFERENCES</b>		66
<b>APPENDICES</b>		
A	Experimental Results	75
B	Experimental Equipment	82

## LIST OF TABLES

<b>Table No.</b>	<b>Title</b>	<b>Page</b>
2.1	Membrane separations and materials process	7
2.2	Gas separation membrane applications	10
2.3	Typical characteristics of membrane modules	16
2.4	Materials for gas separating membranes	21
2.5	Most important glassy and rubbery polymer in gas separation membrane	22
3.1	Stability of the commercial membrane polymer	25
3.2	Properties of polysulfone	27
3.3	Properties of N-Methyl-2-Pyrrolidone (NMP)	29
3.4	Properties of N,N-dimethylformamide (DMF)	30
3.5	Properties of N,N-dimethylacetamide (DMAc)	31
3.6	Properties of pure methane (CH <sub>4</sub> ) and carbon dioxide (CO <sub>2</sub> )	31
3.7	Properties of water	32
3.8	Properties of methanol	32
3.9	Properties of liquid nitrogen	33
4.1	Casting solution formulations	40
4.2	Average separation properties of polysulfone asymmetric membrane at different type of solvent	41
4.3	Molecular weight (Da) and kinetic diameter (A°) of gases encountered in membrane gas separation	42
4.4	Permeation properties of different type of solvent at pressure 1 Bar.	44
4.5	Permeation properties of different type of solvent at pressure 2 Bar	47
4.6	Permeation properties of different type of solvent at pressure 3 Bar	50
4.7	Permeation properties of different type of solvent at pressure 4 Bar	53

## LIST OF FIGURES

<b>Figure No.</b>	<b>Title</b>	<b>Page</b>
1.1	Technology screening for CO <sub>2</sub> gas acid removal	2
2.1	Historical development of membrane in gas separation	6
2.2	The basic concept of membrane separation process	11
2.3	Membrane classification according to the morphology	13
2.4	Cross sectional view of an asymmetric membrane	14
2.5	Schematic representation of phase inversion process. (A) Dry phase inversion, (B) Wet phase inversion, (C) Dry/wet phase inversion	15
2.6	Schematic drawing for flat sheet plate and frame module	17
2.7	Schematic drawing for spiral wound module	18
2.8	Schematic diagram of a tubular module	19
2.9	Schematic diagram of hollow fiber membrane module	19
2.10	Schematic representations of (A) Polymeric Membrane (B) Molecular Sieve Membrane (C) Mixed Matrix Membrane	20
3.1	The experimental workflow of research study	26
3.2	Chemical structure of polysulfone	27
3.3	Chemical Structure of N-Methyl-2-Pyrrolidone (NMP)	28
3.4	Molecular structure of N,N-dimethylformamide (DMF)	29
3.5	Molecular structure of N,N-dimethylacetamide (DMAc)	31
3.6	Casting solution preparation system	34
3.7	Casting process polymer solution	34
3.8	Gas permeation system	35
3.9	Permeation cell	36

<b>Figure No.</b>	<b>Title</b>	<b>Page</b>
4.1	Graph of selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub> of polysulfone asymmetric membrane for various type of solvent with different pressure applied	42
4.2	Graph of carbon dioxide (CO <sub>2</sub> ) pressure normalized flux of polysulfone asymmetric membrane for various type of solvent with different pressure applied	43
4.3	Graph of methane (CH <sub>4</sub> ) pressure normalized flux of polysulfone asymmetric membrane for various type of solvent with different pressure applied	43
4.4	Graph of Pressure-Normalized Flux (GPU) of CO <sub>2</sub> with different type of solvent at pressure 1 Bar	45
4.5	Graph of Pressure-Normalized Flux (GPU) of CH <sub>4</sub> with different type of solvent at pressure 1 Bar	45
4.6	Graph of Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub> with different type of solvent at pressure 1 Bar	46
4.7	Graph of Pressure-Normalized Flux (GPU) of CO <sub>2</sub> with different type of solvent at pressure 2 Bar	48
4.8	Graph of Pressure-Normalized Flux (GPU) of CH <sub>4</sub> with different type of solvent at pressure 2 Bar	48
4.9	Graph of Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub> with different type of solvent at pressure 2 Bar	49
4.10	Graph of Pressure-Normalized Flux (GPU) of CO <sub>2</sub> with different type of solvent at pressure 3 Bar	51
4.11	Graph of Pressure-Normalized Flux (GPU) of CH <sub>4</sub> with different type of solvent at pressure 3 Bar	51
4.12	Graph of Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub> with different type of solvent at pressure 3 Bar	52
4.13	Graph of Pressure-Normalized Flux (GPU) of CO <sub>2</sub> with different type of solvent at pressure 4 Bar	54
4.14	Graph of Pressure-Normalized Flux (GPU) of CH <sub>4</sub> with different type of solvent at pressure 4 Bar	54

<b>Figure No.</b>	<b>Title</b>	<b>Page</b>
4.15	Graph of Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub> with different type of solvent at pressure 4 Bar	55
4.16	Scanning electron micrographs of polysulfone membranes cross sections at different type of polymer (i) N-methyl-2-pyrrolidone, NMP (400X) (ii) (ii) N,N-dimethylacetamide, DMAc (350X) and (iii) (iii) N,N-dimethylformamide, DMF (500X) (iv)	57
4.17	Scanning electron micrographs of polysulfone membranes surface layer at different type of polymer at 100X magnification (i) N-methyl-2-pyrrolidone, NMP (ii) (ii) N,N-dimethylacetamide, DMAc and (iii) (iii) N,N-dimethylformamide, DMF (iv)	58
4.18	FTIR spectrum of polysulfone flat sheet membrane using N-methyl-2-pyrrolidone, NMP as solvent	61
4.19	FTIR spectrum of polysulfone flat sheet membrane using N,N-dimethylacetamide, DMAc as solvent	61
4.20	FTIR spectrum of polysulfone flat sheet membrane using N,N-dimethylformamide DMF as solvent	62

## LIST OF SYMBOLS

$(P/l)$	- Pressure-normalized flux ( $\text{cm}^3$ (STP)/ $\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ )
$^{\circ}\text{C}$	-Degree Celcius
$A$	- Membrane structure area( $\text{cm}^2$ )
$D_p$	- Pressure difference across membrane (cmHg),
$i$	- Component $i$
$j$	- Component $j$
$l$	- Membrane thickness or skin layer thickness (cm)
$P$	- Permeability coefficient of gas ( $\text{cm}^3$ (STP) $\text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ )
$p_{ds}$	- Downstream pressure
$p_{us}$	- Upstream pressure
$\alpha$	- Selectivity
$A^{\circ}$	- Armstrong
Da	- Dalton
%	- percent
$Q$	- Volumetric flow rate
GPU	- Gas Permeation Unit, $10^{-6} \text{ cm}^3$ (STP) $\text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$



**LIST OF ABBREVIATION**

CA	- Cellulose Acetate
CH <sub>4</sub>	- Methane
CMS	- Carbon Molecular Sieves
CO <sub>2</sub>	- Carbon dioxide
DMAc	- <i>N,N</i> -dimethylacetamide
DMF	- Dimethylformamide
H <sub>2</sub> O	- Water
H <sub>2</sub> S	- Hydrogen Sulfide
He	- Helium
IPA	- Iso-propanol
LPG	- Liquefied Petroleum Gases
MMMs	- Mixed Matrix Membranes
<i>MW</i>	- Molecular weight (g/mol)
N <sub>2</sub>	- Nitrogen
NMP	- N-Methyl-2-pyrrolidone
NSA	- Nonsolvent additive
O <sub>2</sub>	- Oxygen
PEG	- Poly (ethylene glycol)
PMP	- 4-Methyl-2-Pentyne
PSU	- Polysulfone
SEM	- Scanning Electron Microscope
FTIR	- Fourier Transform Infrared
cm	- centimetre

**LIST OF APPENDICES**

<b>APPENDIX</b>	<b>TITLE</b>	
<b>PAGE</b>		
A	Experimental results	73
B	Experimental equipments	76

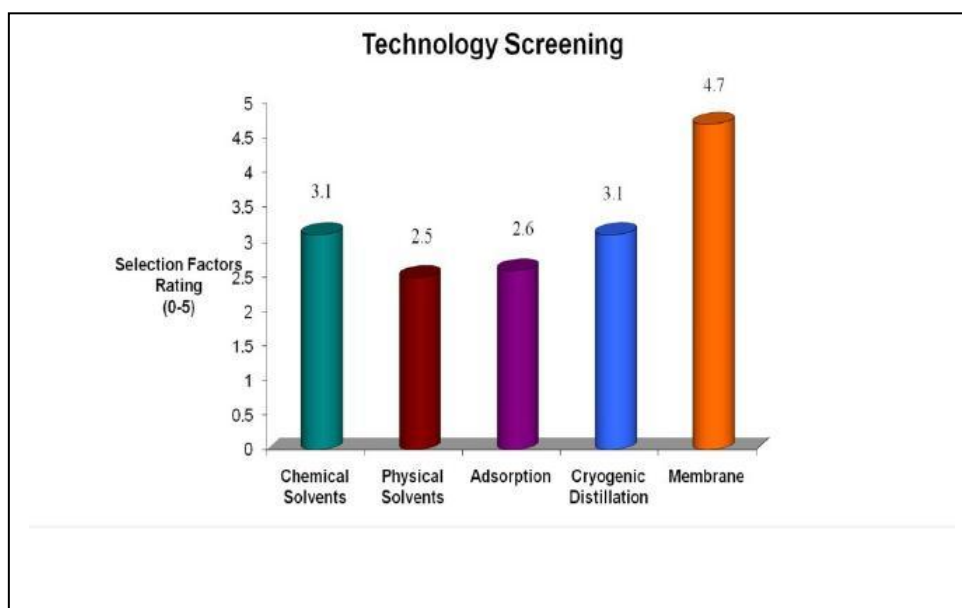
## CHAPTER 1

### INTRODUCTION

#### 1.1 RESEARCH BACKGROUND

Acid gas removal is a very important industrial operation which has been described in many works. Basically, there are five major process acid gas removals that have been used in industrial which solvent absorption, solid adsorption, membrane, direct conversion, and cryogenic fractionation. Membrane gas separation presents major advantages for the offshore industry in the aspect of environment friendly. Otherwise, amine process is too complex for small production, since the membrane system are conducting by installed for small size application and remote locations (Bernardo *et al.*, 2009). Therefore, membrane gas separations are suit for offshore platform natural gas (CH<sub>4</sub>) treatment.

Concern to the production and the environment aspect, Petronas Carogali Sdn Bhd which has wide experiences in developing high CO<sub>2</sub> offshore gas fields projects had made extensive on several process for gas separation such as chemical absorption (amine), physical evaluation, cryogenic distillation, membrane system and the other current technologies. They lead a conclusion that membrane is the most promising efficient and economical way to date for offshore CO<sub>2</sub> removal due its compact size, moderate utility consumption, easy operate and realibility. Figure 1.1 below obviously shown that the membrane process is the optimized technology for CO<sub>2</sub> removal offshore compare to the other technology.



**Figure 1.1:** Technology screening for CO<sub>2</sub> gas acid removal

Source: (Petronas Carigali Sdn. Bhd.)

Membrane gas separation distinguished by the type of material separation which is polymeric membrane, inorganic membrane and mixed matrix membranes (MMMs). Glassy polymer mainly cellulose acetate and polyimide was dominate industrial CO<sub>2</sub> separation applications such as in the separation of CO<sub>2</sub> from CH<sub>4</sub>, CO, N<sub>2</sub> and other hydrocarbon (Bernardo *et al.*, 2009).

The common porous flat membranes are prepared from homogeneous polymer solution by the wet phase inversion methods in which polymer solution is cast on a proper support and absorbed in a coagulation bath containing a non-solvent. Unfortunately, several organic solvent used in membrane preparation are volatile, flammable and many pose a risk to health and the environment (Temtem *et al.*, 2006). Therefore, in order to find the most effective solvent that can show the high performance for removing CO<sub>2</sub> gases are very crucial in membrane gas separation research. Thus the main goal of this research is the study of the solvent affinity and the most selected solvent for membrane separation.

## 1.2 PROBLEM STATEMENT

The different type of solvent and non-solvent additive, type of absorbent, coagulation condition during membrane fabrication played on main role in morphology and separation performance of polymeric membrane (Lai *et al.*, 1996). There are several technique are obtainable to prepare asymmetric porous polymeric films such as sintering, stretching track etching, phase separation, sol-gel process, vapour deposition and solution casting. The greater part of asymmetric porous flat membrane are prepared from a homogeneous polymer solution by the wet-base inversion methods in which polymer solution (polymer plus solvent) is cast on a correct support and immersed in a coagulation bath containing a non-solvent (Temtem *et al.*, 2006). Since the precipitation occurs owed to the exchange of solvent and non-solvent, the proper selection of the pairs of solvents is very important parameter to manage the morphology of membrane. The main goal of work is to study of the solvent affinity on the morphology of polysulfone membrane. The separation performances of these asymmetric membranes were characterized by the measurement of permeability and selectivity of CO<sub>2</sub>/CH<sub>4</sub> separation observed by morphology by scanning electron microscopy (SEM). Therefore, three organic solvent were tested in the membrane formation process of asymmetric polysulfone membrane for gas separation.

## 1.3 RESEARCH OBJECTIVE

Based on the problem statement described in the previous section, therefore the objective of this research are:

- (a) To develop asymmetric flat sheet membrane with high performance and selectivity for gas separation application.
- (b) To study and compare the performance of different type of solvent in the fabrication asymmetric membrane.
- (c) To characterize flat sheet membrane by using scanning electron microscopic (SEM).

#### **1.4 SCOPE OF RESEARCH**

In order to achieve the above mentioned objective, the following scope has been drawn:

- (a) Developing a best formulation solution for rise high selectivity of polysulfone membrane.
- (b) Testing the developed membrane using pure carbon dioxide and methane as gases.
- (c) Quantitative measurement of the permeability and selectivity in polysulfone membrane by using gas permeation system.

#### **1.5 RATIONAL & SIGNIFICANT OF STUDY**

- (a) To increase the permeability and selectivity of CO<sub>2</sub> gas separation by membrane system.
- (b) To develop the economical process for CO<sub>2</sub> capture to sustain supply the increasing gas demand.
- (c) Build up extremely versatile capable medium to produce porous membrane for all separation stage .
- (d) The carbon free on polysulfone asymmetric membranes will prompt the industrial application of natural gas reforming the new technology and environmental protection area.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 MEMBRANE DEFINITION

The word membrane comes from Latin “membrana” that means a skin of Parchment. Membranes can be classified as a layer of material which propose as a selective barrier between two phases and stand impermeable to specific particles, molecules or substances when exposed to the action of a driving force. Some component is permitted passage by the membrane into a permeable stream, whereas other are retained by and accumulate in the retentate stream which is part of solution that does not cross the membrane (Khulbe *et al.*, 2008). In general, a membrane process requires two essential uniform bulk phases ( two liquid phases, two gas phases or a liquid and a gas phase) separated by a third phase, the membrane which is physically and or chemically distinctive from both of them (Ismail *et al.*, 2002). Membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure, may be solid or liquid, carry positive or negatives charges or be bipolar or neutral in ion exchange or electrodialysis separation based on their physical or chemical properties. Transport through a membrane may involve by convection or by diffusion of individual molecules, induced by an electrical field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 100 µm to several mms (Mulder *et al.*, 2000; Nunes *et al.*, 2006).

## 2.2 MEMBRANE TECHNOLOGY REVIEW

### 2.2.1 History Development of Membrane

Systematic studies of membrane phenomena can be traced to the 18<sup>th</sup> century philosopher scientist. It begin by Abbe Nolet was discover the word ‘osmosis’ to describe permeation of water through a diaphragm in 1748. Then membranes had no industrial or marketable uses through the 19<sup>th</sup> and early 20<sup>th</sup> centuries, but were used as laboratory tools to arise physical/chemical theories. In 1887, Maxwell and others was used the concept of a perfectly selective semipermeable membrane in developing the kinetic theory of gases (Richard *et al.*, 2004).

Thomas Graham was the father of membrane science and he performed the first recorded experiments on the transport of gases and vapors in polymeric membranes. Fick proposed the quantitative description of material transport through boundary layer of pore size in 1855 and in 1866 the principles for gas permeation in term of a solution diffusion mechanism were published. Later on, polymer membranes were used for the separation of gases, etc. Since the early 1960’s, synthetic membranes have been used successfully in a wide variety of industrial applications. Figure 2.1 shows the summary of the historical development of the membrane technology since 1850’s.

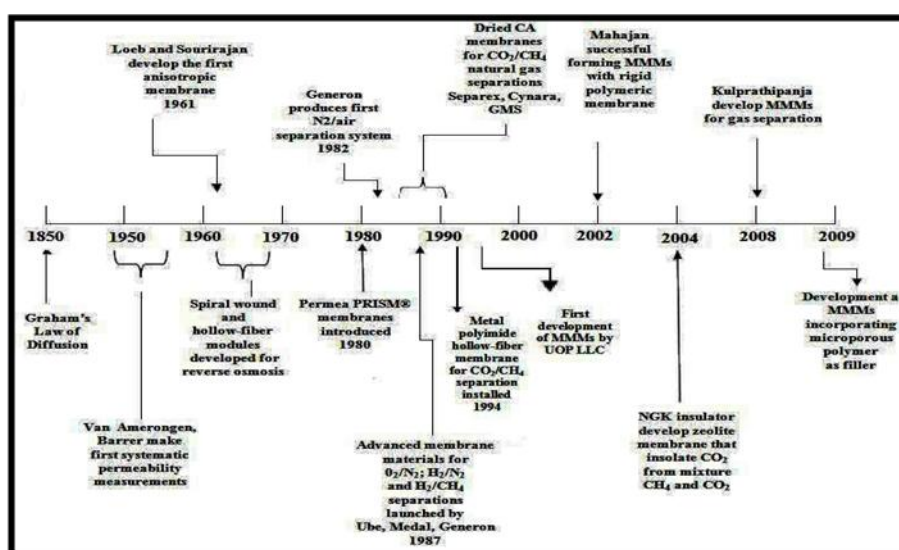


Figure 2.1: Historical development of membrane in gas separation



### 2.2.2 Membrane Process

Various types of membrane separation process have been developed for specific industrial application and their number will certainly increase. Ismail and group find that there are six major membrane processes, which are widely used, in industrial application which is microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation (Ismail *et al.*, 2002). Gas separation is known as a developing process and most gas separation membranes are of the solution-diffusion mechanism type. The selectivity, permeability and durability are the key membrane performance variables. For solution-diffusion membranes, permeability is defined as the product of the solubility and diffusivity. Traditionally, there has been a trade off between selectivity and permeability; high selectivity membranes tend to exhibit less permeability and vice versa.

Transport of selected species through the membrane is achieved by applying a driving force across the membrane. This gives a broad classification of membrane separations in the way or mechanism by which material is transported across a membrane. The industrially important membrane processes with the general classification of membranes used are shown in Table 2.1.

**Table 2.1:** Membrane separations and materials process

<b>Membrane Separation</b>	<b>Membrane Type</b>	<b>Driving Force</b>	<b>Applications</b>
Microfiltration	Symmetric microporous	Hydrostatic pressure	<ul style="list-style-type: none"> <li>• Purification of fluids in semiconductor manufacturing industry</li> <li>• Clarification and biological stabilization in the beverage industry</li> <li>• Sterilization ( in the food and pharmaceutical industries)</li> </ul>

**Table 2.1:** (Continue..)

<b>Membrane Separation</b>	<b>Membrane Type</b>	<b>Driving Force</b>	<b>Applications</b>
Ultrafiltration	Asymmetric microporous	Hydrostatic pressure	<ul style="list-style-type: none"> <li>• Electrodialysis pretreatment</li> <li>• Electrophoretic paint</li> <li>• Cheese whey treatment</li> <li>• Juice clarification</li> <li>• Recovery of textile sizing agents</li> <li>• Wine clarification</li> <li>• Separation of oil/water emulsion</li> <li>• Concentration of latex emulsion from wastewater</li> <li>• Dewaxing</li> <li>• Deasphalting</li> <li>• Egg-white preconcentration</li> <li>• Kaolin concentration</li> <li>• Affinity membranes</li> <li>• Reverse osmosis pretreatment</li> </ul>
Nanofiltration	Asymmetric microporous	Hydrostatic pressure	<ul style="list-style-type: none"> <li>• Water treatment</li> <li>• Product and chemical recovery</li> <li>• Concentration/dewatering</li> <li>• Fractionation of monovalent and divalent cations</li> <li>• Water softening</li> </ul>
Reverse osmosis	Asymmetric skin	Hydrostatic pressure gradient vs osmotic pressure gradient	<ul style="list-style-type: none"> <li>• Water desalination,</li> <li>• Wastewater treatment</li> </ul>
Gas permeation	Asymmetric or composite, homogeneous or porous polymer	Hydrostatic pressure, concentration gradient	<ul style="list-style-type: none"> <li>• Hydrogen separation</li> <li>• Oxygen/nitrogen separation</li> <li>• Carbon dioxide/methane separation</li> <li>• Helium recovery</li> <li>• Removal of acid gases from light hydrocarbons</li> <li>• Biogas processing</li> </ul>

**Table 2.1:** (Continue..)

<b>Membrane Separation</b>	<b>Membrane Type</b>	<b>Driving Force</b>	<b>Applications</b>
Dialysis	Symmetric microporous	Concentration gradient	<ul style="list-style-type: none"> <li>• Separation of microsolute and salts from macromolecular solutions</li> </ul>
Pervaporation	Asymmetric, composite	Concentration gradient vapour pressure	<ul style="list-style-type: none"> <li>• Removal of organics from water</li> <li>• Water removal from liquids organics</li> <li>• Organics/organic separation</li> </ul>
Vapor permeation	Composite	Concentration gradient	<ul style="list-style-type: none"> <li>• Removal of organics from air</li> </ul>
Electrodialysis	Ion-exchange, homogeneous or microporous polymer	Electrical potential	<ul style="list-style-type: none"> <li>• Desalination of brackish water</li> <li>• Production of table salt</li> <li>• Waste water treatment</li> <li>• Concentration of RO brines</li> <li>• Applications in the chemical, food, and drug industries</li> </ul>
Electro-osmosis	Microporous charged membranes	Electrical potential	<ul style="list-style-type: none"> <li>• Dewatering of solutions of suspended solids</li> </ul>
Electrophoresis	Microfiltration	Electrical potential, hydrostatic pressure	<ul style="list-style-type: none"> <li>• Separation of water and ions from colloidal solutions</li> </ul>
Liquids membranes	Microporous, liquids carriers	Concentration, reaction	<ul style="list-style-type: none"> <li>• Separation of ions and solutes from aqueous solutions</li> </ul>

Sources: (Khulbe *et al.*, 2008; Scott *et al.*, 1996).

