EFFECT OF DIFFERENT TYPE OF POLYMER CONCENTRATION
ON ASYMMETRIC POLYSULFONE MEMBRANE
FOR CO$_2$/CH$_4$ SEPARATION

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To Mak and arwah Ayah
"I will love you forever"
To my siblings: Kak Ini, Kak Ngah, Kak Syani, Kak Soh, Abe and Imah
"Thanks for Your Supporting"
To my Amir, Amin, and Shamil
"You're my Heroes forever"

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ABSTRACT

The objective of this study is to developed polysulfone (PSU) asymmetric membrane for gas separation and to identify the concentration of polysulfone in dope solution to produce high selectivity membrane for CO_2/CH_4 gas separation. Polysulfone was selected as the polymer material in this research since it is glassy type polymer that exhibit good mechanical properties compare to others while 1-Methyl-2-Pyrrolidone (NMP) is chosen as the solvent because it is low toxicity and completely miscible with water, organic acid and alcohol. Polysulfone asymmetric membrane was prepared by mixing a dope, where polysulfone polymer was mixed with 1-Methyl-2-Pyrrolidone (NMP). Three sample of solution was prepared with different type of concentration of polysulfone polymer which is 20 wt%, 25 wt% and 30 wt% respectively. Before perform gas permeation test, polysulfone membrane was coating with PDMS and n-hexane with the composition 3 wt% and 97 wt% respectively. Permeation test was carried out by using single gas permeation test by testing gas carbon dioxide (CO_2) and methane (CH_4). The membranes were characterized by using Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Through SEM analysis, the morphology and structure of the membrane at 20 wt% concentration of polysulfone shows structural pores using 1000 magnification. Membranes with 30 wt% of PSU exhibits the most selective membrane with selectivity about 2.619 while membrane with 20 wt% shows the lowest selectivity that is 1.22. This is because the increasing polysulfone polymer concentration resulted a denser and thicker skin layer of membrane so that the membrane with high polysulfone concentration become more selective but less permeability to the gas separation.

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan membrane asimetrik polysulfone untuk tujuan pengasingan gas CO_2/CH_4 dan untuk mengenal pasti kepekatan polymer yang dapat menunjukkan ciri-ciri selektif yang paling baik. Polysulfone dipilih sebagai material untuk polymer dalam penghasilan membrane kerana ia menunjukkan ciri-ciri mekanikal yang baik berbanding polymer lain manakala 1-Methyl-2-Pyrrolidone (NMP) dipilih sebagai pelarut kerana ianya kurang toksid dan dapat terlarut sepenuhnya bila bergabung dengan air. Membrane asimetrik Polysulfone disediakan dengan mencampurkan larutan dope, dimana polysulfone dicampur bersama 1-Methyl-2-Pyrrolidone (NMP). Tiga jenis sampel untuk larutan disediakan pada kepekatan polymer yang berbeza iaitu masing masing 20 wt%, 25 wt% and 30 wt% . Sebelum menjalankan ujian penyerapan gas, polysulfone membrane dilapisi menggunakan PDMS and n-hexane dengan kandungan material masing-masing 3 wt% and 97 wt%. Ujian penyerapan gas dijalankan menggunakan alat ujian penyerapan gas dengan menguji gas karbon dioksida (CO_2) dan methane (CH_4). Kesemua membrane menjalani ujian menggunakan Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) untuk melihat struktur membrane. Melalui analysis SEM, struktur membrane pada kepekatan polysulfone 20 wt% menunjukkan struktur kaviti yang besar pada magnifikasi 1000. Membrane dengan kepekatan polymer 30 wt% menunjukkan ciri yang paling selektif dengan nilai selektiviti 2.619 manakala membrane dengan kepekatan 20 wt% menunjukkan selektiviti paling rendah iaitu pada 1.22. Hal ini kerana penambahan kepekatan polymer menyebabkan struktur membrane menjadi semakin padat dan tebal dan menyebabkan membrane menjadi semakin selektif.

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CHAPTER 1

INTRODUCTION

1.1   BACKGROUND OF STUDY

In natural gas processing, it involved the separation of some of the components contain in natural gas such as water, acid gas and heavy carbon in order to satisfy the commercial specifications. Carbon dioxide (CO_2) which falls into category of acid gases is commonly found in natural gas stream at level as high as 80 percent. In combination with water, it is highly corrosive and rapidly destroys pipeline and equipment unless it is particularly removed or expensive construction materials are used. Carbon dioxide reduces the heating value of natural gas. In LNG plant, carbon dioxide must be removed to prevent freezing in low temperature chiller.

There are various types of acid gas removal process such as solvent absorption, solid adsorption, direct conversion, cryogenic fractionators and membranes. This research will focus on membranes separation process.

The membrane processes have the some characteristic as the alternative technology. According to Baker (2000), membrane technology is continuity and simplicity process compared to conventional separation technology. Besides, this technology is flexibility in designed because it can be combined with each other and with other separation technologies to meet complex demand in separation technology. The other characteristic of membrane technologies that give significant advantages to the industries is the compactness of it design that suitable for the plant that limited in area.

At the moment, the most widely used membrane materials for gas separation are polymers. Polysulfone (PSU) was chosen as the polymer for this study since it is used commercially as a gas separation membrane material, and its gas transport properties have been extensively studied (Ahn *et al*., 2008).

This research will be concentrate about effect of polymer concentration on the development of polysulfone membrane for acid gas removal.

1.2   PROBLEM STATEMENT

The separation of carbon dioxide from methane is one of the important processes in many industrial areas such as natural gas processing, biogas purification, enhanced oil recovery and flue gas treatment. Carbon dioxide in natural gas must be removed because it causes pipe corrosion, reduces the heating value, takes up volume in the pipeline and is able to solidify in cryogenic process. Besides, being a greenhouse gas, the emission of carbon dioxide from the combustion of fossil fuel is a serious concern associated with global climate change. Conventional absorption processes are generally operated in the contactor devices, example, packed and plate columns, which require huge space and high investment cost. In addition, they also suffer from several operational limitations including flooding, entrainment and foaming. Membrane gas permeation process is an alternative separation process for capturing carbon dioxide, but low gas flux and methane loss are the two main problems in gas permeation process. Thus, it is imperative to develop more efficient processes for upgrading low quality gases than presently available ones.

Typically, polymers which are highly permeable to gases have low permselectivity and vice versa. It is hard to find high performances with both selectivity and permeability. Most of membranes selectivity is inversely proportional with permeability (Ridzuan *et al*., 2004). Studies on the relationship between polymer materials and gas separation properties were carried out to understand membrane permeability and selectivity in order to maximize the membrane efficiency and to provide directions for new membranes or new processes. The polymer concentration is one of the significant factors in determining the membrane performances. Different type

of polymer concentration used in the casting solution result in the difference morphology and separation performance in CO_2/CH_4 gas separation. In order to get high purity of methane, so the membrane that exhibit the highest selectivity is needed to achieved the goal.

1.3   OBJECTIVES

The objectives of this study are to develope the asymmetric polysulfone membrane and to identify the concentration of asymmetric polysulfone membrane to produce high selectivity membrane for CO_2/CH_4 gas separation.

1.4   SCOPE OF STUDIES

In order to achieve the set objectives, several scopes of work have been identified.

    a. Study of different polymer concentration to produce asymmetric polysulfone membrane.

    b. Used gas permeation test to test the develop membrane.

    c. Characteristic study of membrane morphology by using Scanning Electron Microscope (SEM).

    d. Identify functional group contains in membrane by using Fourier Transform Infrared Spectroscopy (FTIR).

CHAPTER 2

LITERATURE REVIEW

2.1   MEMBRANE SEPARATION PROCESS

A membrane is a permeable or semi-permeable phase, often a thin polymeric solid, which restricts the motions of certain species. Generally, a membrane is a phase or a group of phase that lies between two different phases, which is physically or chemically distinctive from both of them and which due to its properties and the force field applied (driving force), is able to control the mass transport between these phases (Paul and Yampol, 1994). In simple words, membrane can be defined as a barrier between two fluids, which allows selective transfer of some species through a driving force.

According to Pabby (2008), membranes can be classified as homogeneous or heterogeneous, symmetrical or asymmetrical, and porous or non- porous. Besides, they can be organic or inorganic, liquid or solid. There are three different types of pore size classifications: microporous (dp < 2nm), mesoporous (2nm < dp < 50nm) and macroporous (dp > 50nm) (Mccusker and F. Liebau, 2001).

The historical development of membrane has started at eighteenth century. Membrane technology has been developed from a laboratory technique to a large-scale industrial application. Today membrane technology is applied in a wide range of applications such as in water purification, food industry, dairy, pharmaceutical, textile industry, petrochemical industry and many other applications. Table 2.1 shows some early contributions in the development of membrane.

Table 2.1: Early contributions in the development of membrane (Cardew and Lew, 1994)

Contributions	Membrane Process	Contributors	Years
Observations	Osmosis	Nollet	1748
	Electro osmosis	Reuss, Porret	1816
	Dialysis	Graham	1861
Relations	Diffusion	Fick	1885
	Osmotic pressure	Van't Hoff	1887
	Electrolyte transport	Nernst Planck	1889
Theoretical considerations	Osmotic pressure	Einstein	1905
	Membrane potentials	Henderson	1907
	Membrane equilibrium	Donnan	1911
	Anomalous osmosis	Sollner	1930
	Irreversible thermodynamics	Kedern, Katchalsky	1964
Transport model	Ionic membrane	Teorell	1937
	Pore model	Schmid	1950
	Solution diffusion model	Lonsdale	1965

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 flow of material across a membrane has to be kinectically driven, by the application of either mechanical, chemical or electric work. The driving forces are either pressure, concentration, temperature potential. In many cases the transport rate (permeation) is proportional to the driving force and the membrane can be categorized in terms of an appropriate permeability coefficient. The use of driving force as means of classification is not altogether satisfactory because apparently different membrane

process can be applied for the same separation, for example electrodialysis, reverse osmosis and pervaporation in the desalination of water. All the process use membrane which are micropous in nature.

There are the most simple form of membrane regarding mode of separation and consist of solid matrix with defined pores ranging from 100nm to 50μm in size. Table 2.2 lists the membrane processes and the driving force.

Table 2.2: Membrane separations and materials (Matsuura, 1996)

Process	Application	Driving Force
Microfiltration	Separation of suspended particles.	Hydrostatic pressure
Ultrafiltration	Concentration and purification of solvents from macromolecular solutions.	Hydrostatic pressure
Nanofiltration	Concentration and purification of solvents from medium molecular weight solutes.	Hydrostatic pressure
Membrane distillation	Desalination and concentration of solutions.	Temperature
Electro dialysis	Desalination and deacidification.	Electric potential
Reverse osmosis	Desalination, concentration of low molecular weight solutes.	Hydrostatic pressure
Gas permeation	Gas separation	Hydrostatic pressure Concentration gradient
Pervaporation	Separation of azeotropes and liquid mixtures.	Concentration gradient Vapor pressure
Liquid membranes	Separation of ions and solutes from liquids.	Concentration Reaction

Nowadays, membrane technology is becoming an established part of several industrial processes. The technology is largely applicable in the food industry, in the manufacture of dairy products and in the gas processing industries. Membranes important in water industry and avoid people from suffering kidney disease. The markets of membrane in Asia and South America are growing fast. According to study, hemodialysis/hemofiltration alone had sales of over US 2200 million in 1998.

Reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) had sales over 1.8 billion dollars respectively in 1998. Membranes and modules were sold for US 400 million each year world wide for use in reverse osmosis. Ultrafiltration membranes and modules brought about US 500 million insales in 1998 with an expected growing rate of 10% a year. Sales of microfiltration equipment and membrane is 2.5 billion in 2008. Gas separation accounted for about US 230M. (Nunes *et al*, 2006). Figures 2.1 below shows the membrane and the types module sales according to the application used.
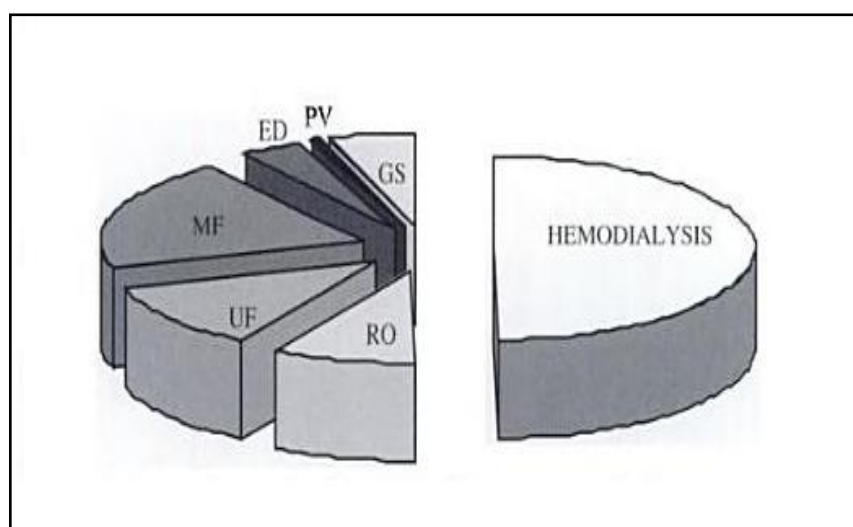
Figure 2 .1: Membrane and Modules sales for different process application
(Nunes *et al*, 2006)

2.2   TYPES OF MEMBRANE PROCESS

2.2.1   Ultrafiltration

Ultrafiltration (UF) is the process that involved the separating of small particles and dissolved molecules from fluids. The process separation is depends on molecular

size. The molecules with the same size can not be separated by ultra filtration. The range of materials from 1K to 1000K molecular weight (MW) is retained by certain ultrafiltration membranes, while salts and water will pass through. Colloidal and particulate matter can also be retained. Materials that is significantly smaller than the pore size rating pass through the filter and can be depyrogenated, clarified and separated from high molecular weight contaminants. Materials larger than the pore size rating are retained by the filter and can be concentrated or separated from low molecular weight contaminants. Usually, the process of ultrafiltration is involved in the proteins separating from buffer components for buffer exchange, desalting, or concentration. Ultrafilters are also practicalin the process of removing or exchange of sugars, non-aqueous solvents, the separation of free from protein-bound ligands, the removal of materials of low molecular weight, or the rapid change of ionic and/or pH environment (Munir, 2006).