### 2.3 MEMBRANE APPLICATION

Membrane process cover a broad range of application in fluids separation and are now considered as a new and emerging separation technology for industrial applications areas because of its advantages in separation, low capital cost, low energy consumption operation, cost effectiveness even at low gas volumes and good weight

and space efficiency. Table 2.2 shows the main application of gas membrane application area.

**Table 2.2:** Gas separation membrane applications

<b>Common Gas Separation</b>	<b>Application</b>
O <sub>2</sub> /N <sub>2</sub>	Oxygen enrichment, inert gas generation
H <sub>2</sub> /Hydrocarbons	Refinery hydrogen recovery
H <sub>2</sub> /N <sub>2</sub>	Syngas ratio adjustment
CO <sub>2</sub> /Hydrocarbons	Acid gas treatment, landfill gas upgrade
H <sub>2</sub> O/Hydrocarbons	Natural gas dehydration
H <sub>2</sub> S/Hydrocarbons	Sour gas treating
He/Hydrocarbons	Helium separation
He/N <sub>2</sub>	Helium recovery
Hydrocarbons/Air	Hydrocarbon recovery, pollution control
H <sub>2</sub> O/Air	Air dehumidification

## 2.4 MEMBRANE SEPARATION PROCESS

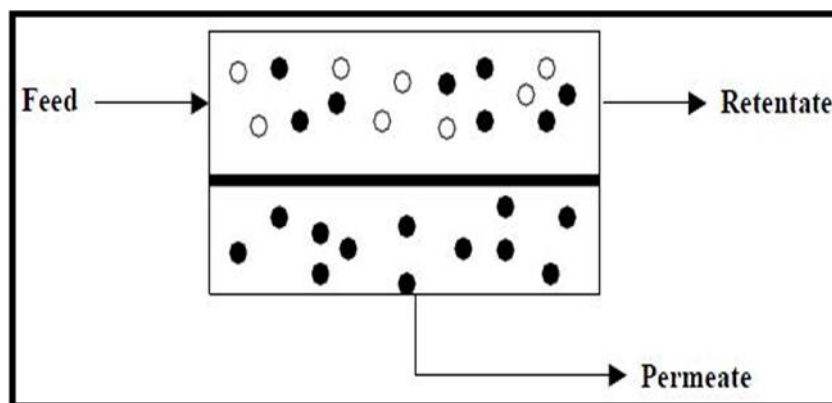
The problems of separating mixtures components are one often encountered in the chemical process industry. Membranes principles carry out most of the separation processes like distillation, extraction, fractionation and adsorption (Van *et al.*, 2004). The key membrane performance variables are permeability, selectivity and durability. The permeation of molecules through membrane is controlled by two major mechanisms. There are diffusivity (D) and solubility (S). Diffusivity is the mobility of individual molecules passing through the holes in a mechanism material and solubility is the number of molecules dissolved in a membrane material. Permeability (P) defined in equation 2.1, is a measure of a membrane's ability to permeate molecules

$$(P) = (D) \times (S) \quad (2.1)$$

The ability of a membrane to separate two molecules, for example A and B, is the ratio of the their permeabilities called the membrane selectivity  $\alpha_{ab}$ .

$$\alpha_{ab} = (P_A)/(P_B) \quad (2.2)$$

The higher the permeability of the membrane used, the smaller is the membrane area required, on the other hand, the higher the selectivity, the lower the driving force required. Figure 2.2 demonstrates the basic concept of a membrane separation process, in which the driving force is often pressure or concentration gradient across the membrane (Ismail *et al.*, 2009).



**Figure 2.2:** The basic concept of membrane separation process

The remains gases is one of the most technologically challenging factor that are subject related to the selection of membrane materials for a given separation complex depending on the application. The other criteria to be taken into consideration are productivity, durability and mechanical integrity at the operating conditions that must be balanced against cost (Ismail *et al.*, 2009).

Various mechanism of gas transport across membrane has been proposed depending on the properties of both the permeance and the membrane. These mechanisms included Knudsen diffusion, convective flow, the molecular sieve effect and a solution diffusion mechanism. Most of these models however, have been found to be applicable only to a limited number of gas and material systems. Lower selectivity of asymmetric membranes can be results of pores or defect or enhanced free volume in the ultrathin skin layer.

In asymmetric and composite membrane, the hydrodynamic resistance is mostly determined by the thin dense top layer. This top layer must avoid defects because a few

defect can significantly reduce the selectivity without having much influence on the flux. But it is very difficult to make an ultrathin defect free top layer from a glassy polymer by enhancing flux. However, two phase inversion methods such as dual methods and the evaporation methods can be used to prepare defect free asymmetric membrane. These processes include dry phase separation, dry/wet phase separation and wet/wet phase separation.

Lee *et al.*, (2000) was conducted the research on a wet/wet phase separation in combination with two series nonsolvent bath which is iso-propanol (IPA) and water to prepare ultrathin and defect free asymmetric polysulfone membrane for gas separation. The skin layer thickness increased from about 2  $\mu\text{m}$  to 13  $\mu\text{m}$  as the immersion times increased from 10 sec to 80 sec by changing the immersion time of the first IPA bath.

## 2.5 MEMBRANE PRINCIPLE

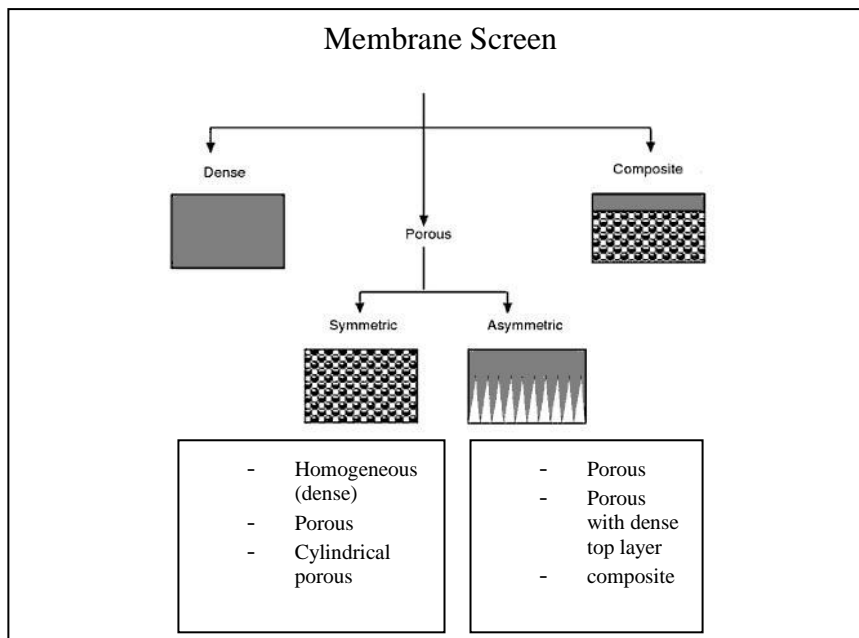
Membrane can be prepared from both polymeric materials and ceramics or inorganic material. Ceramics materials have several advantages over polymeric materials such as higher chemical and thermal stability. However, the market share of polymeric membranes is far greater than ceramic membranes as the polymeric materials which are less expensive and easier to process (Porter *et al.*, 1990). Different methods of polymer membrane preparation have been covered in several reviews. Membranes can be classified, according to the cross section structure as shown in Figure 2.3.

Dense homogeneous polymer membranes are usually prepared

- i. From solution by solvent evaporation only
- ii. By extrusion of the melted polymer

However, dense homogeneous membranes only have a practical meaning when made of highly permeable polymers such as silicone. Usually the permeant flow across the membrane is quite low, since a minimal thickness is required to give the membrane mechanical stability. Most of the presently available membranes are porous or consist of a dense top layer on a porous structure. The preparation of membrane structures with

controlled pore size involves several techniques with relatively simple principle but which are quite tricky (Nunes *et al.*, 2006).



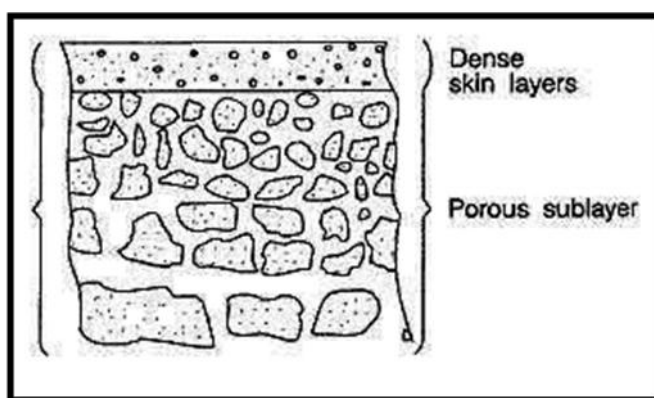
**Figure 2.3:** Membrane classification according to the morphology

### 2.5.1 Asymmetric Membranes

Most membranes used in industries have an asymmetric structure. In this membrane, the two basic properties required membrane with high mass transport rates for certain components and good mechanical strength for physically separation (Khulbe *et al.*, 2008). An asymmetric membrane is composed of a thin, dense layer supported by a thicker and porous substructure layer. The very thin skin represents the actual membrane. Symmetric membranes are constructed of a single (homogeneous) material while, composite membrane use different (heterogeneous) material. Asymmetric membrane may be either homogeneous or heterogeneous.

The first reported asymmetric membrane was developed for the reverse osmosis demineralization of saline water by Loab and Sourijan. There are two technique are used to make asymmetric membrane which is develop the phase inversion process which leads to an integral structure and the other resemble a composite structure where

an extremely thin polymer film is deposited on a microporous substructure (Costa *et al.*, 1991). Figure 2.4 shows schematically a typical cross section view of an asymmetric membrane. It consists of two layer which the top layer is a very thin dense (top skin layer) and bottom one is a porous sublayer. The top dense layer governs the performance (permeation properties) of the membranes while the porous sublayer only provides mechanical strength to the membrane. In asymmetric membrane, when the material of the top layer and porous sublayer are the same, the membrane is called an integrally skinned asymmetric membrane (Wise 2000; Khulbe *et al.*, 2008).



**Figure 2.4:** Cross sectional view of an asymmetric membrane

Sources:(Khulbe *et al.*, 2008)

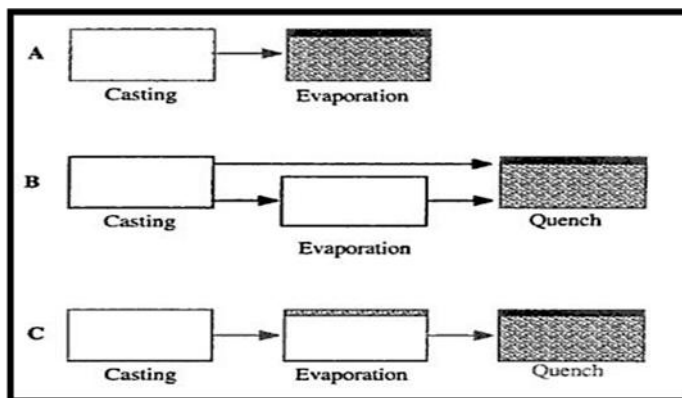
The asymmetric design of the membrane combine the advantage of high selectivity of a dense membrane with high permeation rate of both porous membrane and thin dense membrane that can chosen separately to optimize the overall performance. Asymmetric membrane is cast in a single step process in which the thin barrier film becomes an integral part of the microporous substrate, making it easier to fabricate and handle. However, a major drawback with the asymmetric membrane is the presence of pinholes and other defect in the dense barrier make a lower separation process. But some asymmetric membranes have a graded construction which the porous structures gradually decrease in density from the feed to the filtrate side of the membrane. In other, asymmetric membrane may be district transition between the dense layer and support structure (Allgeier, 2003; Ohya *et al.*, 1996). The following are



researchers that have been done studies on the development of defect free and thin skin asymmetric membrane.

## 2.6 PHASE INVERSION IN MEMBRANE GAS SEPARATION

The term phase inversion has already been introduced in terms of the compositionally driven phase separation processes in the membrane separation section. For convenience, the major approaches that have been found useful in order to obtain the asymmetric membrane which is include dry phase inversion, wet phase inversion and dry/wet phase inversion. Figure 2.5 illustrated the schematic representation of phase inversion process.



**Figure 2.5:** Schematic representation of phase inversion process. (A) Dry phase inversion, (B) Wet phase inversion, (C) Dry/wet phase inversion

Sources: (Paul *et al.*, 1994).

Asymmetric membrane is normally made by dry/wet phase inversion technique. Membrane must dry before being used. Solvent exchange is necessary to dry the polymer membrane. In addition, for asymmetric membrane to be effective in gas separation, the thin selective layer at the top of the membrane should be perfect (Paul *et al.*, 1994).

## 2.7 MEMBRANE MODULE

The membrane modules are largely used for industrial applications are including plate and frame module, spiral wound module, tubular module and hollow fiber module. The applications in Table 2.4 shows great differences in the module present with their technical and economical significant for membrane processes.

**Table 2.3:** Typical characteristics of membrane modules

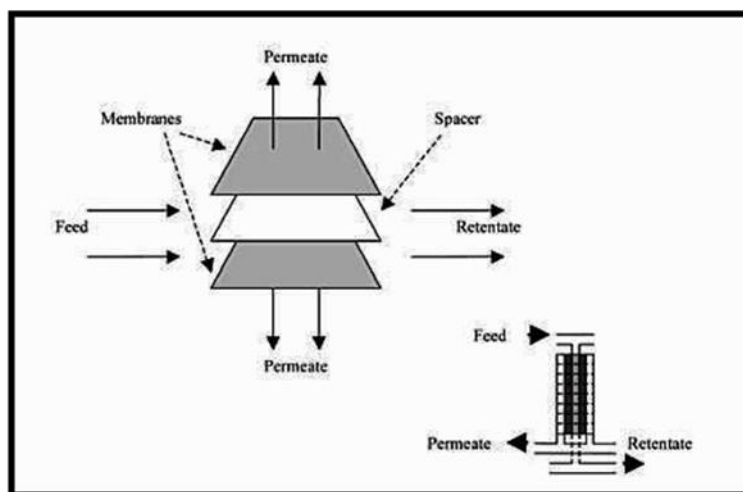
Characteristic	Plate and frame	Spiral wound	Tubular tube	Hollow fiber
Membrane area per volume ( $m^2/m^3$ )	400 – 600	800 – 1000	600 – 1200	5000 - 40000
Price	High	Low	Low	Very low
Controls of concentration polarization	Fair	Poor	Good	Very bad
Application	F, PV, GS, RO, D, MF	UF, RO, P GS, MF, D V,	UF, LM, PV, RO	RO, GS, UF, D
Resistance to fouling	Good	Moderate	Very good	Poor
Ease of cleaning	Good	Fair	Excellent	Poor
Membrane material choices	Many	Many	Few	Few
Packing Density	Low	Moderate	Low	High
Suitable for high pressure operation	Can be done with difficulty	Yes	Can be done with difficulty	Yes
Limited to specific types of membranes	No	No	No	Yes

F= Filtration, PV=Pervaporation, GS=Gas Separation, RO=Reverse Osmosis, D=Dialysis, MF=Microfiltration, UF=Ultrafiltration, LM=Liquid Membrane.

Sources: (Baker *et al.*, 1991).

### 2.7.1 Flat Sheet Plate and Frame Module

Inorganics or metallic membranes for gas separations are usually prepared as dies or flat sheets. This type of module appeared in the earliest stage of industrial membrane applications. Polymeric flat sheet membranes are easy to prepare, handle and mount. For gas separation, the flat sheet membrane is composite with a selective polymer coated on a support (Pabby *et al.*, 2009). Figure 2.6 shows the set of two membranes are placed in a sandwich like fashion with their feed sides facing each other. The membranes permeate is collected for each support plate.



**Figure 2.6:** Schematic drawing for flat sheet plate and frame module

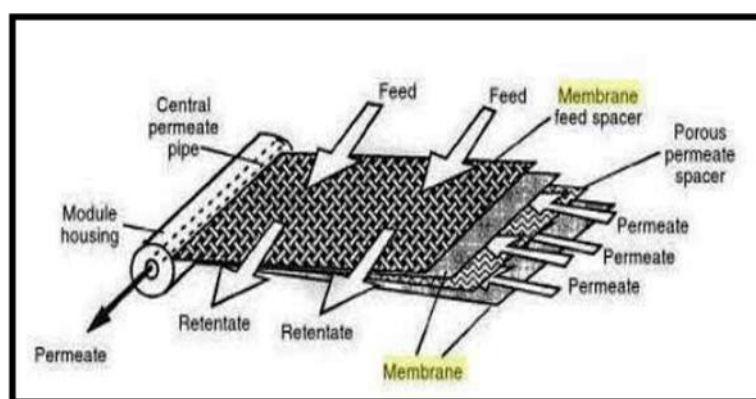
Sources: (Wang *et al.*, 2006)

### 2.7.2 Spiral Wound Module

The spiral wound module is in fact a plate and frame system wrapping around a central collection pipe similar to a sandwich roll consists membrane, spacer (providing a permeate channel), membrane and a new spacer (providing a feed channel). The feed side spacer acts as a turbulence promoter, whereas on the permeate side the flow is directed toward the central pipe. The spiral wound membrane will typically be a polymer composite materials and used for liquid separations (Pabby *et al.*, 2009; Wang

*et al.*, 2006; Valentas *et al.*, 1997). Figure 2.7 illustrated the schematic drawing for spiral wound module. The spiral wound module is featured by

- A compact structure
- High pressure durability
- Less concentration
- Less pressure drop at the permeate channel
- Minimum concentration polarization
- Susceptible to fouling by suspended particle



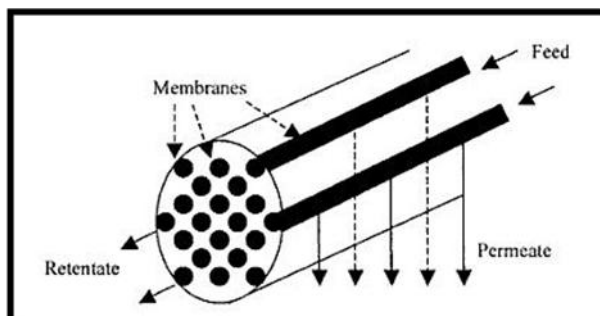
**Figure 2.7:** Schematic drawing for spiral wound module

Sources: (Pabby *et al.*, 2009)

### 2.7.3 Tubular Module

Tubular modules consist of membranes produced inside typically 6 to 25mm in diameter and are of three basic types. Self supporting tubular modules consist of several membranes tubes held simultaneously as a pack and connected to common headers and permeate vessels. This type is limited by its structural strength to low pressure applications. Externally supported tubular membrane modules consist of tubular membranes held inside individual porous support tubes. Besides that, tubular module can withstand high pressures and is therefore used in reverse osmosis. Otherwise, in monolithic tubular module several tubular channels are formed in porous block of material and the membrane layer is formed inside the tube. All types of tubular modules

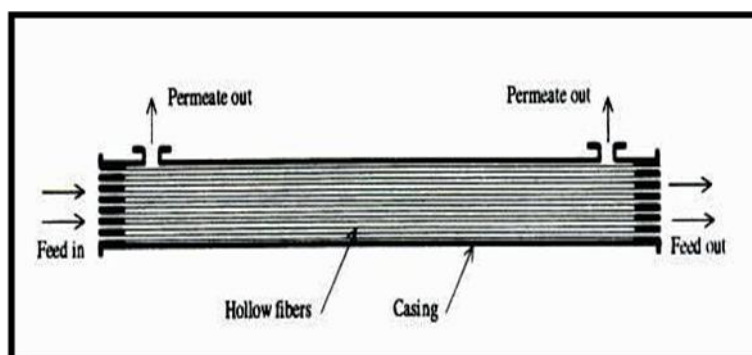
can accommodate suspended particles (Wang *et al.*, 2006). Figure 2.8 illustrate the schematic diagram of tubular shape module.