2.2.2 Microfiltration

Micro filtration (MF) is the process of removing particles or biological entities in the range of 0.025 μm to 10.0μm by passage through a microporous medium such as a membrane filter. Membrane filters has been used for final filtration. Membrane and depth filters offer certain advantages and limitations. They can complement each other when used together in a microfiltration process system or fabricated device. The retention boundary defined by a membrane filter can also be used as an analytical tool to validate the integrity and efficiency of a system. Microfiltration also can be used in sample preparation to remove intact cells and some cell debris from the lysate. For this type of separation, the membrane pore size cut-offs used are typically in the range of 0.05 μm to 1.0 μm (George, 2009).

2.2.3 Reverse Osmosis

Reverse osmosis (RO) is the process of separating salts and small molecules from low molecular weight solutes (typically less than 100 daltons) at relatively high pressures using membranes with NMWLs of 1 kDa or lower. RO membranes are normally rated by their retention of sodium chloride while ultrafiltration membranes are

characterized according to the molecular weight of retained solutes. Millipore water purification systems employ both reverse osmosis membranes as well as ultrafiltration membranes. Reverse osmosis systems are primarily used to purify tap water to purities that exceed distilled water quality. Ultrafiltration systems ensure that ultrapure water is free from endotoxins as well as nucleases for critical biological research (Munir, 2006). The commercialization of membrane technology and the date commercialize is summarized in table 2.3.

Table 2.3: Approximate date for commercialization of membrane technology for various applications (Perez and Zhang, 1997)

Technology	Industrial application	Commercialization
Electrodialysis	Desalination of Brackish water	1952
Reverse Osmosis	Desalination of Brackish/ sea water	1965
Ultrafiltration	Paint Recovery (Electrocoat)	1965
Electrosynthesis	Chlorine / caustic production	1972
Gas separation	Hydrogen recovery	1979
Pervaporation	Alcohol removal from water	1979
Nanofiltration	Softening of hard water	1990
Microfiltration	Filtration of potable water	1994

2.3   MEMBRANE MODULE

In industrial application of membrane process, large surface areas are required. A practical solution for providing this large surface area is packing the membranes into a small unit call module. The typical of membranes module that largely used for industrial application such as plate and frame module, spiral wound module, tubular module and hollow fiber module.

2.3.1   Plate and Frame Module

This type of module is a simplest structure and easy for membrane replacement. General advantages of this module include low volume hold-up per unit membrane area (attractive for recovering valuable biological) and the ability to process highly viscous solution because of the thin channel height (0.3 – 0.6 mm) (Belfort, 1988). This design provides a configuration which is closest to the flate membranes used in the laboratory. Sets of the two membranes are placed in a sandwich-like with their feed sides facing each other. In each feed and permeate compartment thus obtained a suitable spacer is placed. The numbers of sets needed for a given membrane area furnished with sealings rings and the two end plates then builds up to a plate and frame stack.
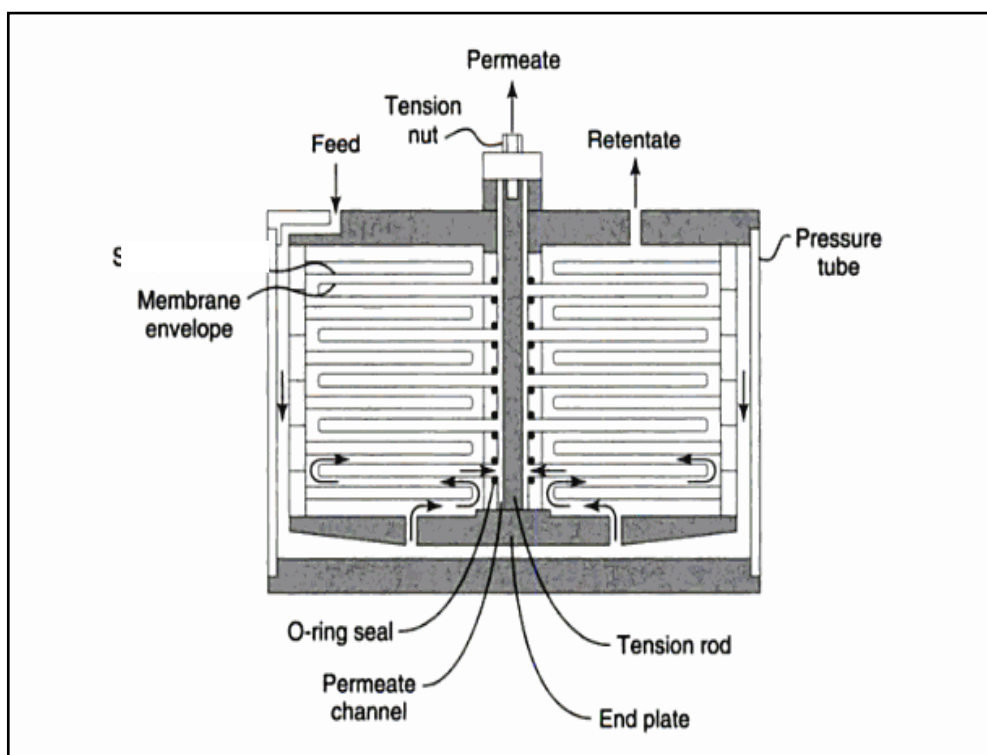
Figure 2.2: Schematic of the plate and frame module (Baker, 2000)

2.3.2   Tubular Module

In this type of module, a number of membrane of tubular shape are encased in a container. The feed solution always flows through the center of the tubes while the permeate flows through the porous supporting tube into the module housing. Ceramic membranes are mostly assembled in such tubular module configurations. Tubular module is convenience membrane replacement and easy cleaning of surface contamination. Besides, the energy consumption is high according to per unit amount of liquid treated.