**Figure 2.8:** Schematic diagram of a tubular module

#### 2.7.4 Hollow Fiber Module.

Formation of membranes into hollow fibers has many advantages and the most important advantage is the capability to form compact modules with very high surface areas. Hollow fibers are commonly on the order of 25-200  $\mu\text{m}$  in diameter. They can make with a homogeneous dense structure or more preferably as a microporous structure having a dense permselective layer on the outside or inside surface. Since no breaks or defects are allowed in a module, this requires very high standards of reproducibility and quality controls (Baker *et al.*, 1991). Figure 2.9 shows the schematic diagram of hollow fiber membrane.

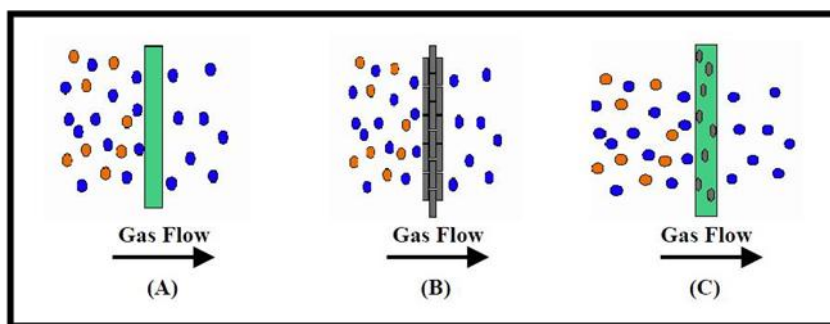


**Figure 2.9:** Schematic diagram of hollow fiber membrane module

## 2.8 MEMBRANE IN GAS SEPARATION

Search for a higher selectivity and permeability material with high resistance against aggressive conditions is the challenge face by current application of gas separation membrane. Wahab *et al.*, (2004) describe a new glassy polymeric membranes, now been tailored to give attractive properties, but their performances deteriorate under aggressive conditions shows in Figure 2.10 (A). While, thermally and chemically stable molecular sieve membrane such as carbon molecular sieve (CMS) and zeolite with performances well above the upper bound trade-off curve, are difficult and expensive to fabricate. Schematic for molecular sieves membrane are shown in Figure 2.10 (B) below.

They are also discussing about the mixed matrix membrane (MMMs). Mixed matrix membrane is a blend of molecular sieving particles in polymer matrix that combine the superior gas separation properties of rigid molecular sieving materials with the processability of the polymer. The embedded molecular sieves are expected to improve membrane properties, and because of their unique crystalline microporous pore structure, surface chemistry and mechanical strength (Wahab *et al.*, 2004). Figure 2.10 (C) shows the schematic of mixed matrix membrane gas flow.



**Figure 2.10:** Schematic representations of (A) Polymeric Membrane (B) Molecular Sieve Membrane (C) Mixed Matrix Membrane

Nunes *et al.*, (2006) proposes that organic polymers are the dominating materials for gas separation membranes. Many polymers exhibit sufficient gas selectivity and they can be easily processed into membranes. The only inorganic materials that are

currently used for gas separation (ultrapure hydrogen generation) in the beginner is palladium alloys on a commercial scale. However, during the last decade inorganic materials have been developed with exciting unmatched selective for certain gas mixtures and some of the inorganic membranes (Van *et al.*, 2004). Table 2.5 shows relevant membrane materials for gas separation.

**Table 2.4:** Materials for gas separating membranes

<b>Organic polymers</b>	<b>Inorganic materials</b>
Polysulfone, polyethersulfone	Carbon molecular sieves
Celluloseacetate	Nanoporous carbon
Polyimide, polytherimide	Zeolites
Polycarbonate (brominated)	Ultramicroporous amorphous silica
Polyphenyleneoxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydimethylsiloxane	
polyvinyltrimethylsilane	

### 2.8.1 Polymeric Membrane

Ismail *et al.*, (2009) have been investigate that polymeric membranes are the dense type membranes, which can be further categorized based on rubbery or glassy polymers. Rubbery polymer is soft and elastic due to the flexibility of the polymer backbone segments that can rotate freely around their axis. Glassy polymer a rigid and tough polymer resulted from the steric hindrance along the polymer backbone that prohibits the rotations of polymer segments. Polymer membranes, particularly glassy polymers have received considerable attention because they possess advantages of mechanical properties and relative economical processing capability. A transport model for permeation in polymer membrane is the application of solution-diffusion model that is applicable to a broad range of membrane separation processes. The major physicochemical factors affecting the permeability and selectivity of a polymer membrane are as follows:

- (a) the mobility of polymer chains,
- (b) the intersegmental spacing that is indicated by the means free volume of the polymer and
- (c) the penetrant–polymer interactions

Polymeric membranes are most commonly produced in the form of flat sheets, but they are also widely produced as tubes of diameter 10-25 mm and in the form of hollow fibres of diameter 0.1-2.0 mm (Richardson *et al.*, 2002). Typically, polymeric membranes present high selectivities and low throughput when compared to porous material due to the low free volume. Eventhough the large number of polymeric materials investigated and developed for gas separation applications, the total of polymers used in industrial is still limited. The main glassy and rubbery polymers employed for gas separation membranes are listed in Table 2.6.

**Table 2.6:** Most important glassy and rubbery polymer in gas separation membrane

<b>Glassy Polymer</b>	<b>Rubbery Polymer</b>
<ul style="list-style-type: none"> <li>• Cellulose acetate</li> <li>• Polyperflourodioxoles</li> <li>• Polycarbonates</li> <li>• Polyimides</li> <li>• Poly(phenylene oxide)</li> <li>• Polysulfone</li> </ul>	<ul style="list-style-type: none"> <li>• Poly(dimethylsiloxane)</li> <li>• Ethylene oxide/propylene oxide-amide copolymer</li> </ul>

### 2.8.2 Inorganic Membranes

In general, inorganic membranes can be categorized as dense and porous. Porous inorganic membranes such as zeolite and carbon molecular sieve are favored where rendered by their excellent selectivity which is significantly higher compared to that of polymeric membranes (Ismail *et al.*, 2009). Dense inorganic membranes are gastight layers. In the past decade for gas separation was studied by the first group about the metallic membrane type which is primarily palladium alloy membranes for H<sub>2</sub>/CO<sub>2</sub> separation. The most extensively was a study in the next group includes the oxygen ionic conductive and mixed oxygen ionic and electronic conductive ceramic membranes. A third group was emerged from high temperature hydrogen semi permeable dense ceramic membranes in the early 1980's. These membranes are based on proton-conducting ceramics (Donk *et al.*, 2008).

Abundant research and study are developed about the inorganic membranes including the dual-phase of membrane and etc. Inorganic membranes that are formed



from metals, ceramic or pyrolyzed carbon have several advantages for many industrial compare to the polymer membranes. In other hand, inorganic have more interest according to their characteristic such as high solvent-resistant properties, thermal and pore structure ability.

### **2.8.3 Mixed Matrix Membranes**

A mixed matrix membrane is a where molecular sieve is dispersed in an inorganic polymer matrix with the objective increasing the selectivity over that of the polymer alone (Cejka *et al.*, 2007). Proper selection of both of the polymer matrix and the molecular sieving material is required to obtain mixed matrix membrane with enhanced gas transport properties increase in diffusivity, selectivity, and permeability. Permselectivity will be obtained in mixed matrix membrane containing molecular sieves with precise pore opening. Miller and co-worker have prepared mixed matrix membrane based molecular sieves, when these molecular sieves are properly dispersed in a continuous phase polymer, the membrane exhibit a mixed matrix membrane effect which is a selectivity increase of at least 10% relative to a neat membrane containing no molecular sieve.

## **CHAPTER 3**

### **METHODOLOGY**

This chapter describes the experimental methods used to develop and the effect of different type of solvent on polysulfone mixed matrix membrane. Transparent asymmetric membranes were prepared by several type of solvent including N-methyl pyrrolidone (NMP), dimethyl formamide (DMF) and dimethyl acetamide (DMAc) and were characterized by using Scanning Electron Microscope (SEM).

Keskes *et al.*, 2009 was discover that there are many solvents have been used for the absorption of CO<sub>2</sub> and H<sub>2</sub>S including, formulations of tributyl phosphate, polycarbonate, methylcyanoacetate, and n-formyl morpholine. There are major two disadvantages with such solvents which include that solvent are not easily disposable (for offshore operations) and could be involved in side reactions with other natural gas constituents. The most frequently polymer that are commercial used in the industrial are summarized in Table 3.1.

**Table 3.1:** Stability of the commercial membrane polymer

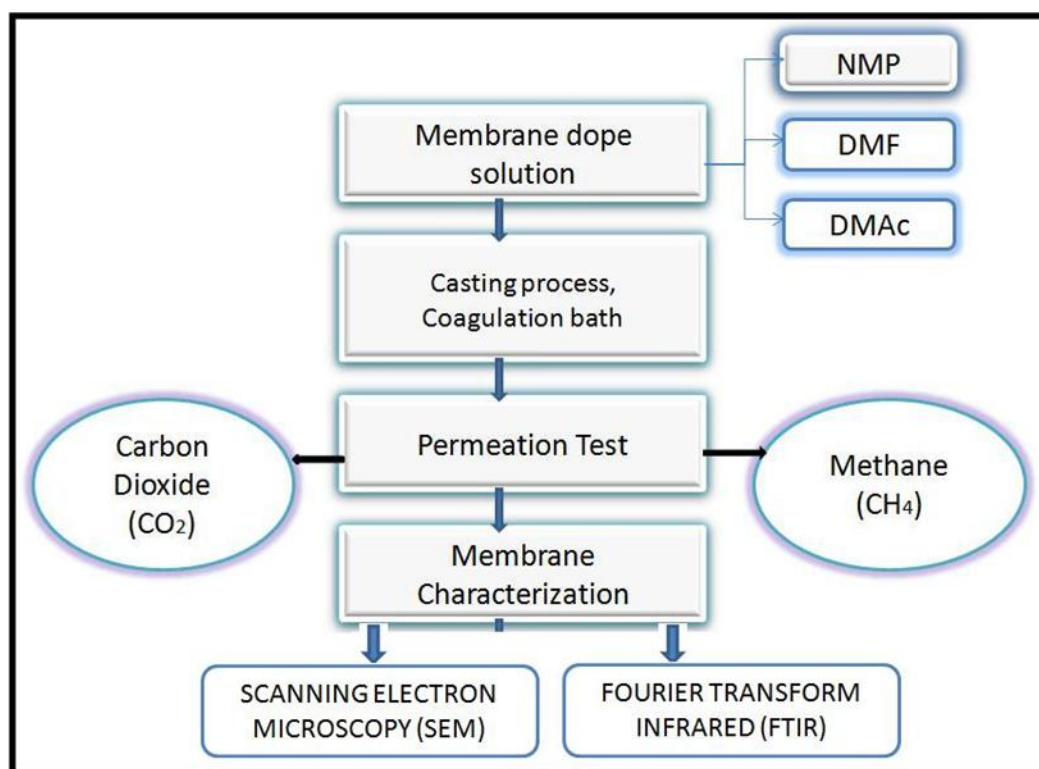
<b>Membrane polymer</b>	<b>Common solvent</b>	<b>Temperature (°C)</b>	<b>pH range</b>
Polysulfone	DMAc, DMF, DMSO, NMP	198	2 - 13
Polyethersulfone	DMAc, DMF, DMSO, NMP	225	2 - 13
Polyvinylidene fluoride	DMAc, DMF, DMSO, NMP	40, ( $T_m \sim 175$ )	2 - 11
Polyacrylonitrile	DMAc, DMF, nitric acid	100	2 - 10
Cellulose acetate	DMAc, DMF, DMSO, NMP, Acetone, dioxin	High crystalline	3 - 7

DMAc = Dimethyl acetamide, DMF = Dimethyl formamide, DMSO= Dimethylsulfoxide, NMP = N-methyl pyrrolidone.

Drioli *et al.*, 2009 was described that the solvent must be miscible with the nonsolvent (aqueous system). A polar solvent like N-methyl 2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc) or dimethylsulfoxide (DMSO) is preferable for rapid precipitation (instantaneous demixing) upon immersion in the nonsolvent water.

### 3.1 RESEARCH DESIGN

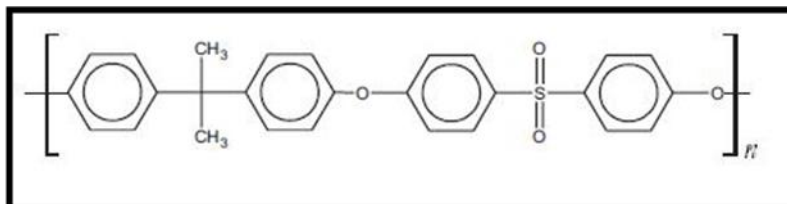
The experimental work involved in this study is depicted in a flowchart as shown in Figure 3.5.



**Figure 3.1:** The experimental workflow of research study

## 3.2 MATERIAL SELECTION

### 3.2.1 Polysulfone



**Figure 3.2:** Chemical structure of polysulfone

Figure 3.1 shows the main chemical structure of polysulfone. Polysulfone has excellent transport properties, high glassy transition temperature, strong mechanical strength and good chemical resistance. (Kim *et al.*, 2000; Chen *et al.*, 2007). It also has superior combination of high performance properties that consist of transparency, heat stabilized, medium viscosity, platable, good flow, good dimensional stability, high rigidity, impact modified and high heat resistance. Besides that, it also shows impact resistance, no discoloration by food contact, high mechanical strength and toughness and sterilizable and long-term dishwasher safe. Thus, it is suitable participant for preparation for mixed matrix membrane which can apply for gas separation in this study. The basic properties of polysulfone polymer are illustrated in Table 3.1.

**Table 3.2:** Properties of polysulfone

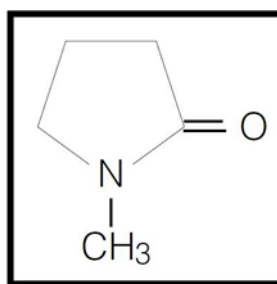
Properties	Value
Molecular weight, (g mol <sup>-1</sup> )	442.52
Density, (g cm <sup>-3</sup> )	1.24
Glass Transition temperature, (°C)	185 (min) 266 (max)
Thermal conductivity, <i>k</i> (W m <sup>-1</sup> K <sup>-1</sup> )	0.29
Solubility parameter (MPa)	20.26
Water Absorption, (%)	0.33
Specific heat capacity, (J/g °C)	0.442
Tensile strength (yield) (MPa)	81.2
Tensile Elongation (%)	77

Filler content (%)	16.7
Melt mass flow rate (g/10 min)	7.3

### 3.2.2 N-Methyl-2-Pyrrolidone

N-Methyl-2-Pyrrolidone with formula molecular of  $C_5H_9NO$  was also known as NMP. N-Methyl-2-Pyrrolidone has high chemical and thermal stability and is totally miscible with water at all temperatures. N-Methyl-2-Pyrrolidone can perform as a cosolvent with water, alcohols, glycol ethers, ketones, and aromatic/chlorinated hydrocarbons. N-Methyl-2-Pyrrolidone is a powerful solvent for use in numerous applications including graffiti removal, automotive and industrial cleaning, water borne coatings, and photoresist stripping. The chemical structure and typical properties of N-Methyl-2-Pyrrolidone are shown in Figure 3.2 and Table 3.2 respectively.

Van't Hof *et al.*, (1991) have been studied the effect of with N-methylpyrrolidone as a solvent and water as a nonsolvent additive in the dope solution (Polyethersulfone in N-methylpyrrolidone) on the performance of polyethersulfone (PES) hollow fiber membrane gas separation. The authors observed high selectivity were easily obtained for feed gas 25 vol. % of carbon dioxide in methane with intrinsic selectivity of polyethersulfone [ $\alpha(CO_2/CH_4) = 50$ ] without necessity additional coating step.



**Figure 3.3:** Chemical Structure of N-Methyl-2-Pyrrolidone (NMP)

**Table 3.3:** Properties of N-Methyl-2-Pyrrolidone (NMP)

Properties	Value
Molecular weight, ( $\text{gmol}^{-1}$ )	99.13
Purity, (%)	99.8 (min)
Water, (ppm)	300 (max)
Density @ 25°C, ( $\text{gcm}^{-3}$ )	1.027
Boiling point @ 760 Torr, (°C)	202
Vapor pressure, (mm Hg)	< 0.3
Melting point, (°C)	-25

### 3.2.3 N,N-Dimethylformamide

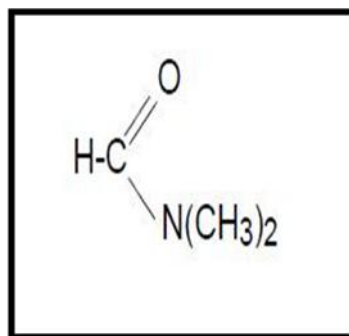
**Figure 3.4:** Molecular structure of N,N-dimethylformamide

Figure 3.3 shows the molecular structure of N,N-dimethylformamide. N,N-dimethylformamide with formula molecular of  $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$  was also known as DMF. N,N-dimethylformamide is a colorless, high-boiling point, polar liquid with a faint, characteristic odor. It does not decompose on distillation and is freely miscible with water, alcohols, ethers, ketones, esters, carbon disulfide and chlorinated and aromatic hydrocarbons. N,N-dimethylformamide is an extremely suitable solvent for salts or compounds with a high molecular weight due to the combined action of its small molecule, its high dielectric constant, its electron donor properties, and its ability to form complexes. N,N-dimethylformamide can be absorbed through the skin and can cause liver damage. The properties of N,N-dimethylformamide were covered in Table 3.3.

**Table 3.4:** Properties of N,N-dimethylformamide (DMF)

Properties	Value
Molecular weight, (gmol <sup>-1</sup> )	73.10
Density @ 20°C, (gcm <sup>-3</sup> )	0.949
Boiling point, (°C)	153
Melting point, (°C)	-61
Flash point, (°C)	58
Vapor pressure @20°C, (kPa)	0.3

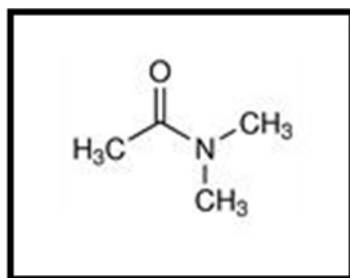
Blinka *et al.*, 1990 prepared the asymmetric membrane by casting from a 23% by weight solution of the 6FDA/AMPS polymer, 41% acetone, 36% DMF and 2% maleic acid. The author shows the dimethylformamide perform high permeability for carbon dioxide separation but low selectivity of carbon dioxide/methane gases. White *et al.*, 1995 has studied the carbon dioxide and methane permeabilities for dense film and asymmetric membrane prepared from 10% aromatic polyimide (6FDA/DMB) in dimethylformamide and drying under vacuum at 90°C. However, the author shows the performance of dope solutions do not demonstrates high selectivities because dense layer is formed precipitation.

### 3.2.4 N,N-Dimethylacetamide

N,N-dimethylacetamide with formula molecular of CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub> was also known as DMAc. It is dissolved in most of organic solvents including alcohols, ethers, ketones, chlorinated and aromatic solvents except aliphatic hydrocarbons. N,N-dimethylacetamide is produced from acetic acid and dimethylamine. N,N-dimethylacetamide is less toxic than N,N-dimethylformamide. The good water solubility and excellent solvent power particularly for high molecular weight polymers and resins make N,N-dimethylacetamide as a common solvent in man-made fibre and polyurethane production. N,N-dimethylacetamide is also used as a solvent for production of X-ray and photo-resist stripping compounds. N,N-Dimethylacetamide is a dipolar aprotic solvent with a high boiling point. N,N-dimethylacetamide is a good reaction medium and catalyst. The molecular structure and typical properties of N,N-dimethylacetamide are shown in Figure 3.4 and Table 3.4 respectively.



Texas Commission on Environmental Quality has studied the performance of nanocomposite membrane gas separation with using minimal amount of N,N-dimethylacetamide (DMAc) solvent and silica as nanocomposite. However, the permeability and selectivity behavior begin to decrease only in small amount from the CO<sub>2</sub>/CH<sub>4</sub> pure gas selectivity.



**Figure 3.5:** Molecular structure of N,N-dimethylacetamide.(DMAc)

**Table 3.5:** Properties of N,N-dimethylacetamide (DMAc)

Properties	Value
Molecular weight, (gmol <sup>-1</sup> )	87.12
Density @ 20°C, (gcm <sup>-3</sup> )	0.949
Boiling point, (°C)	165
Melting point, (°C)	-20
Flash point, (°C)	64
Vapor density	3
Purity (%)	99.8
Ignition temperature, (°C)	345

### 3.2.5 Methane and Carbon Dioxide Gases

The membranes were tested using pure carbon dioxide and methane as test gases. Table 3.5 shows the properties of pure carbon dioxide and methane.

**Table 3.6:** Properties of pure methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>)

Properties	Methane (CH <sub>4</sub> )	Carbon dioxide (CO <sub>2</sub> )
Molecular weight, (gmol <sup>-1</sup> )	16.043	44.01
Melting point, (°C)	-182.5	-78
Critical temperature, (°C)	-82.7	31
Critical pressure, (bar)	45.96	73.825

### 3.2.6 Nonsolvent Additives (NSA)

Water of co-solvent was used in this study. Table 3.6 shows the properties of water.

**Table 3.7** Properties of water

<b>Properties</b>	<b>Value</b>
Molecular weight, (gmol <sup>-1</sup> )	18.02
Density, (kg/m)	998
Melting point, (°C)	0
Boiling point, (°C)	100
Critical Temperature, (°C)	386
Critical Pressure, (Bar)	221.2
Specific Heat Capacity, (KJ/KgK)	4.187

### 3.2.7 Coagulation Medium

Methanol (industrial grade) as a coagulation medium was used in this study. Table 3.7 shows the properties of methanol.

**Table 3.8:** Properties of methanol

<b>Properties</b>	<b>Value</b>
Molecular weight, gmol <sup>-1</sup>	32.04
Melting point, (°C)	-98
Boiling point, (°C)	65.04
Density, (kg/m)	790

### 3.2.8 Liquid Nitrogen

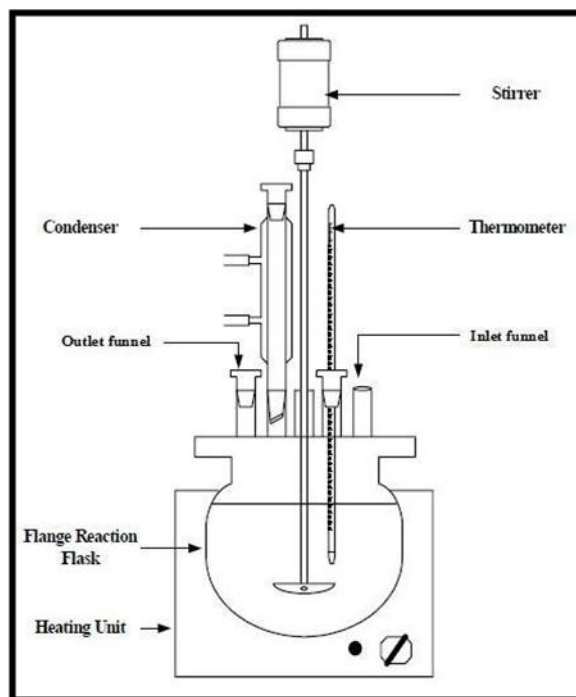
Liquid nitrogen is a cold, liquefied gas with a temperature of -321 °F. Nitrogen makes up 70% of the air we breath so it will not harm human. Liquid nitrogen is used to freeze and destroy skin growth. Table 3.8 shows the properties of liquid nitrogen.

**Table 3.9:** Properties of liquid nitrogen.

<b>Properties</b>	<b>Values</b>
Molecular weight , $\text{gmol}^{-1}$	28
Melting point, ( $^{\circ}\text{C}$ )	-210
Boiling point, ( $^{\circ}\text{C}$ )	-196
Critical temperature ( $^{\circ}\text{C}$ )	-147
Relative density, gas	0.97 (air = 1)
Relative density, liquid	0.8 (water = 1)
Solubility mg/l water	20
Appearance/ Colour	Colourless liquid
Odour	No Odour warning properties

### 3.3 PREPARATION OF CASTING SOLUTION (DOPE)

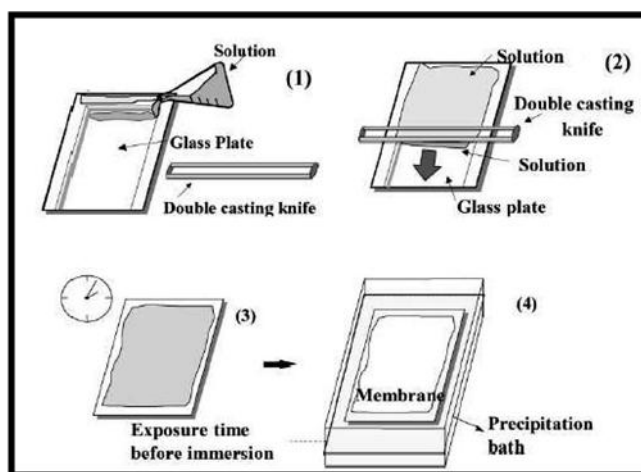
Figure 3.6 illustrated the apparatus for preparing the casting solutions (dope). Polysulfone was first dried in a vacuum oven overnight at temperature of about  $60 \pm 2^{\circ}\text{C}$  in order to eliminate all absorbed water vapor before used in making dope solution. The polysulfone, solvent and nonsolvent (water) were weighted according to the required solution percentage on an electronic scale and keep inside aluminium foil sealed beaker. The necessary equipment to be used in the dope solution preparation were cleaned and dried. Firstly, the solvent was poured into the round bottom reaction vessel until the temperature is increased to about  $60^{\circ}\text{C}$  with medium speed stirred. The solution temperature was measured by thermometer and the required temperature range was controlled by the heating mantle and condenser to cool down the temperature. When the temperature of the solvent has reached 50 to  $55^{\circ}\text{C}$ , polymer pellets were added slowly into the vessel to avoid the accumulation or agglomeration. After almost an hour, non-solvent, water is poured slowly into the vessel and stirring process is continuing for several hours. Typically, the whole process to prepare casting solution is about 6-7 hours. After the solution has fully dissolved, it was poured into a clean schott bottle. Finally, the homogeneous solution was degassed using ultrasonic to remove any micro bubble before casting.



**Figure 3.6:** Casting solution preparation system

### 3.4 MEMBRANE CASTING

Asymmetric polysulfone membranes were prepared according to dry/wet phase separation process using casting technique. Figure 3.7 printed the casting process used in this study for producing flat sheet membranes.

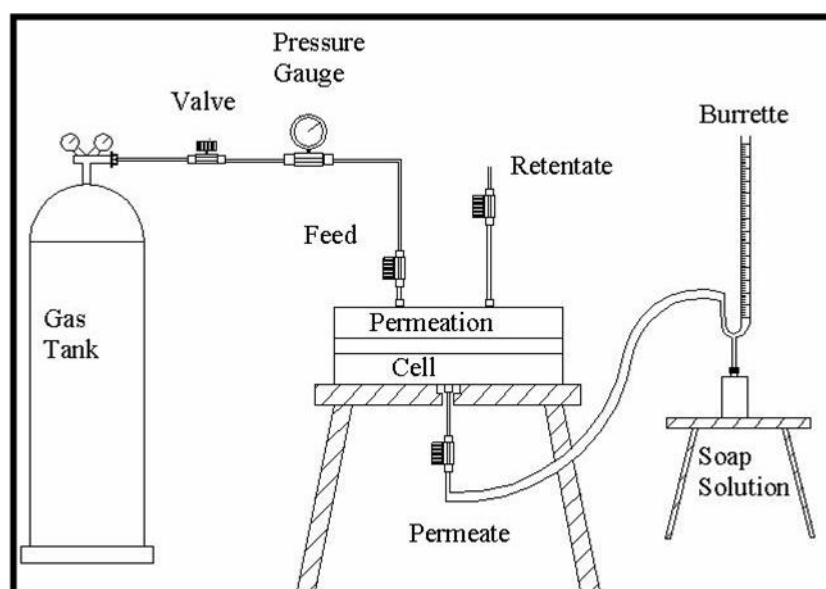


**Figure 3.7:** Casting process polymer solution

The casting process was conducted at room temperature ( $30\pm 2^{\circ}\text{C}$ ) and approximately 84% relative humidity. A small amount of casting solution was poured onto a glass plate with the casting block. The casting solutions were cast on the glass plate for gap setting of  $400\mu\text{m}$  at an appropriate casting shear. During the casting solution, convective evaporation phenomena were induced on membrane before being immersed into the coagulation medium. The glass plate with the membrane casting solution then were immersed into the coagulation bath (water as coagulation medium) to peel off the membrane from the surface plate. Finally, the membranes were transferred to water bath for 1 day and lastly pretreated with methanol for 24 hours before air dried for at least 48 hours at room temperature to remove any residual organic compounds.

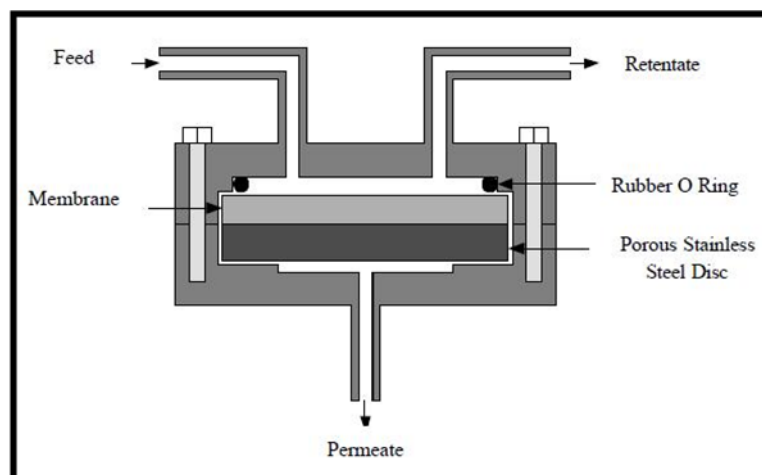
### 3.5 Gas Permeation Tests

Figure 3.8 illustrated the overall gas permeation system used in this study. The system was included the flexible hose, permeation cell, needle valve, pressure regulator and bubble flow meter. Gas permeation system was made up to measure pure gas permeation rate for asymmetric flat sheet membrane and approximately their selectivity.



**Figure 3.8:** Gas permeation system

Figure 3.9 shows the permeation cells that were used in this study to measured flux of the flat sheet membranes. Pure carbon dioxide and methane gases were utilized in the permeation test. Volumetric gas permeation rates were measured with soap bubble flow meter. These experiments were carried out at ambient temperature ( $30\pm 2^\circ\text{C}$ ) by various pressures at 1-4 bar pass through the membrane.



**Figure 3.9:** Permeation cell

Gas permeability rate can be calculated by

$$P_i = \frac{Q_i l}{A \Delta p} \quad (3.1)$$

where  $P_i$  is permeability coefficient for gas  $i$ ,  $Q_i$  is volumetric flow rate of gas  $i$ ,  $A$  is membrane effective surface area and  $l$  is membrane skin thickness.  $\Delta p$  is pressure different across membrane, which is given by  $\Delta P = P_{us} - P_{ds}$ , where  $P_{us}$  and  $P_{ds}$  are upstream and downstream pressure respectively. The common unit of permeability coefficient is Barrer, where

$$1 \text{ Barrer} = 10^{-10} \text{ cm}^3 (\text{STP}).\text{cm}/\text{cm}^2.\text{s}.\text{cmHg}$$

Instead, total gas permeation rate through asymmetric membrane is usually expressed as below

$$\frac{P_i}{l_i} = \frac{Q_i}{A\Delta p} \quad (3.2)$$

where  $(P/l)_i$  is defined as pressure-normalized flux or permeability for gas  $i$ .  $Q_i$  is volumetric flow rate of gas  $i$ ,  $\Delta p$  is pressure difference across membrane,  $A$  is membrane effective surface area and  $l$  is membrane skin thickness. The common unit of pressure-normalized flux is GPU, where

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

Selectivity (unitless) of asymmetric membrane can be determined by relative permeability of components  $i$  and  $j$ .

$$\alpha_{ij} = P_i/P_j = (P/l)_i / (P/l)_j \quad (3.3)$$

## 3.6 MEMBRANE CHARACTERIZATION METHODS

### 3.6.1 Scanning Electron Microscopic (SEM)

Scanning Electron Microscopy is an apparatus that is capable of magnifying a very discrete surface into a larger and clearer image. This method is used to analyze the membrane surface to examine the morphology or specifically the membrane structure, pore distribution, defect and presence of impurities. A small piece of the tested membranes were cut and were dried then immersed to leave an undeformed structure and mounted on sample stubs. The samples were recovered with a thin platinum layer (Baltec) and placed on a support in the SEM. The morphologies (cross section and surface layer) were then viewed with scanning electron microscopy (Carl Zeiss EVO50) with potential of 20kV under magnifications ranging from 50X to 6000X.

### **3.6.2 Fourier Transform Infrared (FTIR)**

FTIR were performed in order to study the chemical structure of organic molecules and potential structural changes that occur as a result of the membrane chemical treatment or degradation. FTIR spectra of thin films were recorded. These can be seen from the spectrum observed (in term of the wave number and the wave length) in order to know the different occurred in the membrane.



## **CHAPTER 4**

### **RESULT AND DISCUSSION**

One important goal in membrane technology is to control membrane structure and thus membrane performance. Polysulfone membranes were prepared by a dry/wet phase inversion process from casting solutions containing of polysulfone, nonsolvent additive (water) and various type of solvent ( 1-methyl-2-pyrrolidone, Dimethylacetamide and Dimethylformamide). Therefore, this chapter discusses the characteristic and separation performance of flat sheet asymmetric membrane developed. The aim of this study is to obtain high performance flat sheet asymmetric membrane with optimum Pressure Normalized Flux or Permeability and Selectivity. It is hoping that this study can produce locally made asymmetric membrane for CO<sub>2</sub>/CH<sub>4</sub> separation as well as other gas separation field.

#### **4.1 EFFECT OF SOLVENT ON MEMBRANES GAS SEPARATION**

##### **4.1.1 Composition of Dope Solution**

In order to prepare of asymmetric polysulfone membrane dope solutions that are suitable for flats sheet casting, several solvent were selected. From literature, high performance polysulfone membrane for gas separation were prepared from casting solution containing of 10 to 30 percent polymer, 35 to 70 percent solvent and 15 to 30 percent pore forming agents. In this study, the parameter that involved to achieve the aim of this study are involved the different type of solvent and the pressure that was applied during the permeation test. For the purpose, three type of dope solutions were successfully cast containing of 20% of polysulfone polymer and 3% of water as non-

solvent additive with 77% of different type of solvent were produced as tabulated in Table 4.1. The solvent were used are N-methyl-2-pyrrolidone, (NMP), N-N-dimethylacetamide, (DMAc), and N-N-dimethylformamide, (DMF). The dope solutions were used to test with a single test gas after casting process.

**Table 4.1:** Casting solution formulations

<b>Polymer Solution Composition</b>	<b>Dope Solution 1</b>	<b>Dope Solution 2</b>	<b>Dope Solution 3</b>
Polysulfone (PSU)	20%	20%	20%
N-methyl-2-pyrrolidone (NMP)	77%	-	-
N,N-dimethylacetamide (DMAc)	-	77%	-
N-N-dimethylformamide (DMF)	-	-	77%
Water (H <sub>2</sub> O)	3%	3%	3%

#### 4.1.2 Performance of Asymmetric Polysulfone Membrane

Gas separation through asymmetric membrane depends on differences in the permeabilities of various gases through a given membrane. The selectivity of membranes for mixed gas has been different compared to the selectivity based on single gas.

Separation performances of membrane were tested in gas permeation rig. Single feed gases were used by passing through a flexible hose before feeding it to the membrane module. A flat sheet membrane was employed in this study. A membrane (diameter of 24 cm) was mounted between the permeate chamber and the feed gas chamber supported by a porous metal disk and sealed with rubber O-rings. Flow rate and pressure were recorded and controlled by flow meter. The permeation rate was measured by a bubble flow meter. Various polysulfone asymmetric flat sheet membrane listed as PSU/NMP/H<sub>2</sub>O, PSU/DMAc/H<sub>2</sub>O and PSU/DMF/H<sub>2</sub>O were prepared based on composition of three casting solutions developed as listed in Table 4.1 were exhibit a clear difference on the CO<sub>2</sub>/CH<sub>4</sub> separation performance as shown in Table 4.2.

Membranes were coated using a standard coating procedure in order to seal the skin layer defects. The advantage of using this coating technique is that it circumvents the difficulty of membrane with a perfect skin. Asymmetric membranes usually contained few defects, which attributed to the complete coalescence of the nodule aggregates of the composed skin layer. The average pressure-normalized fluxes of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) for coated asymmetric membranes with different pressure applied are shown in Table 4.2.

**Table 4.2:** Average separation properties of polysulfone asymmetric membrane at different type of solvent

Solvent	Pressure (bar)	Pressure-normalized flux of CO <sub>2</sub> (GPU)	Pressure-normalized flux of CH <sub>4</sub> (GPU)	Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub>
NMP	1	266.98	36.35	7.34
	2	240.11	83.55	2.87
	3	236.28	111.78	2.11
	4	189.88	137.67	1.38
DMAc	1	178.28	32.03	5.57
	2	128.40	54.58	2.35
	3	126.84	67.86	1.89
	4	123.76	82.82	1.49
DMF	1	98.37	26.23	3.75
	2	72.07	32.13	2.24
	3	64.61	34.41	1.88
	4	63.32	34.25	1.85

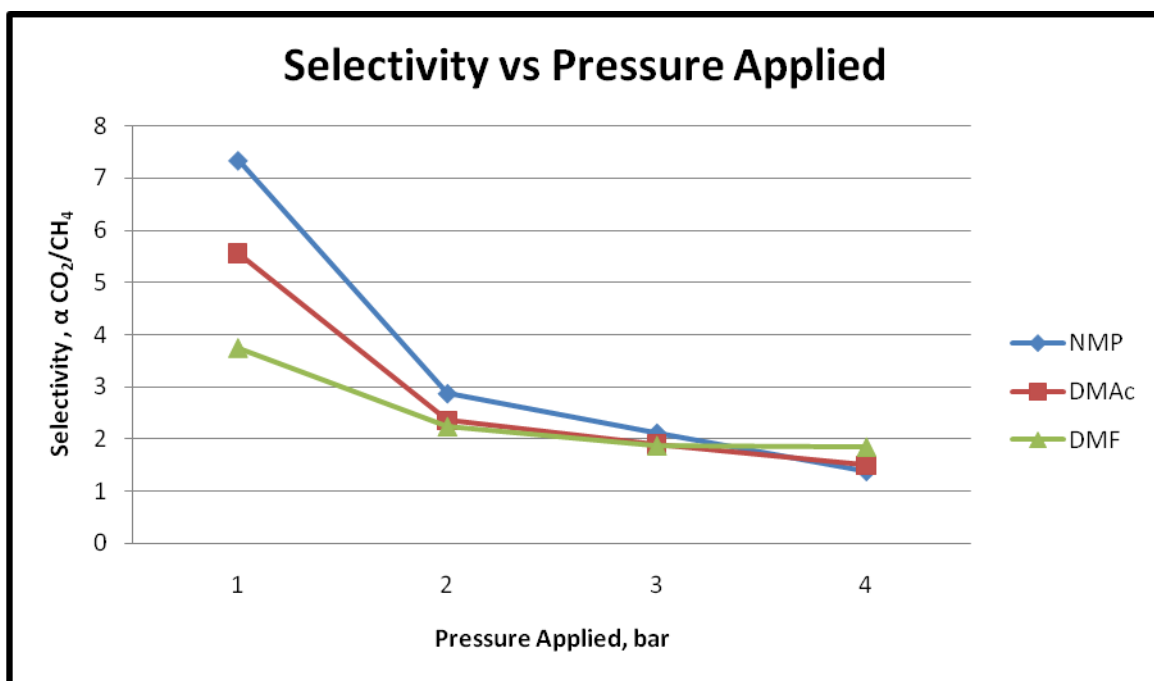
The calculated results are shown in Figure 4.1, Figure 4.2 and Figure 4.3 respectively. Each data presented an average result of at least four experimental data points. Selectivity of CO<sub>2</sub>/CH<sub>4</sub> had same trend, which slightly decrease with the increase of pressure. With the number of gaseous mixtures, the real separation factor is not equal to the ideal separation factor because of plasticization which may occur at high (partial) pressure when permeating gas exhibits a high chemical affinity for the polymer. Because of the plasticization, the permeability increase but the selectivity decrease generally. While the performance of CO<sub>2</sub> reasonable increased to the addition of feed pressure.

As shown in Table 4.2, N-methyl-2-pyrrolidone shows the highest selectivity with 7.34 compared to the other solvent which is 5.57 for N,N-dimethylacetamide and 3.75 for N,N-dimethylformamide at sama pressure as 1 bar. The carbon dioxide pressure-normalized flux were higher than methane pressure-normalized flux due to their kinetic diameter as illustrated in Table 4.3.