Figure 2.3:   Tubular module for ultrafiltration

Tubular module commonly used in ultrafiltration application since this module is resistance to membrane fouling and exhibits good hydrodynamics, resulting in lower cost of production. This module is non-self supporting membrane but it have supported by a tube from outside. The flow in tubular membrane is inside out since the location of tubular membrane is inside a tube. Large numbers of tubes are manifolded in series. The feed fed through all the tubes connected in series, typically at high velocity with typical operating pressures of 20 to 80 psi, which is sufficient to maintain turbulent flow. Clean fluid passes through the pores membrane, while suspended particulates remain in the retentive stream. Permeate is removed from each tube and sent to a permeate collection header. The turbulent flow of the retentive stream prevents the cake formation on the inner surface of the tube resulting high flux and longer shelf life (Prasad, 2010).
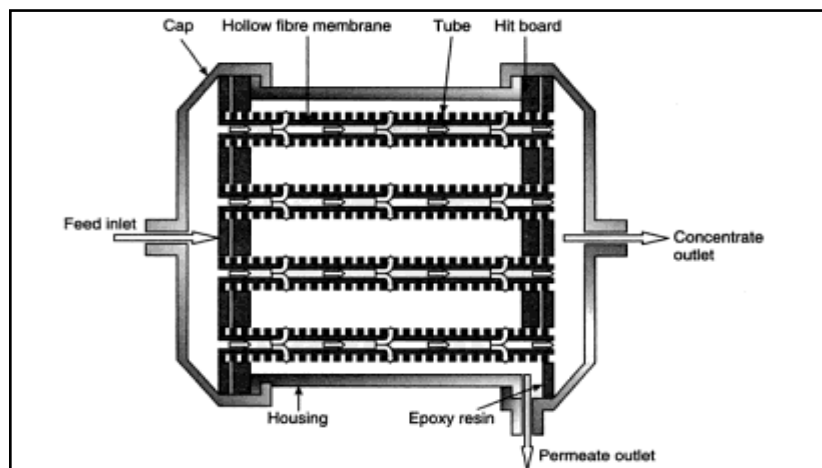
Figure 2.4: Schematic diagram of tubular module

2.3.3   Hollow Fiber Module

Hollow fiber module consists of a large number of fibers assembled together in a module. The free ends of the fibers are often potted with agents such as epoxy resins, polyurethanes, or silicon rubber. The membranes are self supporting for this module. There are two basic types of arrangement for this module :

1) Inside out where the feed solution passes through the bore of the fiber and the permeate is collected on the outside of the fiber.

2) Outside in where the feed solutions enters the module on the shell side of the fibers and the permeate passes into the fiber bore.

The choice between the two concepts is mainly based on some parameters such as operation pressure, pressure drop or type of membrane available. The hollow fiber module is often used when the feed stream is relatively clean, such as in gas separation and pervaporation. It has also been use for desalination process, but treatment is need.
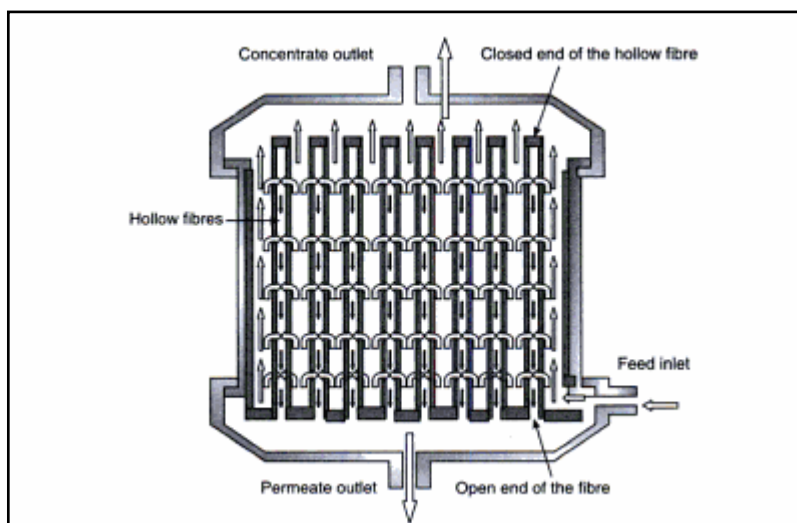
Figure 2.5: Schematic representation of shell side feed type hollow fibre membrane module
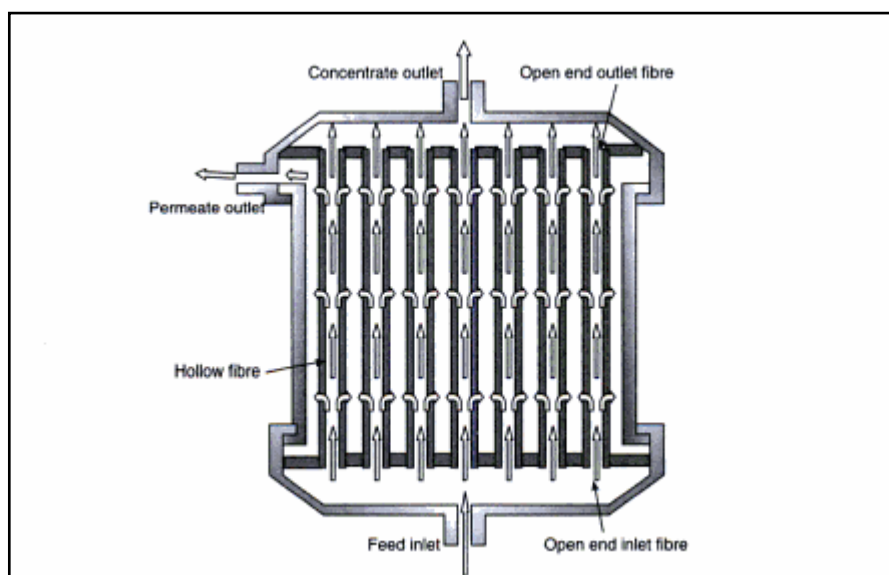
Figure 2.6: Schematic representation of bore side feed type of hollow fibre membrane

module

Hollow fibre membrane modules are available in two basic geometries such as shell side feed design (figure 2.4) and bore side design (figure 2.5). In shell side module, the system is pressurized from the shell side driving permeate through a closed bundle of fibres contained in a pressure vessel, and permeate exits through the open fibre ends. The shell side module is simple, easy and economic. In bore side feed type of hollow fibre module, units are open at both ends for inlet and outlet, and the feed

fluid circulates through the bore of the hollow fibres. The pressure drop inside the hollow fibers is reduced by increasing the diameter of the fine fibers and spinning compared to the shell side feed system (Nath, 2008).

2.4   ADVANTAGES OF MEMBRANE TECHNOLOGY

There are many reasons why numerous fluid separation markets have adopted membrane separation technologies in such a short time. But the most significant reason is that they are more efficient than traditional technologies.

2.4.1   Energy Saving

Energy savings are among the main reasons for selecting membrane technologies. In food processing application, the compact system of membrane can operate at near room temperature, so at the same time, the cooling cost will be reduced. In waste water industries, the usage of membrane will improves wastewater management, aiding the reclamation of salable by-products from waste streams in the food processing businesses. Besides, membrane separation has been recognizing as the energy saving technology and high quality of production.

2.4.2   Clean Energy

The development of advanced technology in membrane separations gives significant effect in the energy and environmental concern. The continuous use of fossil fuels for transportation, as primary energy sources and indiscriminate use of fossil fuel will cause considerable harm to environment. To prevent this from damage, scientists have been actively working on upgrading membranes for fuel cells, which are expected to compete with petroleum-based energy sources particularly in the transportation markets. These enhanced membranes will not only improve hydrogen production for use as a fuel in vehicles, but will also sequester carbon dioxide to reduce the greenhouse

effect and global warming due to burning of fossil fuels. Research in membranes for the energy and environmental markets is particularly intense for fuel cell membranes, hydrogen separation, and carbon dioxide recovery from fossil fuel applications.

2.4.3   The Ability of Connection to Other Processes

To meet the complex demands in fluid separation, membrane technologies can be combined with each other and with other separation technologies. The example of applications that is classified as the challenging application is in the treatment of seawater and brackish water sources and wastewater recovery. Pretreatment with ultra or micro-filtration followed by reverse osmosis is being used for desalination to minimize fouling. In the treatment of wastewater with organic matter, membrane bioreactors are well accepted in many parts of the world.

2.4.4   Good Weight and Space Efficiency

Skid construction can be optimized to the space available, and multiple elements can be inserted into tubes to increase packing density. The space efficiency that is shows in membrane technology is important especially in the limited area of plant such as for offshore environment, where deck area is at a premium, and is the reason why so many new offshore developments have chosen to use membranes for acid gas removal.

2.4.5   Lower Capital Cost

The scope, cost, and time taken for site preparation are minimal since membrane systems are skid mounted, except for the larger pretreatment vessels. Therefore, installation costs are significantly lower than alternative technologies, especially for remote areas. Furthermore, membrane units do not require the additional facilities, such as solvent storage and water treatment, needed by other processes.

2.4.6 Operational Simplicity and High Reliability

Because single-stage membrane systems have no moving parts, they have almost no unscheduled downtime and are extremely simple to operate. They can operate unattended for long periods, provided that external upsets, such as well shutdowns, do not occur. Items in the pretreatment system that could cause downtime, such as filter coalescers, are usually spared so that production can continue while the item is under maintenance. The addition of a recycle compressor adds some complexity to the system but still much less than with a solvent or adsorbent-based technology. Multistage systems can be operated at full capacity as single-stage systems when the recycle compressor is down, although hydrocarbon losses will increase. The start-up, operation, and shutdown of a complex multistage membrane system can be automated so that all important functions are initiated from a control room with minimal staffing (Dortmundt and Doshi, 1999).

2.47 Lower Operating Costs

The only major operating cost for single-stage membrane systems is membrane replacement. This cost is significantly lower than the solvent replacement and energy costs associated with traditional technologies. The improvements in membrane and pretreatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors are usually comparable to those for traditional technologies.

2.4.8 Deferred Capital Investment

Often, contracted sales-gas flow rates increase over time, as more wells are brought on-line. With traditional technologies, the system design needs to take this later production into account immediately, and so the majority of the equipment is installed before it is even needed. The modular nature of membrane systems means that only the membranes that are needed at start-up need be installed. The rest can be added, either into existing tubes or in new skids, only when they are required. Even on offshore

platforms, where all space requirements must be accounted for, space can be left for expansion skids rather than having to install them at the start of the project (Dortmundt and Doshi, 1999).

2.5 MEMBRANE IN GAS SEPARATION

2.5.1 History and Introduction

The study of gas separation has a long history and it becomes a major industrial application of membrane technology during the past 20 years. The study of membrane started with the first description of the solution diffusion model by Thomas Graham and led to Graham's law of diffusion theory. In the 1940s, the other researcher comes out with the modern theories of gas permeation. Next, the development of high flux anisotropic membranes and large surface area membrane modules for reverse osmosis applications in the late 1960s provided the basis for modern membrane gas separation technology.
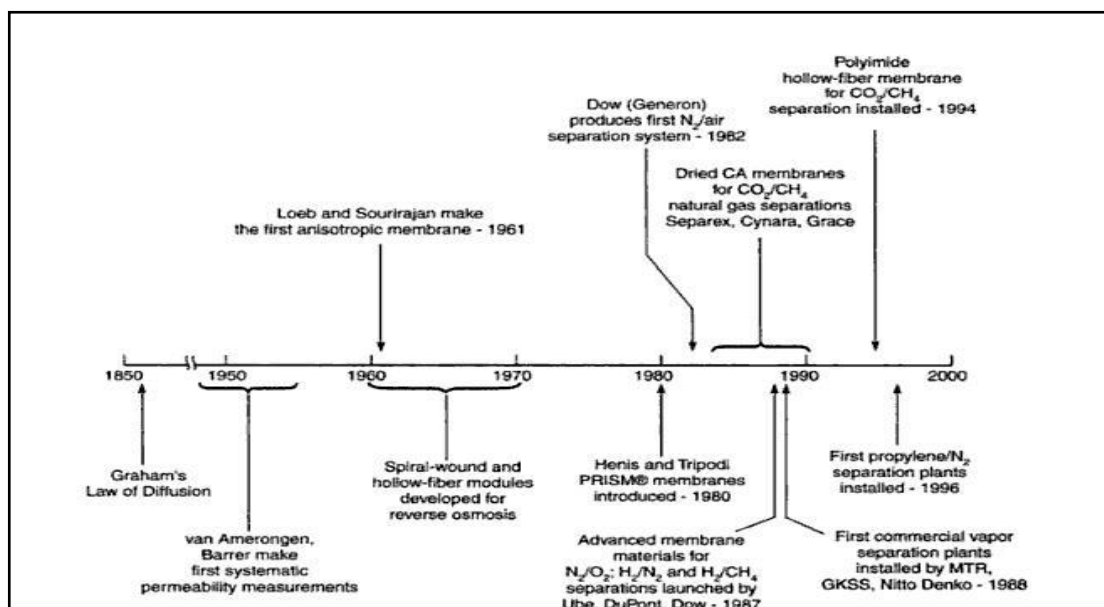
Figure 2.7: Milestone in the development of membrane for gas separation (Baker, 2000)

The separation of carbon dioxide from methane is one of the important processes in many industrial areas such as natural gas processing, biogas purification, enhanced oil recovery and flue gas treatment. Carbon dioxide in natural gas must be removed because it causes pipe corrosion, reduces the heating value, takes up volume in the pipeline and is able to solidify in cryogenic process. Besides, being a greenhouse gas, the emission of carbon dioxide from the combustion of fossil fuel is a serious concern associated with global climate change. Figure 2.7 shows the milestone in the development of membrane for gas separation.

Table 2.4: Applications of the membrane for gas separation in industries

Types of Industries	Applications
Oil refinery industries	• Hydrogen recovery • Hydrocarbon recovery from gas streams • Sour gas sweetening
Gas industries	• Sour gas sweetening • Natural gas drying, hydrocarbon and dew point adjustment Helium separation • Separation of nitrogen from natural gas
Petrochemical industries	• Hydrogen recovery • Monomer recovery (in polymerization processes) • Separation of nitrogen from air

2.5.2 Permeability and selectivity

The performance or efficiency of membranes in gas separation is determined by selectivity and the flux through membrane. The flux or the permeation rate is defined as the volume flowing through the membrane per unit area and time. The selectivity of a membrane towards a mixture is generally expressed by retention (R) or the separation factor (α). Selectivity can be considered for two phase which is solute and particulates in liquids and gases; retention is the fraction of solute in the feed retained by the membrane. For mixtures of miscible liquids and gases, selectivity is the separation factor that is the ratio of the concentration in the permeate divided by that in the feed for two components (scott, 1996)

Membrane with higher permeability leads to higher productivity and lower capital cost, whereas membrane with higher selectivity leads to more efficient separations, higher recovery and lower power cost. So, membrane that simultaneously posses high values of selectivity and permeability would lead to the most economical gas separation process.