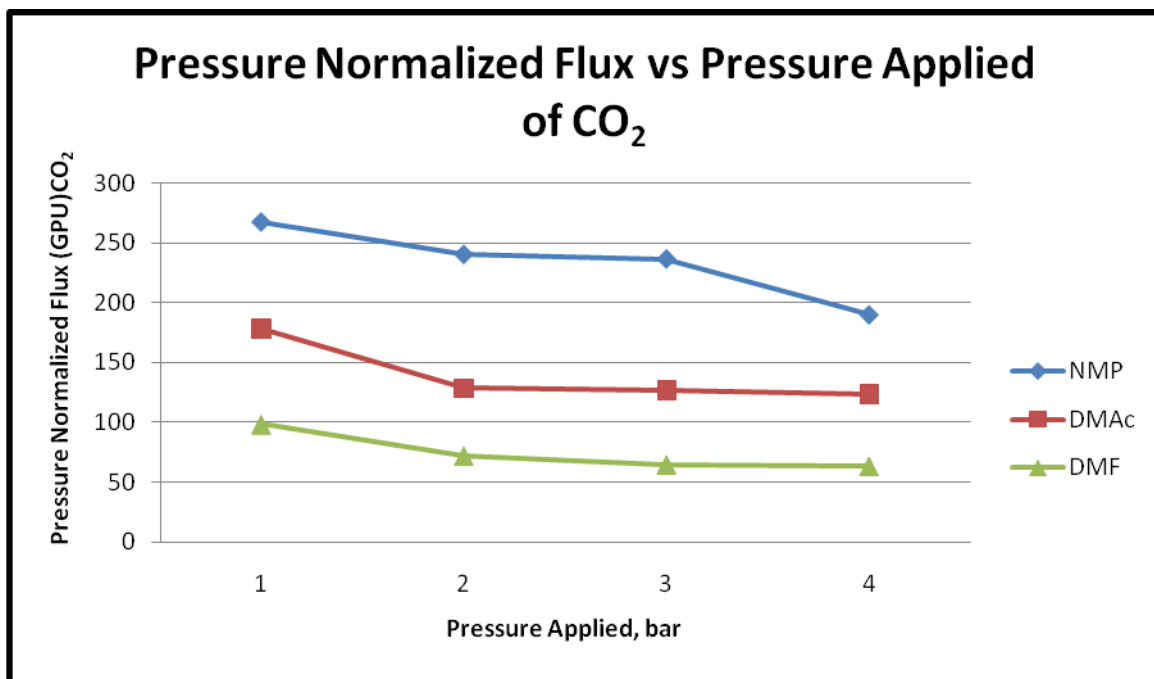
**Table 4.3:** Molecular weight (Da) and kinetic diameter ( $\text{\AA}$ ) of gases encountered in membrane gas separation

Molecule	Molecular Weight	Kinetic Diameter ( $\text{\AA}$ )
CO <sub>2</sub>	44	3.3
CH <sub>4</sub>	16	3.8

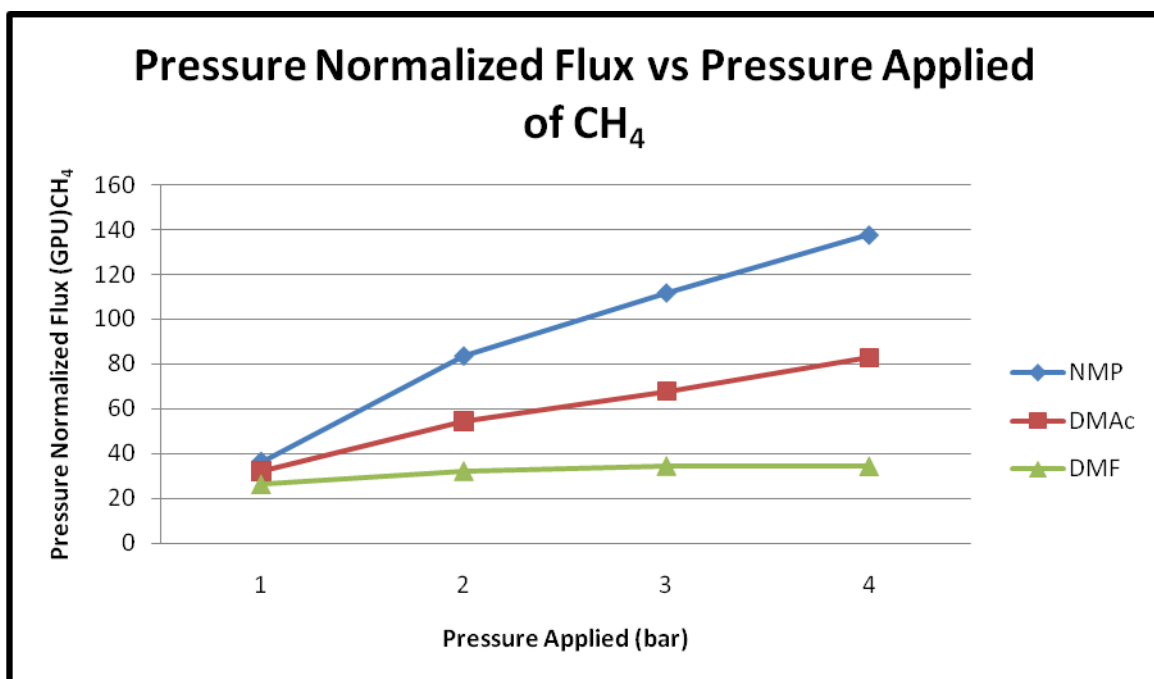
Sources: (Scholes *et al.*, 2008)



**Figure 4.1:** Graph of selectivity,  $\alpha$  CO<sub>2</sub>/CH<sub>4</sub> of polysulfone asymmetric membrane for various type of solvent with different pressure applied.



**Figure 4.2:** Graph of carbon dioxide (CO<sub>2</sub>) pressure normalized flux of polysulfone asymmetric membrane for various type of solvent with different pressure applied.



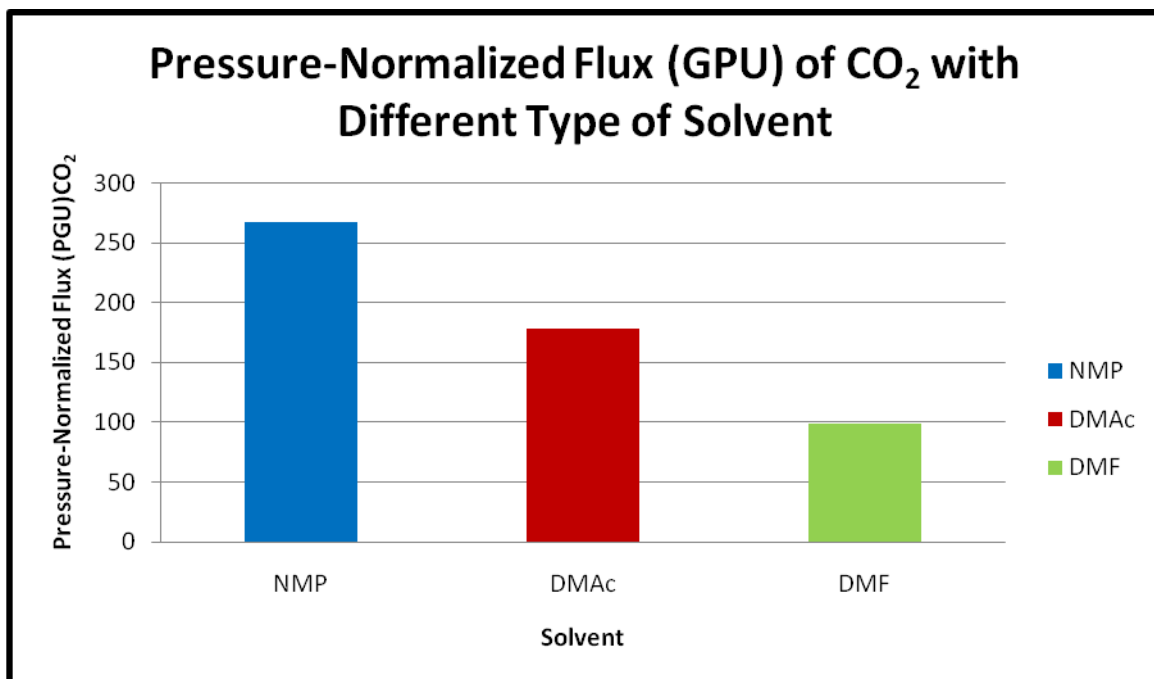
**Figure 4.3:** Graph of methane (CH<sub>4</sub>) pressure normalized flux of polysulfone asymmetric membrane for various type of solvent with different pressure applied.

### 4.1.3 Performance of Asymmetric Polysulfone Membrane of Different Pressure

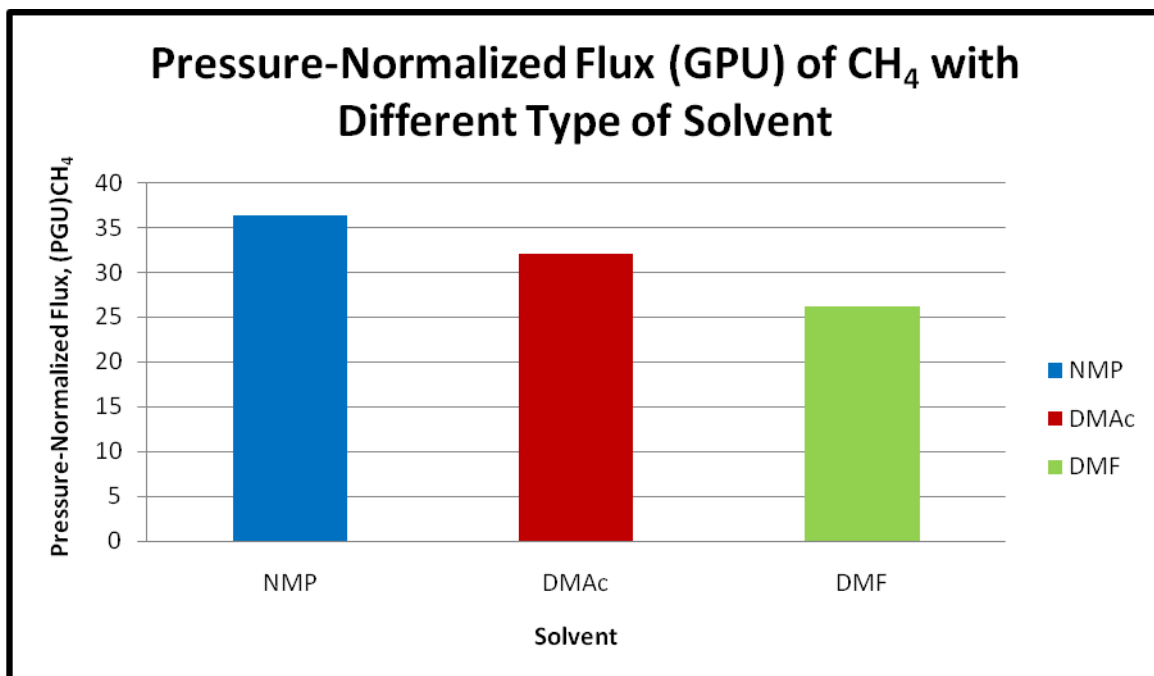
Pressure-normalized flux and selectivity of asymmetric membrane were measured by using pure carbon dioxide and methane. Every membrane sample from different type of formulations was tested to observe the effect of different pressure applied on the performance of polysulfone asymmetric flat sheet membranes. The data results of this study had been tabulated in Table 4.3, Figure 4.4, Figure 4.5 and Figure 4.6 respectively. As shown in Table 4.3, N-methyl-2-pyrrolidone shows the highest selectivity with 36.82 compared to the other

**Table 4.4:** Permeation properties of different type of solvent at pressure 1 Bar.

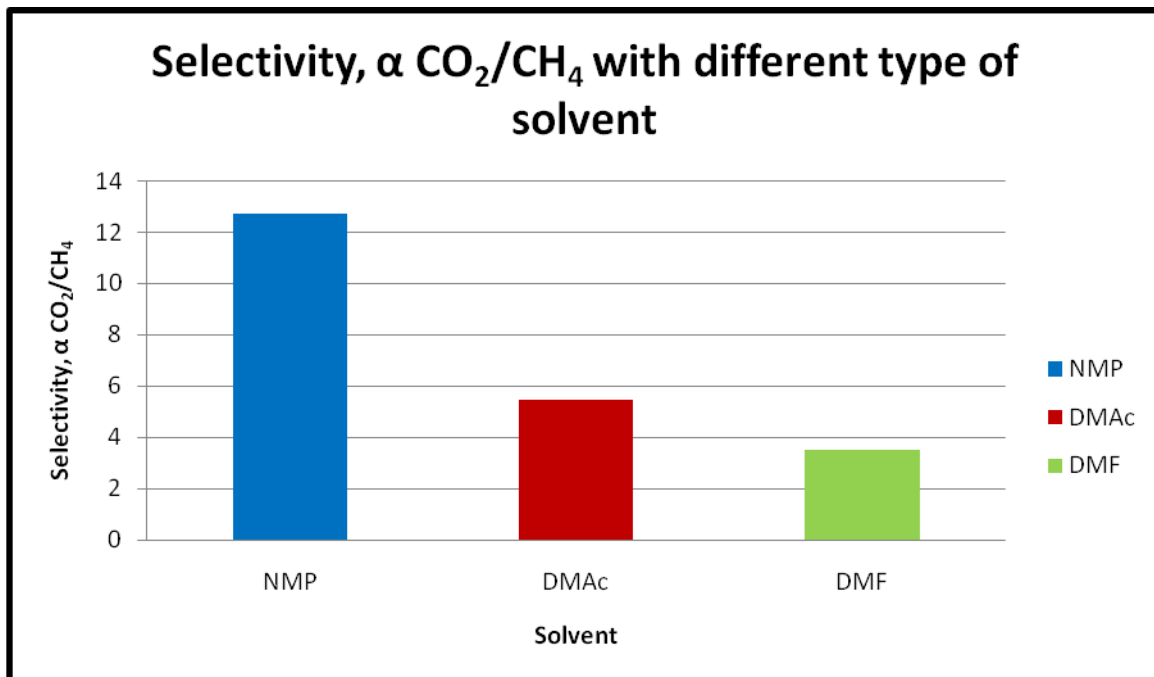
Type of Solvent	Membrane Type	Pressure-normalized flux of CO <sub>2</sub> (GPU)	Pressure-normalized flux of CH <sub>4</sub> (GPU)	Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub>
NMP	M1	130.97±96.17	31.76±3.25	4.12±6.09
	M2	246.72±14.33	68.00±22.38	3.63±6.44
	M3	482.23±152.20	13.10±16.44	36.82±17.03
	M4	208.02±41.70	32.54±2.69	6.39±4.49
	Average	266.98±76.10	36.35±11.91	12.74±8.51
DMAc	M1	241.11±44.43	36.08±2.86	6.68±0.85
	M2	106.09±51.05	23.42±6.09	4.53±0.67
	M3	179.81±1.08	36.58±3.22	4.92±0.40
	M4	186.12±5.54	32.05±0.01	5.81±0.23
	Average	178.28±25.52	32.03±3.05	5.48±0.54
DMF	M1	70.73±19.54	35.25±6.37	2.01±1.07
	M2	225.72±90.05	34.90±6.13	6.47±2.09
	M3	46.74±36.51	16.50±6.88	2.83±0.48
	M4	50.28±34.00	18.30±5.62	2.75±0.54
	Average	98.37±45.03	26.23±6.25	3.51±1.04



**Graph 4.4:** Graph of Pressure-Normalized Flux (GPU) of CO<sub>2</sub> with different type of solvent at pressure 1 Bar.



**Graph 4.5:** Graph of Pressure-Normalized Flux (GPU) of CH<sub>4</sub> with different type of solvent at pressure 1 Bar.



**Graph 4.6:** Graph of Selectivity,  $\alpha$  CO<sub>2</sub>/CH<sub>4</sub> with different type of solvent at pressure 1 bar.

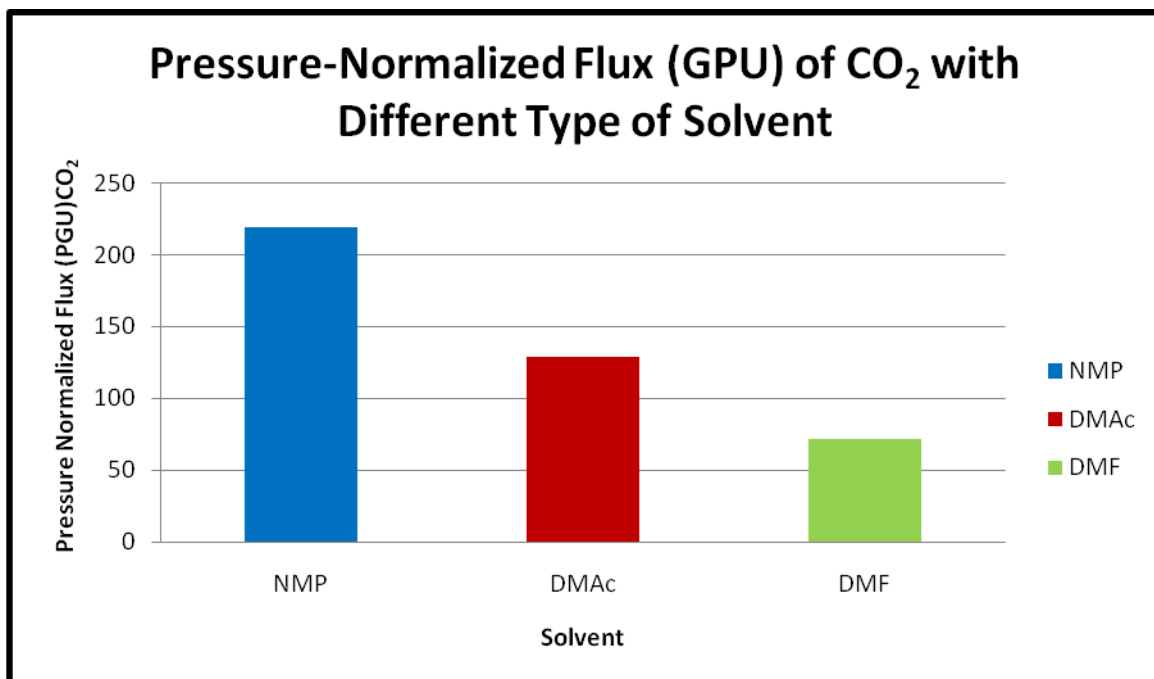
An ideal gas separation membrane must have high permeability and high selectivity. The gas permeation properties of polymer membrane have been extensively studied and a wide variety of polymers have been synthesized to be more permeable and selective (Li *et al.*, 2008). Fujioka (2009) has been studied that gas separation in membrane is driven by a pressure difference across the membrane. To obtain a adequate pure steam of CO<sub>2</sub> the selectivity for CO<sub>2</sub> must facility. In addition, high permeability is required to produce a compact membrane permeate through multiple membrane stages to achieve the desired flow rate and purity. In achieve high selectivity and permeability, the disadvantage of the phenomena is their tendency to plasticize even at a partial CO<sub>2</sub> pressure of 8-10 bar. In membrane studies, plasticization is generally defined as an increase in the segmental motion of polymer chains due to the presence of one or more sorbates, such that the permeability of both components increase and the selectivity decrease. For many new potential applications (such as natural gas upgrading, enhanced oil recovery and landfill gas clearing), CO<sub>2</sub> separations for enhanced oil plasticization resistance is required (Robert, 2006).



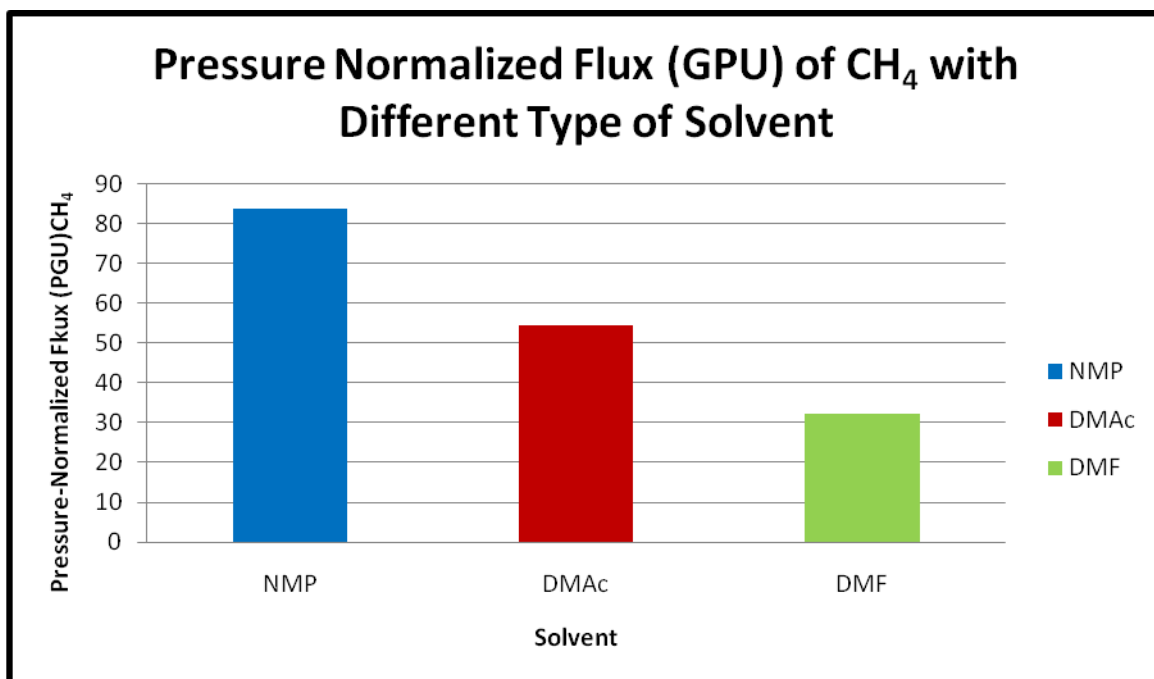
Donald (1996) discussed that the increasing the feed pressure in air separating system increase the permeate purity. However, once CO<sub>2</sub> plasticization begins affecting the selectivity of the polymer, the permeate purity rapidly decrease. As the feed pressure is increased, the increasing differential between inlet and permeate causes the permeate purity to again increase slightly. As shown in Table 4.4, Figure 4.7, Figure 4.8 and Figure 4.9, there was a performance of polysulfone asymmetric flat sheet membrane at pressure 2 bar. Four sample of casting solution for each solvent was tested during gas permeation test in order to minimize the error of casting technique during membrane fabrication process. The data for four samples will calculate to get an average for each type of solvent and the pressure applied.