Membrane can be characterized by permeation experiments and morphological analysis. According to Chakrabarty (2007), the morphology of the prepared membrane can be investigated by microscopic observations and are characterized in terms of pure water flux, equilibrium water content, compaction factor, hydraulic resistance and permeate flux. Two common techniques that have been used to characterized membrane are gas permeation test and scanning electron microscope (SEM).

2.5.2.1 Gas Permeation Test

Gas permeation test is performed with a permeation cell by using pure gases such as hydrogen and nitrogen. Usually an experiment is carried out at ambient temperature (30ºC). Gas permeation rate is measured by a soap flow meter. Gas permeation rate can be calculated using this formula

$$\frac{P}{l} = \frac{Qi}{A\Delta p} \qquad (2.1)$$

Where $\frac{P}{l}$ is defined as pressure normalized flux or permeability for gas *i*. The common unit of pressure normalized gas flux is GPU (1 GPU= 1 x 10^{-6} cm³ (STP) cm/cm² s

cmHg). Qi is volumetric flow rate of gas i, Δp is the pressure difference across membrane, A is membrane surface area and l is membrane skin thickness.
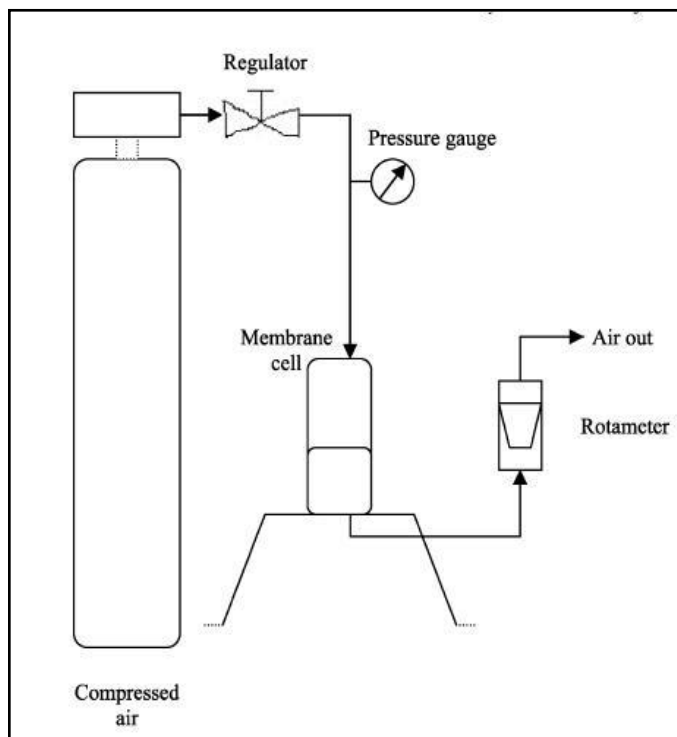
Figure 2.8: Schematic diagram of gas permeation test set up.

2.5.2.2   Scanning Electron Microscope

Scanning electron microscope is used to examine membrane structure and morphology. SEM technique is important because it gives us the information regarding the numbers of pores in different pore size range. SEM stands for scanning electron microscope. The SEM is a microscope that uses electrons instead of light to form an image. Since their development in the early 1950's, scanning electron microscopes have developed new areas of study in the medical and physical science communities. The SEM has allowed researchers to examine a much bigger variety of specimens. The scanning electron microscope has many advantages over traditional microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the

degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today. The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample.
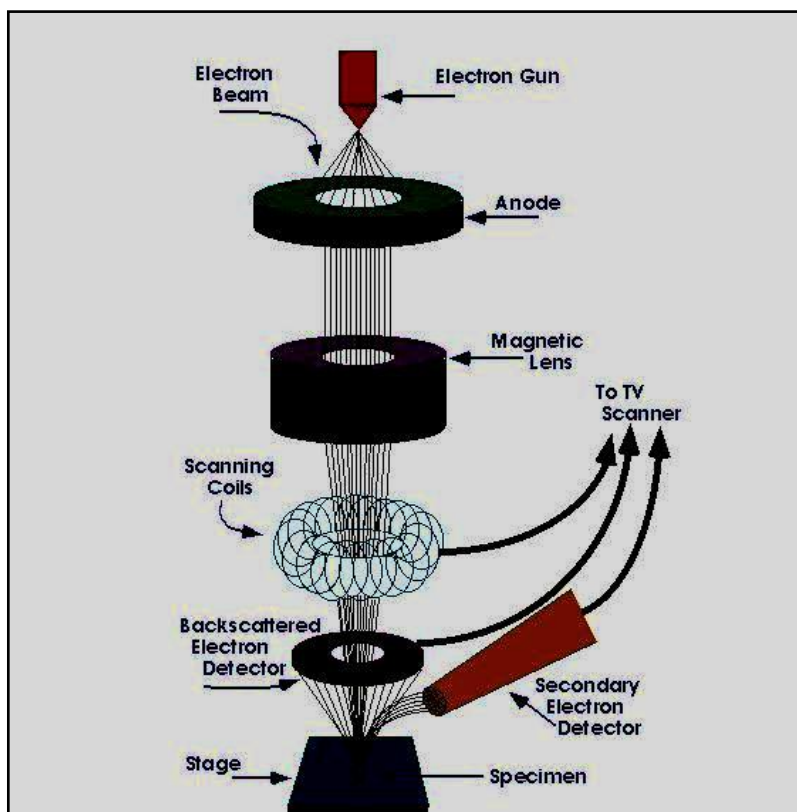
Figure 2.9: Schematic diagram of Scanning Electron Microscope

2.5.2.3   Fourier Transform Infrared (FTIR)

FTIR is the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

2.5.3 Polymer as Membrane Material

Polymer is one of the important materials for gas separation membranes. Polymers exhibit good performances for gas selectivity and easily process into membrane. Polymers are high molecular weight components built up from a number of basic unit, the monomers. The number of structural unit linked together to form the long chain molecule is defined as the degree of polymerization. The molecular weight of a long chain molecule is dependent on the degree of polymerization and on the molecular weight of the basic unit, the monomer. The polymers can be linear or branched. It is also possible to connect two or more chains to each other by means of crosslinks. One characteristics is that the polymer becomes insolubles.

Polymer can be divided into two categories which is rubbery and glassy polymers. Some rubbery polymers are among the most permeable polymers known. However, the true is glassy polymers are more permeable than rubbery polymer (Suzana, 2006). Glassy polymer, compared to rubbery polymer are much more selective, much more mechanically and thermally stable than rubbery polymers, although the permeability of glassy polymers of interest are about two or three orders of magnitude lower than that of rubbery polymers. The low permeability of glassy polymers can, however be compensated by improved membrane fabrication techniques to reduce the membrane thickness.