**Table 4.5:** Permeation properties of different type of solvent at pressure 2 Bar.

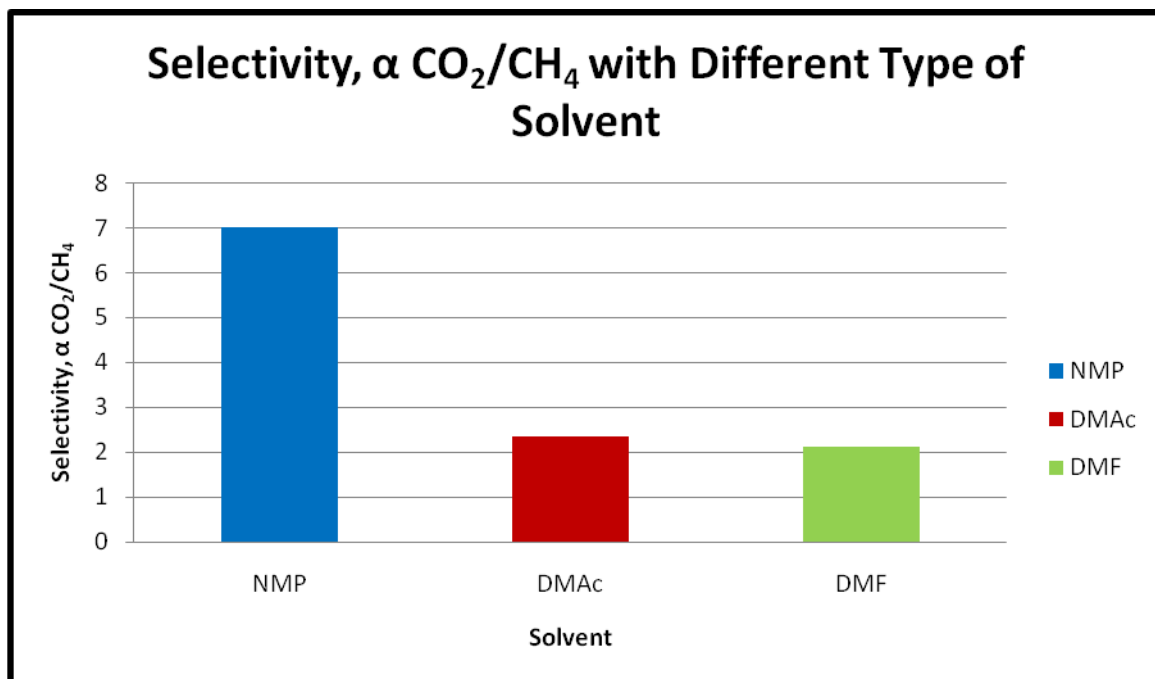
Type of Solvent	Membrane Type	Pressure-normalized flux of CO <sub>2</sub> (GPU)	Pressure-normalized flux of CH <sub>4</sub> (GPU)	Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub>
NMP	M1	104.01±81.69	106.09±15.94	0.98±4.26
	M2	221.02±1.04	70.73±9.07	3.13±2.74
	M3	312.03±65.40	14.03±49.16	22.24±10.77
	M4	241.11±14.25	143.36±42.30	1.68±3.76
	Average	219.54±40.85	85.55±29.11	7.00±5.38
DMAc	M1	182.91±38.55	54.13±0.32	3.38±0.73
	M2	74.71±37.96	51.01±2.53	1.46±0.62
	M3	132.61±2.98	61.68±5.02	2.15±0.14
	M4	123.36±3.56	51.50±2.18	2.40±0.03
	Average	128.40±20.76	54.58±2.51	2.35±0.38
DMF	M1	58.29±9.74	39.29±5.07	1.48±0.44
	M2	151.56±56.21	44.95±9.07	3.37±0.89
	M3	36.33±25.27	18.88±9.37	1.92±0.13
	M4	42.10±21.19	25.38±4.77	1.66±0.32
	Average	72.07±28.10	32.13±7.07	2.11±0.47



**Graph 4.7:** Graph of Pressure-Normalized Flux (GPU) of CO<sub>2</sub> with different type of solvent at pressure 2 Bar.



**Graph 4.8:** Graph of Pressure-Normalized Flux (GPU) of CH<sub>4</sub> with different type of solvent at pressure 2 Bar.



**Graph 4.9:** Graph of Selectivity,  $\alpha$  CO<sub>2</sub>/CH<sub>4</sub> with different type of solvent at pressure 2 Bar.

Permeability falls with increasing permeant size and small molecules permeate preferentially. Separation of gas mixtures by membrane gas separation was achieved shown to be a function of intrinsic selectivity of the membrane and the pressure different across the membrane. In gas separation, the effect of pressure is usually characterized by the pressure ratio across the membrane that is the ratio of feed to permeate pressure (Baker, 2006; Yampolskii *et al.*, 2006). Ahmad *et al.*, (2010) have been discovering the increase in feed pressure improves methane recovery. It is due to the fact that the increased pressure creates a greater driving force across the membrane. As a result, a net increase in permeation through the membrane increases methane recovery.

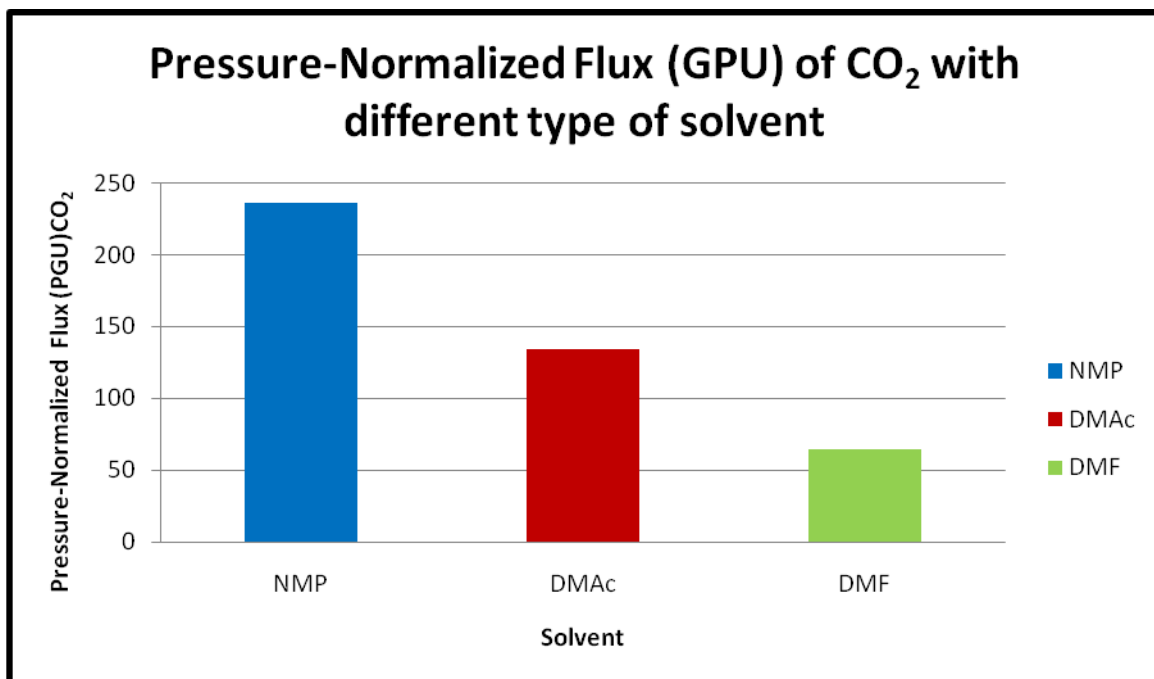
Selective transport of gases can be achieved by use of a polymer which forms channels of a certain sizes. Large channels will allows faster diffusions of gasses through a membrane at the cost of less selectivity between different gases, smaller channel will allow a much greater selectivity at the cost of lower permeation rates. As the methyl group increase (from 0 to 4) a significant increase in the CO<sub>2</sub> permeability is observed (from 9.20 to 440 barrer). A decrease in gas selectivity is also observed upon

addition of extra methyl group. The increase in permeabilities has been subscribed to an increase in the number of large free spaces. The permeability of CO<sub>2</sub> increase with pressure whereas CH<sub>4</sub> permeability decrease slightly with increased pressure as expected from dual mode sorption model (Powell, 2006).

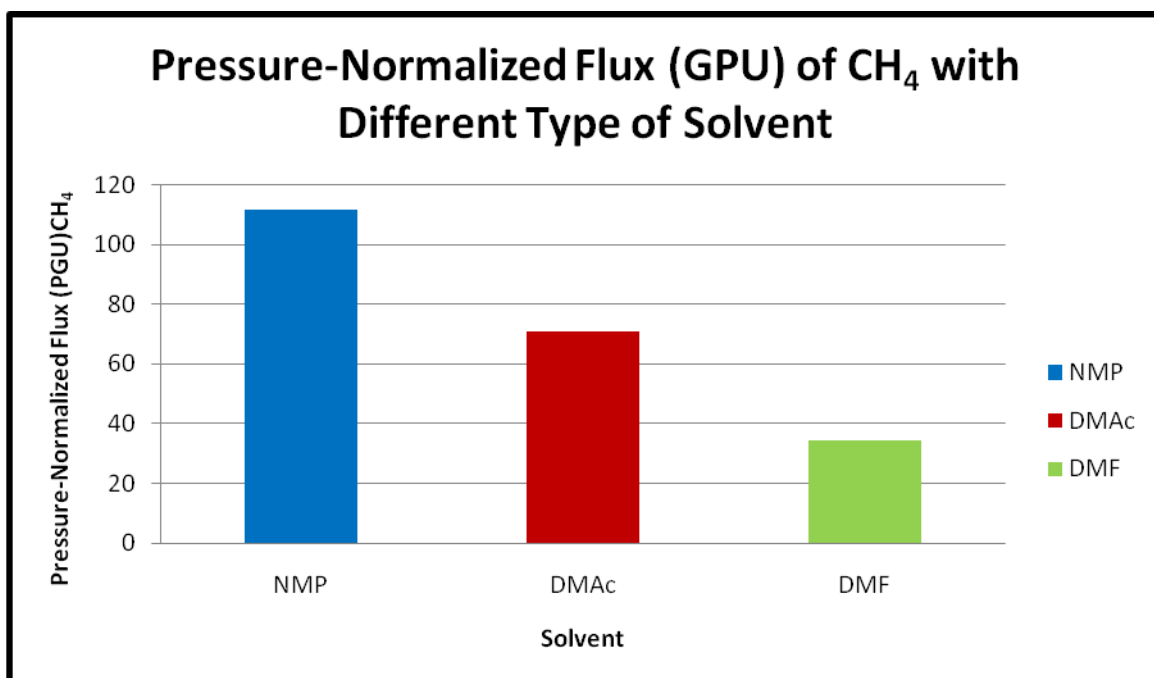
As shown in Table 4.5, Figure 4.10, Figure 4.11 and Figure 4.12, CO<sub>2</sub>/CH<sub>4</sub> selectivities for these membrane varied between 0.7 to 9.36 for N-methyl-2-pyrrolidone, 1.65 to 2.08 for N,N-dimethylacetamide and 1.71 to 2.21 for N,N-dimethylformamide. While for carbon dioxide pressure-normalized flux show performance between (117.88-353.63) GPU, (114.07-160.74) GPU and (37.22-107.16) GPU for N-methyl-2-pyrrolidone, N,N-dimethylacetamide and N,N-dimethylformamide respectively. Besides that, for methane pressure-normalized flux show the separation between (26.99-196.46) GPU, (64.30-78.58) GPU and (21.07-48.44) GPU for the three type of solvent respectively.

**Table 4.6:** Permeation properties of different type of solvent at pressure 3 Bar.

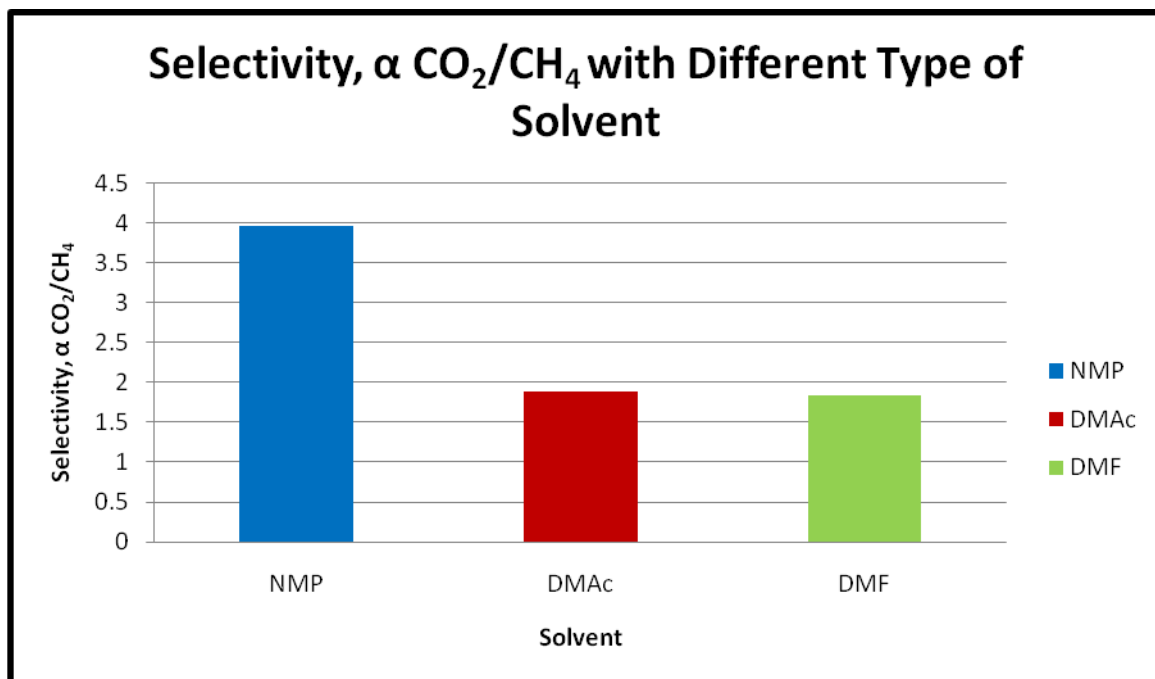
Type of Solvent	Membrane Type	Pressure-normalized flux of CO <sub>2</sub> (GPU)	Pressure-normalized flux of CH <sub>4</sub> (GPU)	Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub>
NMP	M1	117.88±83.72	168.40±40.04	0.7±2.31
	M2	221.02±10.79	55.25±39.97	4±0.03
	M3	252.59±11.54	26.99±59.95	9.36±3.81
	M4	353.63±82.98	196.46±59.88	1.8±1.53
	Average	236.28±47.26	111.78±49.96	3.96±1.92
DMAc	M1	147.35±9.40	70.73±0.01	2.08±0.14
	M2	160.74±18.87	78.58±5.55	2.05±0.11
	M3	114.07±14.13	64.30±4.55	1.77±0.08
	M4	114.07±14.13	69.34±0.99	1.65±0.17
	Average	134.06±14.13	70.74±2.77	1.89±0.13
DMF	M1	62.04±1.82	39.29±3.45	1.58±0.18
	M2	107.16±30.09	48.44±9.92	2.21±0.27
	M3	37.22±19.36	21.83±8.89	1.71±0.09
	M4	52.01±8.91	28.07±4.48	1.85±0.01
	Average	64.61±15.04	34.41±6.69	1.84±0.14



**Graph 4.10:** Graph of Pressure-Normalized Flux (GPU) of CO<sub>2</sub> with different type of solvent at pressure 3 Bar.



**Graph 4.11:** Graph of Pressure-Normalized Flux (GPU) of CH<sub>4</sub> with different type of solvent at pressure 3 Bar.



**Graph 4.12:** Graph of Selectivity,  $\alpha$  CO<sub>2</sub>/CH<sub>4</sub> with different type of solvent at pressure 3 Bar.

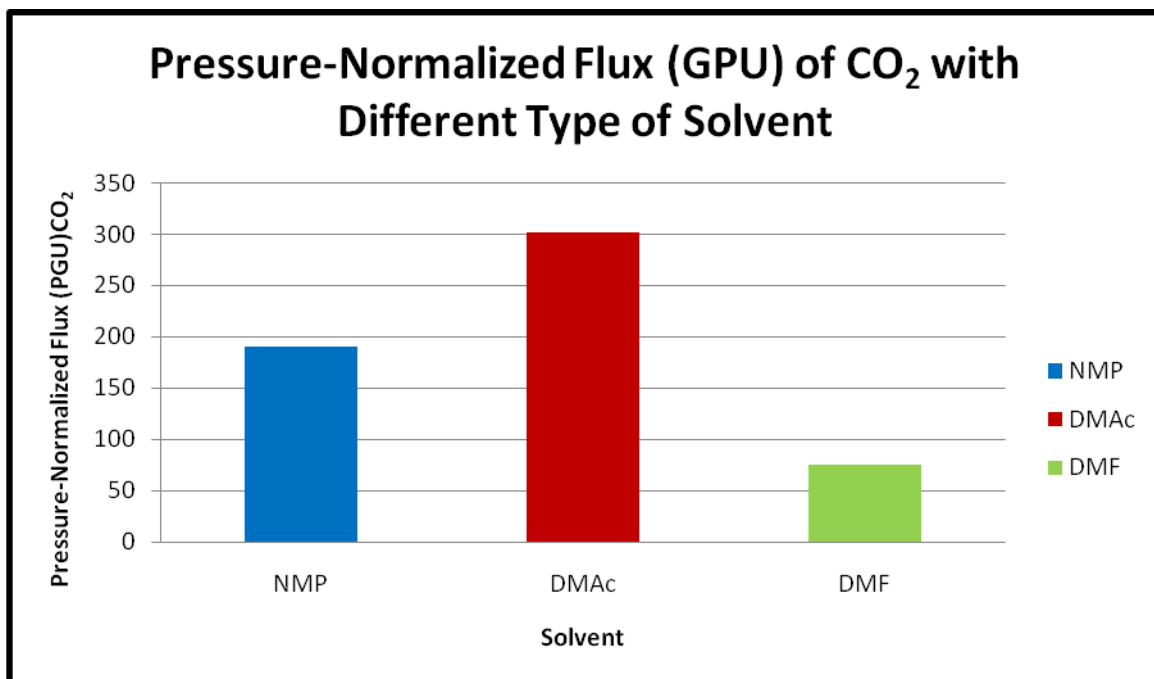
As shown in Table 4.6, Figure 4.13, Figure 4.14 and Figure 4.15, CO<sub>2</sub>/CH<sub>4</sub> selectivities for these membrane varied between 0.59 to 13.18 for N-methyl-2-pyrrolidone, 1.1 to 4.83 for N,N-dimethylacetamide and 1.34 to 3.09 for N,N-dimethylformamide. Otherwise, for carbon dioxide pressure-normalized flux show performance between (120.56-241.11) GPU, (165.76-442.04) GPU and (39.59-120.56) GPU for N-methyl-2-pyrrolidone, N,N-dimethylacetamide and N,N-dimethylformamide respectively. Besides that, for methane pressure-normalized flux show the separation between (18.29-265.22) GPU, (80.37-241.11) GPU and (29.47-53.04) GPU for the three type of solvent respectively.