Polysulfone is one type of glassy polymer. For this research, polysulfone has been selected as polymer for membrane material. Normally, polysulfone can be synthesized by substitutions on the phenylene rings of the phenol in combination with replacing the isopropylidene unit (bisphenol connector group) with another group.
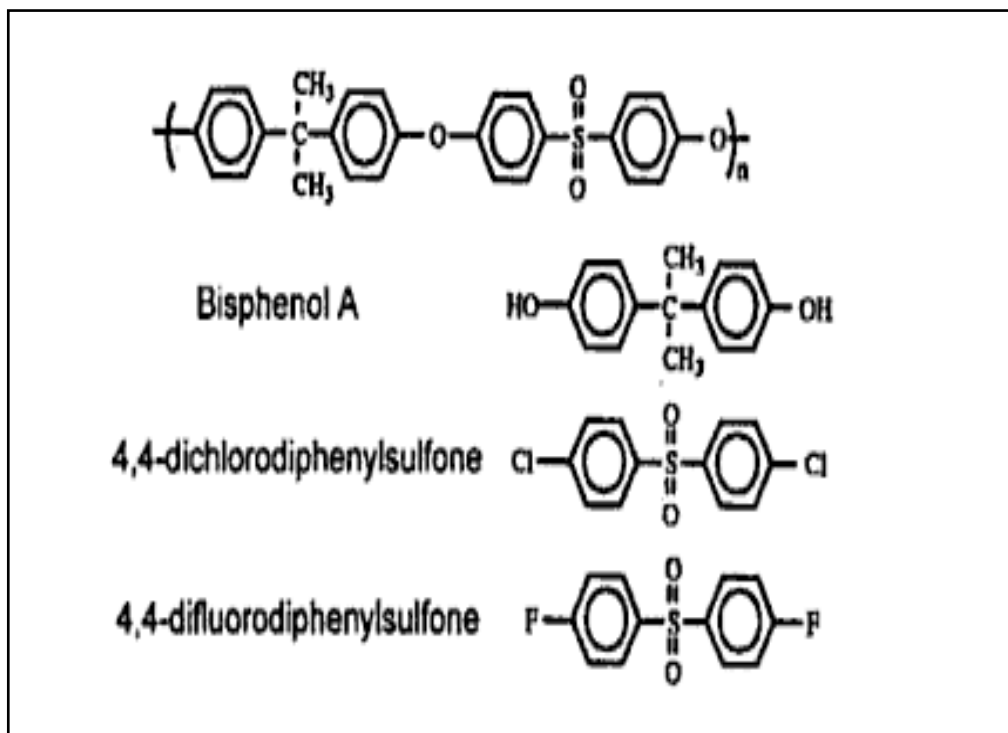
Figure 2.10: Structure of polysulfone and raw material (Tanabe, 1999)

2.6 ASYMMETRIC MEMBRANE

Asymmetric membrane is membranes that consist of an extremely thin nonporous layer mounted on a much thicker and highly porous layer of the same material as shows in figure 2.11. The nonporous layer meets the requirements of the ideal membrane, that is, it is highly selective and also thin. Figure 2.12 shows the SEM images of the asymmetric membrane. The porous layer provides mechanical support and allows the free flow of compounds that permeate through the nonporous layer (Nath, 2004).
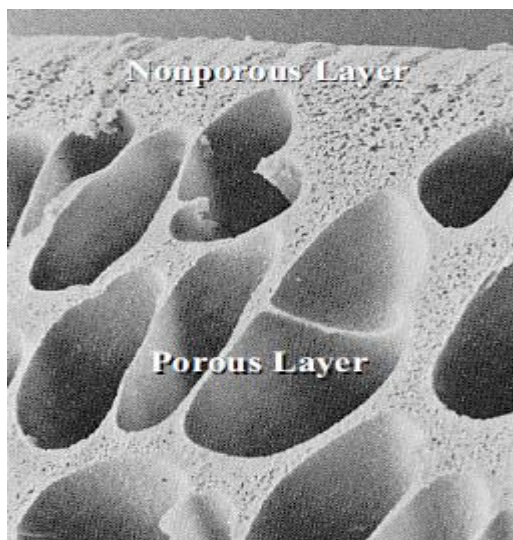
Figure 2.11: Asymmetric membrane structure consist of porous and nonporous layer structure

Figure 2.12: SEM image of an asymmetric polysulfone membrane by solution casting method

Asymmetric gas separation membranes were prepared by a dry/wet phase inversion process. There are three components which is polymer, solvent and non solvent additive that will form membrane casting solution and the coagulant is

introduced into the coagulation bath only during the membrane making process. Figure 2.13 shows the step involved in preparations of dry/wet phase inversion.
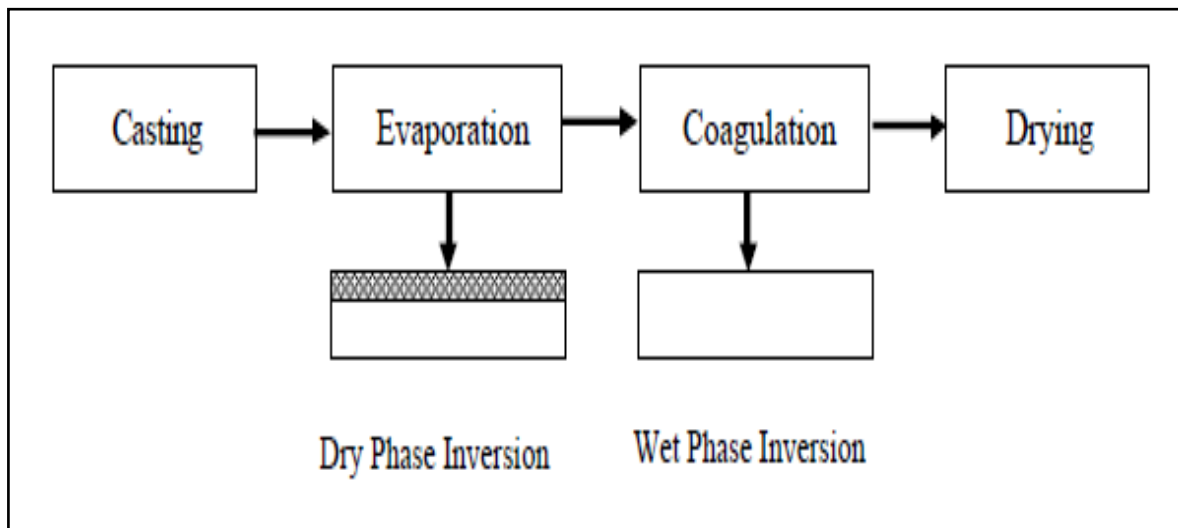
Figure 2.13: Step on preparations of dry/wet phase inversion