A quite different behaviour was exhibit by the membranes prepared using the N-methyl-2-pyrrolidone solvent mixtures at the pressure 4 bar. The experimental data show a decreasing selectivity of CO<sub>2</sub>/CH<sub>4</sub> that shown N,N-dimethylacetamide achieved higher selectivity at pressure 4 bar compared the previous pressure where at pressure 1-3 bar. This Phenomenon has been observed and discussed by many researchers. It has to be given due attention while designing a gas separation module since both permeate and

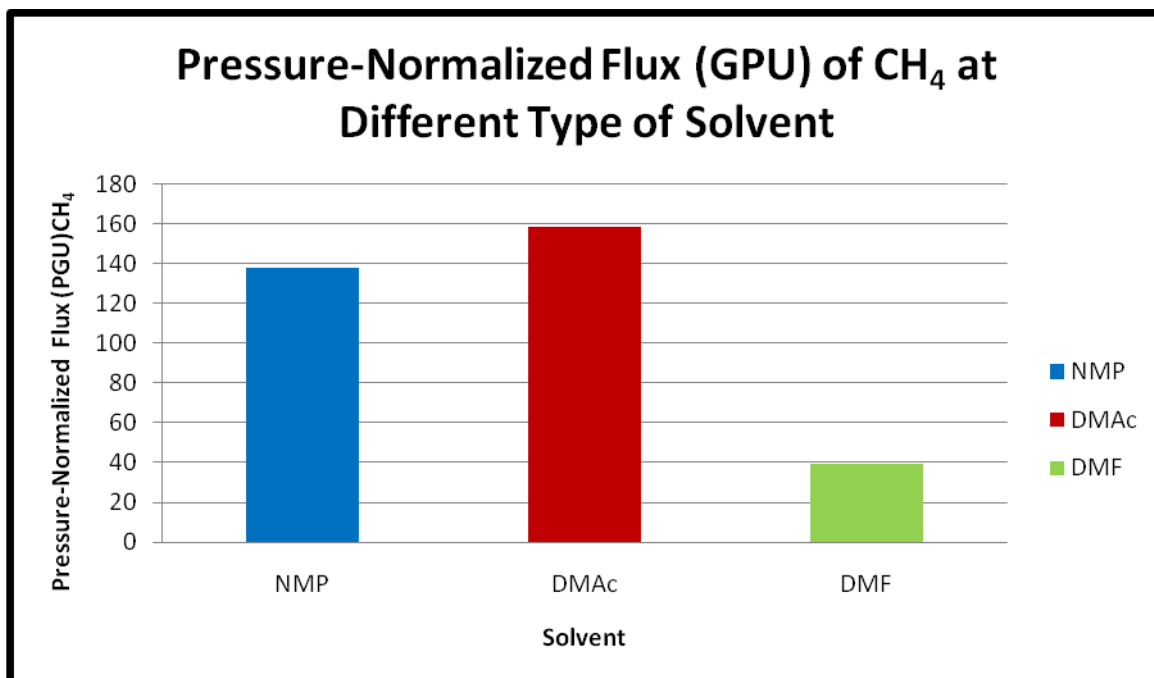
feed-side pressures are liable to variation. The changed pressure effects on these two modes of sorption displayed by the two groups in a mixture coupled with a difference in the diffusivity causes pressure-dependent selectivity (Iqbal, *et al.*, 2008). The CO<sub>2</sub> behaves as a plasticizer in CO<sub>2</sub>/CH<sub>4</sub> separations at elevated pressures resulting in loss in selectivity. The phenomenon has been explained recently by Lee *et al.*, 2009 in term of a plasticization depending upon the pressure and antiplasticization of Matrimid asymmetric fibre relevant to CO<sub>2</sub>/CH<sub>4</sub> separation.

**Table 4.7:** Permeation properties of different type of solvent at pressure 4 Bar.

Type of Solvent	Membrane Type	Pressure-normalized flux of CO <sub>2</sub> (GPU)	Pressure-normalized flux of CH <sub>4</sub> (GPU)	Selectivity, $\alpha$ CO <sub>2</sub> /CH <sub>4</sub>
NMP	M1	120.56±49.02	204.02±46.92	0.59±2.75
	M2	221.02±22.02	63.15±52.69	3.5±0.70
	M3	241.11±36.23	18.29±84.41	13.18±6.15
	M4	176.82±9.24	265.22±90.19	0.67±2.70
	Average	189.88±29.13	137.67±68.55	4.48±3.07
DMAc	M1	331.53±21.49	221.02±44.22	1.5±0.62
	M2	442.04±99.63	91.46±47.40	4.83±1.74
	M3	265.22±25.40	241.11±58.42	1.1±0.90
	M4	165.76±95.72	80.37±55.24	2.06±0.22
	Average	301.14±60.56	158.49±51.32	2.37±0.87
DMF	M1	120.56±31.93	39.01±0.15	3.09±0.84
	M2	88.41±9.20	53.04±9.78	1.67±0.17
	M3	39.59±25.32	29.47±6.89	1.34±0.39
	M4	53.04±15.81	35.36±2.73	1.5±0.28
	Average	75.40±20.57	39.22±4.89	1.90±0.42

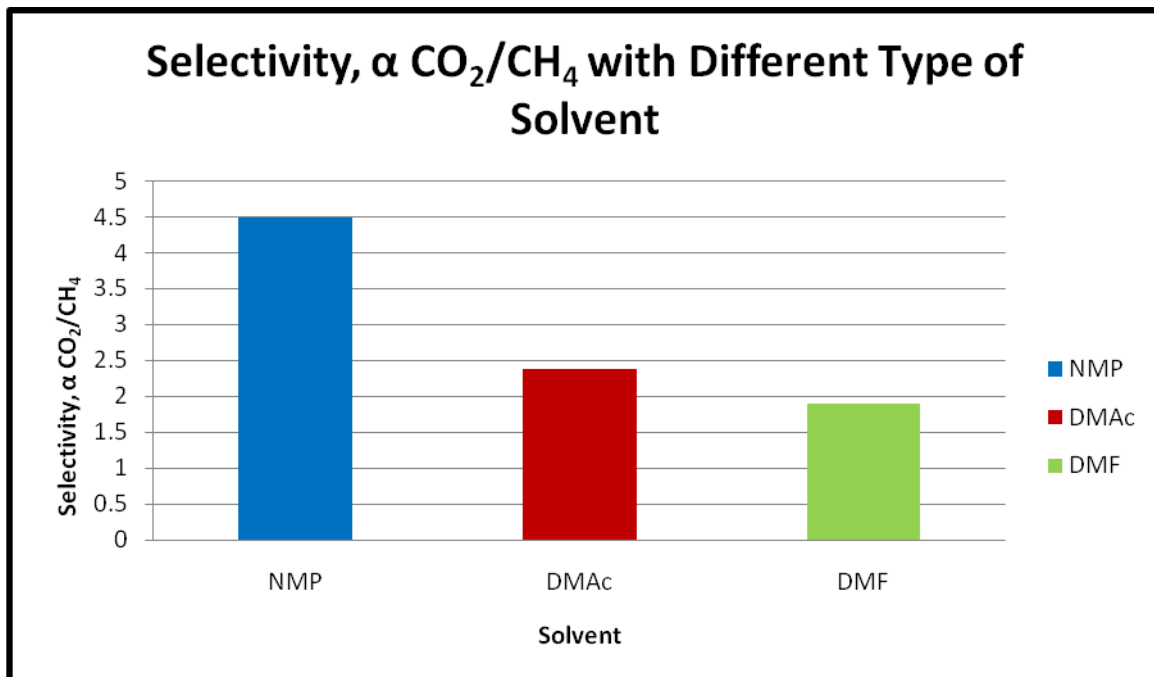


**Graph 4.13:** Graph of Pressure-Normalized Flux (GPU) of CO<sub>2</sub> with different type of solvent at pressure 4 Bar.



**Graph 4.14:** Graph of Pressure-Normalized Flux (GPU) of CH<sub>4</sub> with different type of solvent at pressure 4 Bar.





**Graph 4.15:** Graph of Selectivity,  $\alpha$  CO<sub>2</sub>/CH<sub>4</sub> with different type of solvent at pressure 4 Bar.

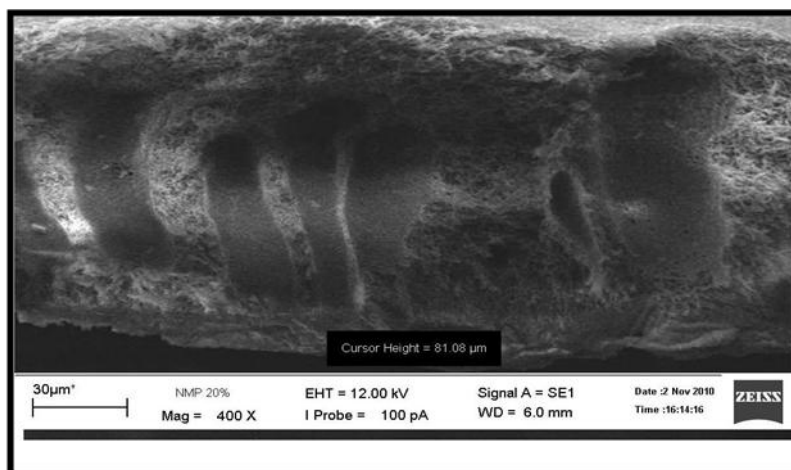
#### 4.2 EFFECT OF SOLVENT ON MORPHOLOGY OF ASYMMETRIC MEMBRANE

In general, the skin layer thickness affected the separation performances of membranes. In addition the membrane formation, the order of the solvent-nonsolvent (water) diffusivity dominates the behaviour of skin layer formation during the dry/wet phase inversion procedures respectively. The morphology of the membrane both on the surface and in the bulk along the permeability and selectivity could be correlated with the solvent characteristics (Guell, *et al.*, 2009). Thus, the effect of different type of solvent on CO<sub>2</sub>/CH<sub>4</sub> separation performance was investigated by using three type of solvent during producing the casting solution. The cross section and surface layer morphologies of the polysulfone asymmetric flat sheet membranes cast from the three casting solution (Table 4.1) based on the different type of solvents was investigated by scanning electron microscopy (SEM).

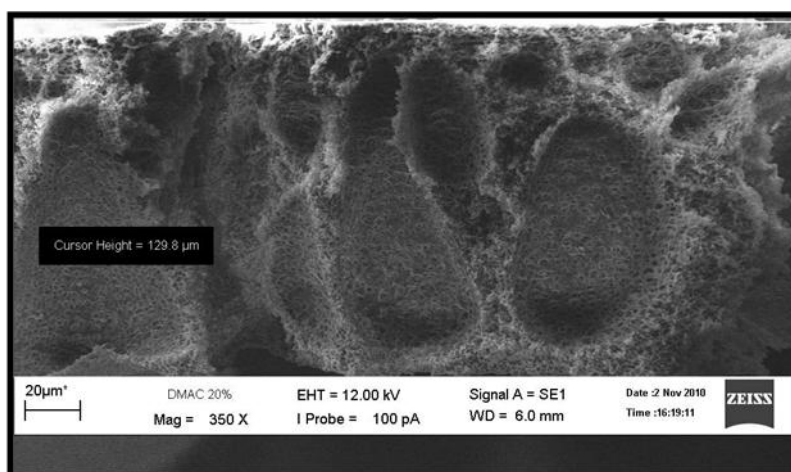
According Arthanareeswaran *et al.*, (2010), the process of formation of surface pores is affected by the thermodynamics properties of a casting solution and kinetics of

membrane formation. The mutual diffusion rate of the solvent-nonsolvent has a very significant influence on the sublayer formation. A very good correlation was found between the pure water fluxes of all membranes with solvents and the pore formation on surface (Arthanareeswaran et al., 2010). The results are illustrated as shown in Figure 4.15 and Figure 4.16. Both SEM images for cross section and surface layer were scanned at range of 350X-500X and 100X respectively.

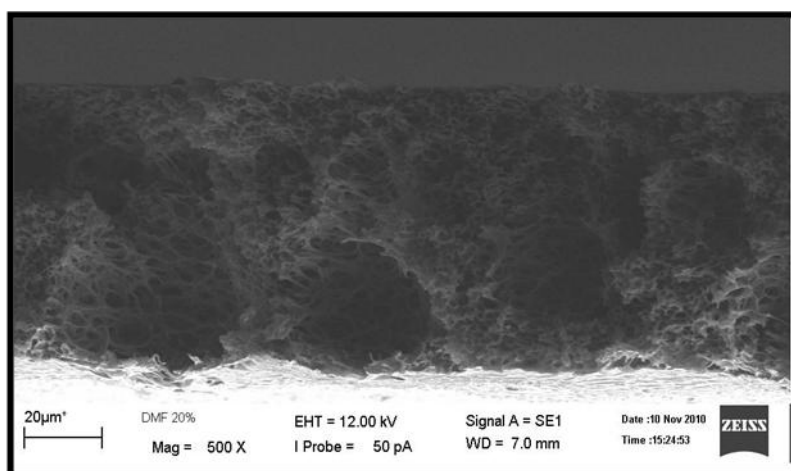
Figure 4.15 and 4.16 illustrate the morphologies of polysulfone asymmetric flat sheet membranes for three different type of solvent. Figure 4.15 show the cross section structure for three type of casting solution. It displayed similar cross sectional with a structure long finger like macrovoids from the skin layer to support region. Analysis on the cross section of these membranes revealed that a thin dense skin layer with highly porous substructure appeared for the membrane. There are many circular macrovoids beneath the thin dense skin layer. These phenomena were due to the transition step take place during the membrane drying process. Figure 4.16 illustrate the top surface layer of coated membrane containing polysulfone, water as nonsolvent and various type of solvent for each membrane.



(i)

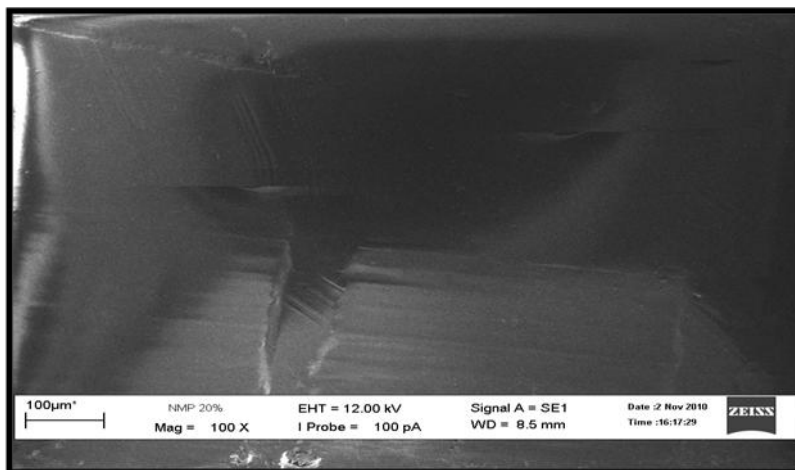


(ii)

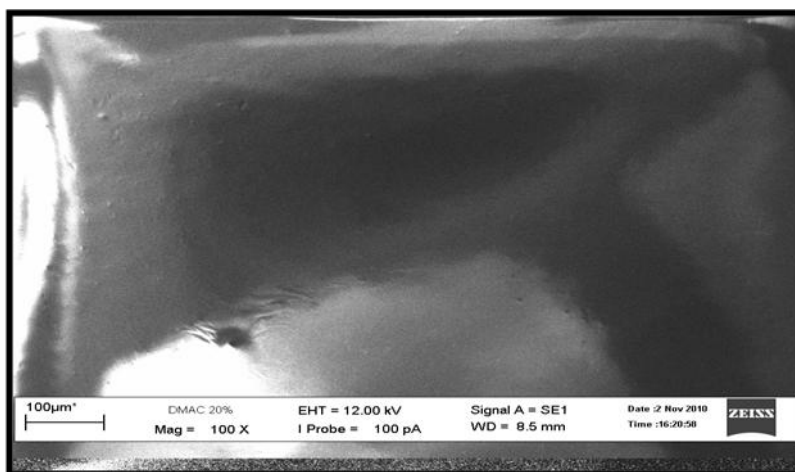


(iii)

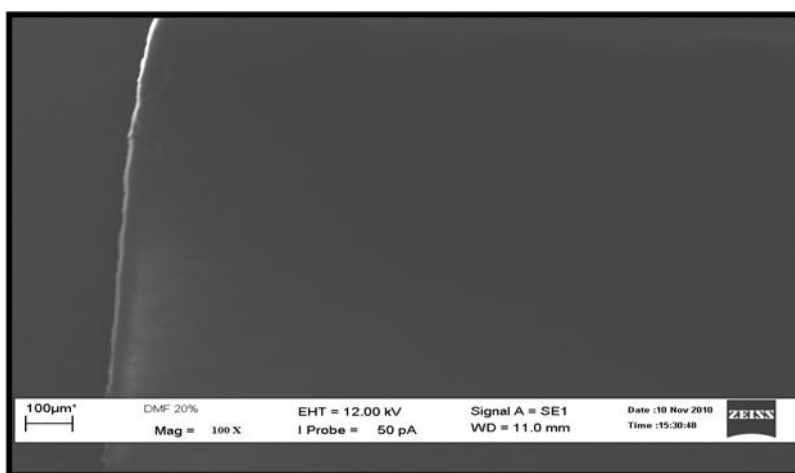
**Figure 4.16:** Scanning electron micrographs of polysulfone membranes cross sections at different type of polymer (i) N-methyl-2-pyrrolidone, NMP (400X) (ii) N,N-dimethylacetamide, DMAc (350X) and (iii) N,N-dimethylformamide, DMF (500X)



(i)



(ii)



(iii)

**Figure 4.17:** Scanning electron micrographs of polysulfone membranes surface layer at different type of polymer at 100X magnification (i) N-methyl-2-pyrrolidone, NMP (ii) N,N-dimethylacetamide, DMAC and (iii) N,N-dimethylformamide, DMF

As shown in Figures 4.15, the cross section of polysulfone membrane using different type of solvent for the ternary casting solution showed different structures for each membranes surface layer. Membranes produced with NMP exhibit the larger pores with size diameter restrained in a broad range. The relative affinity of a polymer and solvents can be assessed invoking the solubility parameter concept which numerical value that indicates the relative solvency behaviour of a specific solvents (Temtem, *et al.*, 2006). Hence, separation process was found to be more successful membrane using NMP compared to DMAc and DMF as solvent based on the membrane morphology.

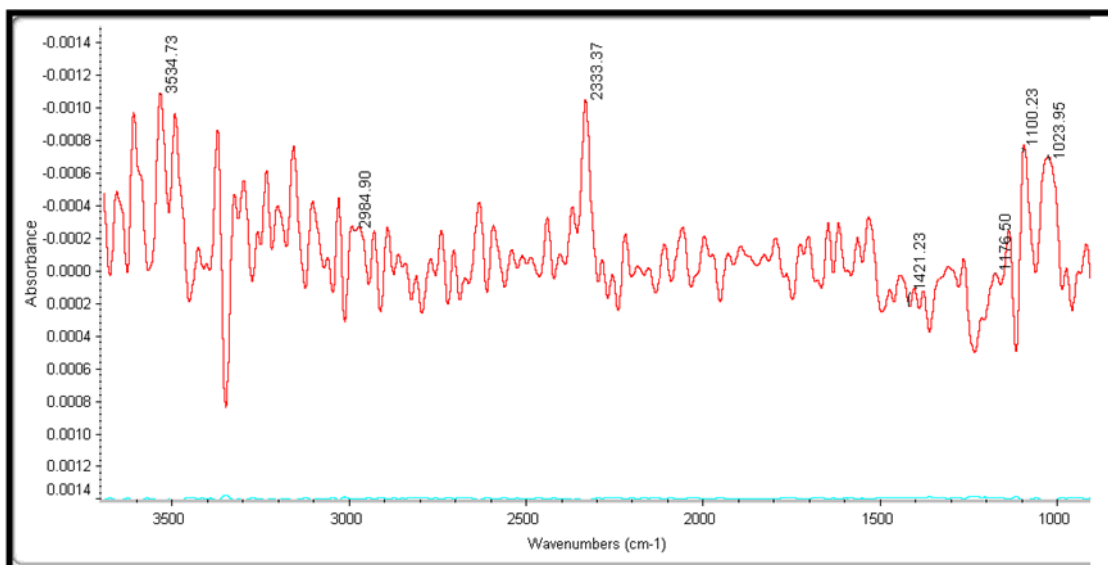
Morphologies of the skin layer surface layer for polysulfone membrane using NMP, DMAc and DMF are shown in Figure 4.16 respectively. The surface layer of those membranes was found quite smooth because it was coated by a solution mixtures of silicone PDMS and n-hexane. Membrane with silicone coating was able to enhance the membrane performance since the defects on the surface are seal smoothly. The process of formation of surface is affected by the thermodynamics properties of a casting solutions and kinetics of membranes of membrane formation. The different in membrane structure and separation performance were identified caused by different type of solvent used in casting solution. When a solvent-non-solvent was interact, it leading to reduction of the dissolving power of the solvent and thus enhanced the polymer-polymer interaction (Ridzuan, 2004; Arthanareeswaran *et al.*, 2010). The different in membrane structure and separation performance were identified caused by different type of solvent used in casting solution. The addition water as a nonsolvent during the coagulation process dissolves the solution to polymer when the casting solution is immersed in coagulant. As a result, membrane with smooth and macrovoids-free structure could be obtained (Wang *et al.*, 1995).

### 4.3 MEASUREMENT OF CHEMICAL STRUCTURE IN POLYSULFONE ASYMMETRIC MEMBRANE

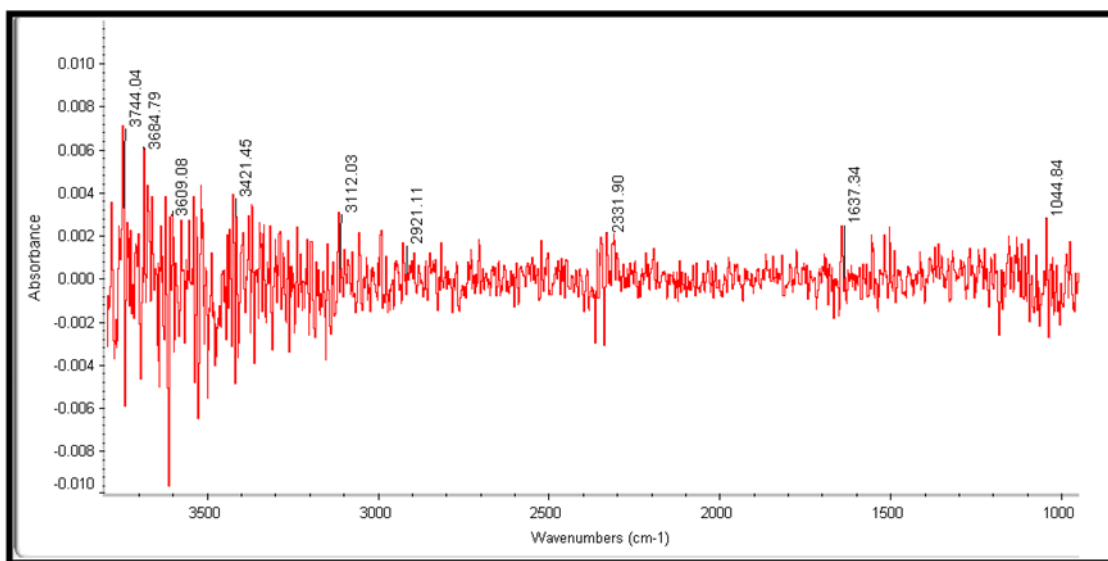
Chemical structure which mechanically induced on polysulfone asymmetric membrane by varying type of solvent during casting solution can be directly measured using Fourier Transform Infrared (FTIR). Shear induced molecular orientation in membranes has been shown to increase selectivity and has been directly measured using plane-polarized Fourier Transform Infrared Spectroscopy (FTIR) (Shilton *et al.*, 1996 and Ismail *et al.*, 1997). The results indicated clearly the presence sulfonic group in the polymer. This can be observed at a peak area  $1027\text{cm}^{-1}$  in Figure 4.17 that is evidence of the  $\text{SO}_3$  stretching of the sulfonic groups. The infrared assignments of polysulfone were illustrated in Table 4.6.

**Table 4.6:** Infrared band of functional group in polysulfone

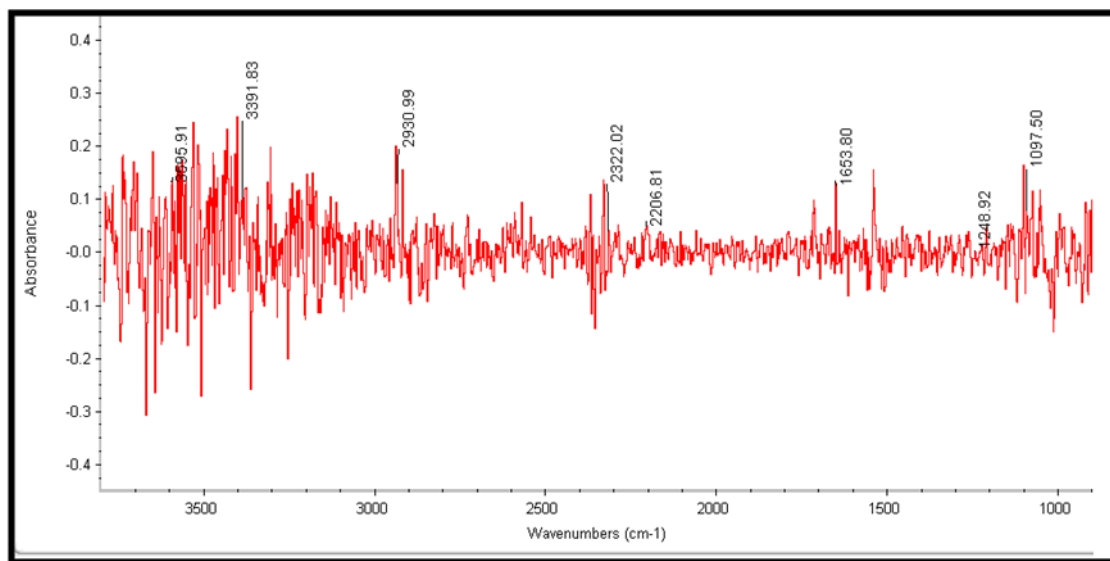
Wave Number ( $\text{cm}^{-1}$ )	Assignments
3600 } 3200 }	O-H stretching vibrations
2980 } 2880 }	Asymmetric and symmetric C-H stretching vibrations involving entire methyl group
1590 } 1485 }	Aromatic C=C stretching
1412	Asymmetric C-H bending deformation of methyl group
1365	Symmetric C-H bending deformation of methyl group
1325 } 1298 }	Doublet resulting from asymmetric O=S=O stretching of sulfone group
1244	Asymmetric C-O-C stretching of aryl ether group
1170	Asymmetric O=S=O stretching of sulfonate group
1150	Symmetric O=S=O stretching of sulfonate group
1107 } 1092 }	Aromatic ring vibrations
1027	Symmetric O=S=O stretching of sulfonate group



**Figure 4.18:** FTIR spectrum of polysulfone flat sheet membrane using N-methyl-2-pyrrolidone, NMP as solvent.



**Figure 4.19:** FTIR spectrum of polysulfone flat sheet membrane using N,N-dimethylacetamide, DMAc as solvent.



**Figure 4.20:** FTIR spectrum of polysulfone flat sheet membrane using N,N-dimethylformamide DMF as solvent.

Figure 4.17 illustrates the stretching band of polysulfone casting solution which made by using NMP, DMAc and DMF respectively. Chemical structure of polysulfone were given in Figure 3.1. The strong absorptions due to the asymmetric stretches of sulfone group in polysulfone molecule were found at round  $1170\text{ cm}^{-1}$  belong to the vibrations of the aromatic  $\text{O}=\text{S}=\text{O}$  in polysulfone molecules.

In contrary, different trends of spectrum were observed when the casting solution prepared by different solvent. There are bands at around  $1107\text{-}1092\text{ cm}^{-1}$  that indicated for the aromatic ring vibrations of PSU/NMP/ $\text{H}_2\text{O}$  as shown as N-methyl-2-pyrrolidone in Figure 3.2. Water absorption effect of the polysulfone membrane samples could be seen clearly in Figure where O-H stretching band of PSU/DMAc/ $\text{H}_2\text{O}$  sample that was detected at frequency around  $3600\text{-}3200\text{ cm}^{-1}$ . Membrane cast from ternary mixture of PSU/DMF/ $\text{H}_2\text{O}$  showed positive attending of asymmetric C-O-C that stretching of aryl ether group at frequency around  $1244\text{ cm}^{-1}$ .

As a conclusion, the highest and positive spectrum at certain peak indicates the polymer backbone is more aligned in the polysulfone asymmetric reaction. The results of FTIR analysis clearly demonstrated the occurrence of each molecular presence in the polysulfone membrane.



## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 CONCLUSIONS**

This chapter presents a brief overview of the result in order to sum up the work and to consolidate the detailed discussions that have been given in the previous chapter.

In the first stage of this study, multi component casting solution formulations that suitable for asymmetric flat sheet membrane for gas separation have been developed. Three different type of solvent was chosen as a solvent to perform the casting solution with fixed the concentration of the component. The fabrication of the asymmetric flat sheet membrane has been discussed in previous chapter. While in the final stage, Scanning Electron Microscopy (SEM) was used to examine the membrane morphology. The result showed the different type of membranes cross-section and membrane surfaces were obtained from different casting solution formulations. The study found the cross section and the surfaces layer was affected by correlation solvent-nonsolvent (water) diffusivity. The mechanisms of chemical structure were investigated by Fourier Transform Infrared (FTIR). There is a trend that seemed to indicate chemical structure of functional group as a different molecular structure in the different solvent.

Based on the results of this study, there is found that high selectivity polysulfone asymmetric flat sheet membrane can be achieved by optimizing the pore sizes factors in membrane formation process. The both mutual affinity between solvent water influencing the permeability and selectivity. Water flux through the membranes

augments pores which may enhance membrane permeability as well as selectivity. N-methyl-2-pyrrolidone showed excellent result compared to the N, N-dimethylacetamide and N, N-dimethylformamide in term of their selectivity.

The selectivity of both gases decrease while their carbon dioxide pressure-normalized flux for decrease and methane pressure-normalized flux increase for feed pressure applied at 1 to 4 bars. Increasing the feed pressure decreasing the selectivity where decrease the pore area inside the membrane. All the membrane type was shown their optimum pressure is during pressure applied at 1 bar. N-methyl-2-pyrrolidone shows the greater selectivity, 7.34 compared to the N,N-dimethylacetamide and N,N-dimethylformamide which their selectivity are 5.57 and 3.75 respectively. Otherwise the performance of carbon dioxide pressure-normalized flux is greater than methane pressure-normalized flux due to their molecular diameter where is 3.3°A and 3.8°A each.

Different type of morphology developed when different types of solvent were used in casting solution. For the cross section, solution containing N-methyl-2-pyrrolidone exhibited larger pores with diameter restrained in a broad range. Therefore, separation process was found to be more successful membrane using NMP compared to DMAc and DMF as solvent based on the membrane morphology. For the membrane surface layer, there is no comparison for the three type of membrane at all. Those membranes show the smooth surface besides the coating membrane. Otherwise, we can make a comparison if included the effect of coated and uncoated membrane.

A rheological study was cried out the investigate the mechanism of chemical structure of the membrane. The FTIR spectrum obviously confirmed the occurrence of polysulfone in the polymer backbone. The stretching band at 1027  $\text{cm}^{-1}$  indicates the proof of the  $\text{SO}_3$  stretching of the sulfonic groups in the membrane structure.

## **5.2 RECOMMENDATIONS**

As a recommendation for future research, further theoretical and practical studies should be extensively carried out in order to investigate and fully comprehend

and progress in a number of aspects of this work. The following are some recommendation that have been identified as a suitable material for flat sheet membrane.

- i. A study on other fabrication parameters of asymmetric flat sheet membrane such as coagulation medium, coagulation temperature, evaporation temperature, air gap length and drying methods must be carried out to further optimize membrane formation process.
- ii. Flat sheet membranes can be casted from other variety ternary casting solution including different of polymer, nonsolvent, coagulation medium and their concentration in order to generalize membrane formation process.
- iii. The permeation test should be continued using gas mixtures. A variety factors can make mixed gases separation results different from those test with only pure gas.
- iv. A comprehensive study on development high performances hollow fiber for gas separation is recommended for future work by using new casting solution which had developed in this study.
- v. Characterization technique of flat sheet membrane should be expanded to include other microscopic methods such Atomic Force Microscopy (AFM), Positron Annihilation Lifetime Spectroscopy (PALS) and Differential Scanning Chromatograph (DSC). AFM is a powerful tool to measures important membrane properties such as pore size, pore distribution of membranes, surface roughness and also the size of macromolar nodules.

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## **APPENDICES**

## **APPENDIX A**

**Permeability and selectivity of polysulfone membrane with different pressure**

Permeability and Selectivity

Dope Formulation: 20% PSU 77% NMP 3% H2O

Type of gas applied: CO2 and CH4

Description: coated

Pressure applied: 1,2,3,4 bar

Volume changes: 10 cm3

Membrane area: 12.568 cm2

Pressure (bar)	Membrane	Time (s)		Permeability CO2 cm/s.cmHg	Permeability CH4 cm/s.cmHg	Pressure normalized flux of CO2 (GPU)	Pressure normalized flux of CH4 (GPU)	Average Pressure	Average Pressure	Average Permeability CO2	Average Permeability CH4	Average Selectivity	Selectivity
		CO2	CH4					Normalized flux of CO2 (GPU)	Normalized flux of CH4 (GPU)				
1	1	81	334	0.000130975	3.17633E-05	130.9747402	31.7633352	266.9846211	36.35243197	0.000266985	3.63524E-05	7.344340026	4.12345679
	2	43	156	0.00024672	6.80061E-05	246.7198595	68.00611511						3.627906977
	3	22	810	0.000482225	1.30975E-05	482.2251799	13.09747402						36.81818182
	4	51	326	0.000208019	3.25428E-05	208.018705	32.54280355						6.392156863
2	1	51	50	0.000104009	0.00010609	104.0093525	106.0895396	240.1110645	83.55328746	0.000240111	8.35533E-05	2.873747662	0.980392157
	2	20	75	0.000265224	7.07264E-05	265.2238489	70.72635971						3.75
	3	17	378	0.000312028	1.4033E-05	312.0280576	14.03300788						22.23529412
	4	19	37	0.000279183	0.000143364	279.1829989	143.3642427						1.947368421
3	1	30	21	0.000117877	0.000168396	117.8772662	168.3960946	236.2807702	111.7769918	0.000236281	0.000111777	2.113858732	0.7
	2	16	64	0.00022102	5.5255E-05	221.0198741	55.25496853						4
	3	14	131	0.000252594	2.69948E-05	252.5941418	26.99479378						9.357142857
	4	10	18	0.000353632	0.000196462	353.6317986	196.4621103						1.8
4	1	22	13	0.000120556	0.000204018	120.556295	204.0183453	189.8761646	137.6705074	0.000189876	0.000137671	1.379207269	0.590909091
	2	12	42	0.00022102	6.31485E-05	221.0198741	63.14853546						3.5
	3	11	145	0.000241113	1.82913E-05	241.1125899	18.29129993						13.18181818
	4	15	10	0.000176816	0.000265224	176.8158993	265.2238489						0.666666667

Permeability and Selectivity

Dope Formulation: 20% PSU 77% DMAc 3% H2O

Type of gas applied: CO2 and CH4

Description: coated

Pressure applied: 1,2,3,4 bar

Volume changes: 10 cm<sup>3</sup>Membrane area: 12.568 cm<sup>2</sup>

Pressure (bar)	Membrane	Time (s)		Permeability CO2 cm/s.cmHg	Permeability CH4 cm/s.cmHg	Pressure normalized flux of CO2 (GPU)	Pressure normalized flux of CH4 (GPU)	Average Pressure	Average Pressure	Average Permeability CO2	Average Permeability CH4	Selectivity	Selectivity
		CO2	CH4					Normalized flux of CO2 (GPU)	Normalized flux of CH4 (GPU)				
1	1	44	294	0.000241113	3.60849E-05	241.1125899	36.08487741	178.2842269	32.03450552	0.000178284	3.20345E-05	5.565380955	6.681818182
	2	100	453	0.00010609	2.34193E-05	106.0895396	23.41932441						4.53
	3	59	290	0.000179813	3.65826E-05	179.8127789	36.58259985						4.915254237
	4	57	331	0.000186122	3.20512E-05	186.1219992	32.05122041						5.807017544
2	1	29	98	0.000182913	5.41273E-05	182.9129993	54.12731611	128.3989492	54.57791095	0.000128399	5.45779E-05	2.35258087	3.379310345
	2	71	104	7.47109E-05	5.10046E-05	74.71094336	51.00458633						1.464788732
	3	40	86	0.000132612	6.168E-05	132.6119245	61.67996487						2.15
	4	43	103	0.00012336	5.14998E-05	123.3599297	51.49977649						2.395348837
3	<u>1</u>	24	50	0.000147347	7.07264E-05	147.3465827	70.72635971	126.8392553	67.85790941	0.000126839	6.78579E-05	1.869188963	2.083333333
	<u>2</u>	22	45	0.000160742	7.85848E-05	160.7417266	78.58484413						2.045454545
	<u>3</u>	35	67	0.000101038	5.27809E-05	101.0376567	52.78086546						1.914285714
	<u>4</u>	36	51	9.82311E-05	6.93396E-05	98.23105516	69.33956835						1.416666667
4	1	16	27	0.000165765	9.82311E-05	165.7649056	98.23105516	123.76099	82.82003024	0.000123761	8.282E-05	1.49433645	1.6875
	2	19	38	0.000139591	6.97957E-05	139.5914994	69.79574972						2
	3	27	32	9.82311E-05	8.28825E-05	98.23105516	82.88245279						1.185185185
	4	29	33	9.14565E-05	8.03709E-05	91.45649963	80.37086331						1.137931034

Pressure applied: 1,2,3,4 bar

Volume changes: 10 cm<sup>3</sup>Membrane area: 12.568 cm<sup>2</sup>

Pressure (bar)	Membrane	Time (s)		Permeability CO2 cm/s.cmHg	Permeability CH4 cm/s.cmHg	Pressure normalized flux of CO2 (GPU)	Pressure normalized flux of CH4 (GPU)	Average Pressure	Average Pressure	Average Permeability CO2	Average Permeability CH4	Selectivity	Selectivity
		CO2	CH4					Normalized flux of CO2 (GPU)	Normalized flux of CH4 (GPU)				
1	1	150	301	7.07264E-05	3.52457E-05	70.72635971	35.24569421	98.36591674	26.23350495	9.83659E-05	2.62335E-05	3.749629222	2.006666667
	2	47	304	0.000225722	3.48979E-05	225.7224246	34.89787486						6.468085106
	3	227	643	4.67355E-05	1.64992E-05	46.73547999	16.49915079						2.832599119
	4	211	580	5.02794E-05	1.82913E-05	50.27940264	18.29129993						2.748815166
2	1	91	135	5.8291E-05	3.92924E-05	58.29095581	39.29242206	72.06962466	32.12575792	7.20696E-05	3.21258E-05	2.243359513	1.483516484
	2	35	118	0.000151556	4.49532E-05	151.5564851	44.95319473						3.371428571
	3	146	281	3.6332E-05	1.88771E-05	36.3320341	18.87714227						1.924657534
	4	126	209	4.2099E-05	2.53803E-05	42.09902364	25.38027262						1.658730159
3	<u>1</u>	57	90	6.20407E-05	3.92924E-05	62.04066642	39.29242206	64.6077234	34.40756833	6.46077E-05	3.44076E-05	1.877718378	1.578947368
	<u>2</u>	33	73	0.000107161	4.84427E-05	107.1611511	48.44271213						2.212121212
	<u>3</u>	95	162	3.72244E-05	2.18291E-05	37.22439985	21.82912337						1.705263158
	<u>4</u>	68	126	5.20047E-05	2.8066E-05	52.00467626	28.06601576						1.852941176
4	1	34	69	7.8007E-05	3.84382E-05	78.00701439	38.43823898	63.32346134	34.24677512	6.33235E-05	3.42468E-05	1.849034285	2.029411765
	2	30	50	8.84079E-05	5.30448E-05	88.40794964	53.04476979						1.666666667
	3	72	136	3.68366E-05	1.95018E-05	36.83664568	19.5017536						1.888888889
	4	53	102	5.00422E-05	2.60023E-05	50.04223565	26.00233813						1.924528302

## **APPENDIX B**

**Experimental equipment work procedure on studying of effect of different type of solvents on asymmetric polysulfone membrane for CO<sub>2</sub>/CH<sub>4</sub> separation**



## APPENDIX B

(i) Preparation casting solution



(ii) Ultrasonic bath to remove microbubble



(iii) Membrane casting



(iv) Coagulation medium (water – 1 day and methanol – 1 day)



(v) Cut a membrane after drying in 2 days with ambient condition (1 atm and 30°C)



(vi) Coating with solution of 3% PDMS and 97% n-hexane



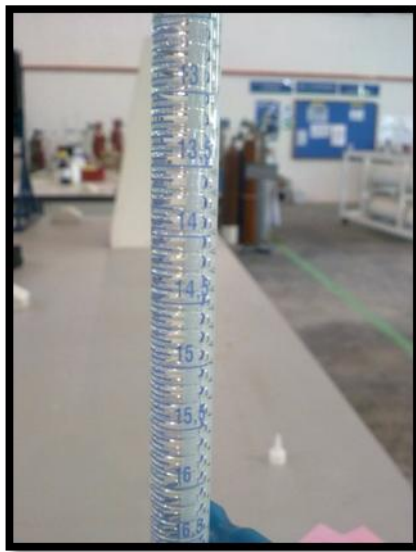
(vii) Drying the membrane coating at ambient condition or 30°C in vacuum oven



(viii) Gas permeation test



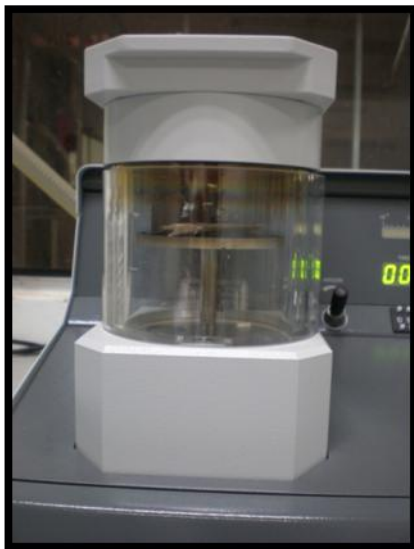
(ix) Bubble flow meter



(x) Liquid nitrogen



(xi) Coating the membrane sample with platinum



(xii) Characterize the structure of the membrane using SEM



(xiii) Characterize the functional group of polysulfone using FTIR



PARAMETER OF THIS STUDY:

- a) N-methyl-2-pyrrolidone (NMP)
- b) N,N-dimethylacetamide (DMAc)
- c) N,N-dimethylformamide (DMF)