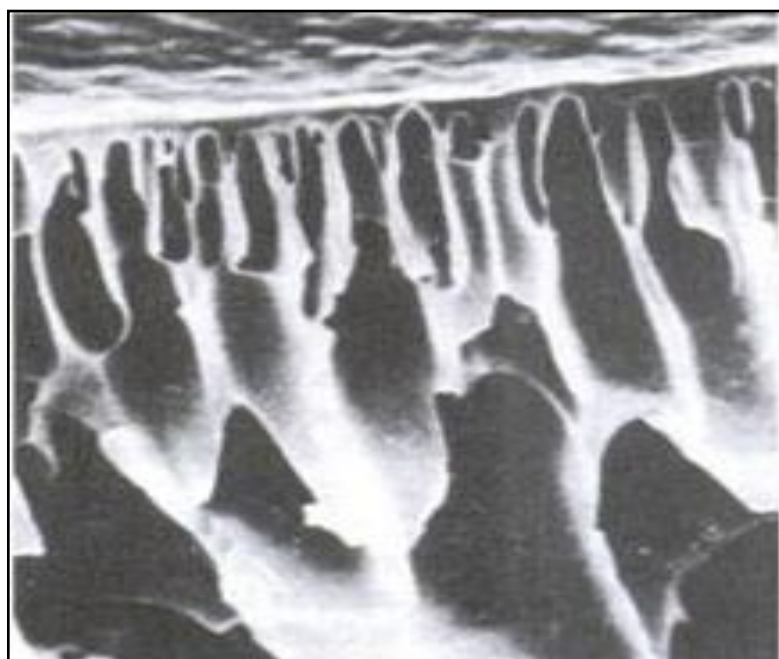The phase inversion process is widely use in the preparation of asymmetric membrane. Phase inversion occurs by bringing the initially thermodynamically stable polymer solution to an unstable state by solvent/non solvent exchange during the coagulation step. The introduction of an evaporation step before immersion in a nonsolvent bath (dry wet phase inversion) seems to be a logical way to prepare defect free asymmetric membranes. The feature of this process is to combine a volatile bad solvent with a non volatile good solvent as solvent system. Both are solvents for the polymer but have quite a different affinity to the nonsolvent, water. The bad solvent has a low affinity for water as can be expressed by a high excess free enthalpy of mixing whereas the good solvent has high affinity for water and a low or sometimes even a negative excess free enthalpy of mixing (Mulder, 1997).

Paul and Yampol (1994) have suggested that the ideal of asymmetric membranes for gas separation must meet the following requirement

1. The selective layer should be defect-free so that gas transport takes places exclusively by solution/ diffusion, not by poorly selective flow through pores.
2. The selective skin layer should be as thin as possib le to maximize the gas fluxes.

3. The supporting substructure should not contribute any resistant to gas transport.

4. The substructure should provide sufficient mechanical strength to support the delicate selective layer in higher pressure operation.

2.6.1   Solution Diffusion Mechanism

This mechanism applies to reverse osmosis, pervaporation and gas permeation in polymer films (Baker, 2000). The movement of any species across the membranes is caused by one or more driving forces. This driving force arises from a gradient of chemical potential or electrical potential. A gradient in chemical potential may due to the concentration gradient or pressure gradient or both. Solution-diffusion separation is based on both solubility and mobility factors. Diffusivity selectivity favors the smallest molecule. Solubility selectivity favors the most condensable molecule. The difference in pressure-normalized flux exhibited by a polymer membrane to different gasses can serve as the basis for separating the components of a gaseous mixture (Ridzuan et al., 2004). The permeation of a polymer membrane by gas takes place in three steps.

> i. The dissolution of the gas at the membrane interface
> ii. The diffusion of the gas through the membrane
> iii. The elution of the gas at the opposite interface.

The diffusion can be defined in terms of a concentration driving force by Fick's first law. Fick's law describes the relation between flow of matter and concentration gradient with the constant of proportionality as the diffusion coefficient.

Fick's law, shown below, is widely used to approximate the solution-diffusion process:

$$J = \frac{k \times D \times \Delta\rho}{\ell}$$

(2.2)

J   is the membrane flux of CO_2, that is, the molar flow of CO_2 through the membrane per unit

area of membrane.

k is the solubility of CO_2 in the membrane.

D   is the diffusion coefficient of CO2 through the membrane.

Δρ   is the partial pressure difference of CO2 between the feed (high pressure) and permeate (low pressure) side of the membrane.

l is the membrane thickness.

To simplify matters further, the solubility and diffusion coefficients are usually combined into a new variable called *permeability* (P). Fick's law can therefore be split into two portions: a membrane-dependent portion (P/l) and a process-dependent portion (Δp). To achieve a high flux, the correct membrane material and the correct processing conditions are needed. P/l is not a constant; it is sensitive to a variety of operating conditions such as temperature and pressure. (Dortmunt and Doshi, 1999)

2.7   INFLUENCE OF VARIOUS PARAMETERS ON MEMBRANE PERFORMANCE

There are several factors or parameters that have been identified in influencing membrane performance such as type of solvent used, type of coagulation bath, type of drying membrane and different type of polymer concentration. Each parameter has significant advantages in determining the performance of membrane. In this research, different type of polymer concentration has been highlight as the parameter that needs to be study.

Polymer concentration has been identified as one of the most influential parameter in determining membrane performance. Previously, there are several studies on the polymer concentration to investigate the effect of concentration of polymer on performance of membrane. Ridzuan et. al, (2004) has study the effect of polymer concentration on development of asymmetric polyethersulfone membrane. The study has reported that, the increasing of polymer concentration in casting solution formed a dense and thicker skin layer, resulting in a more selective but less productive asymmetric membrane for gas separation. The studies also investigate on the effect of coated and uncoated membranes at different polymer concentration and reported that all of the uncoated membrane exhibited higher pressure normalized flux but less of selectivity.

Ismail et al, 2004 also has studying the effect of polymer concentration on membrane properties and structures. The study also reported the same point, the increasing polymer concentration resulted a denser and thicker skin layer of membrane. So it will promote more selective but less productive asymmetric membrane for gas separation process. Besides, when the concentration polymer increased the viscosities of the solution are also increased. Increasing the polymer concentration of casting solution caused a reduction of coagulation value, due to a stronger interaction between solvent and polymer (larger solubility parameter difference between solvent and polymer) and a greater interaction of non solvent and polymer that decreased dissolving power of solvent for polymer. Furthermore, casting solution with higher polymer concentration also exhibited a greater interaction of solvent and non solvent (larger solubility parameter difference between solvent and coagulant), suggesting a retarded diffusional exchange between solvents and nonsolvents.

CHAPTER 3
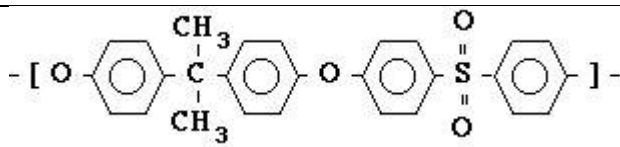
METHODOLOGY

3.1   MATERIALS

3.1.1   Polysulfone

Polysulfone, PSU (average weight about 15000 Dalton) is selected as membrane material in this study. PSU is a glassy type polymer that has higher selectivity and good mechanical properties compare to rubbery type polymer (Ahn, *et al*., 2008). Table 3.1 listed the properties of polysulfone.

Table 3.1: Properties of Polysulfone

Properties	Values
Molecular formula	$C_{27}H_{22}O_4S$
Glass transition temperature	185 °C
Molecular Weight of repeat unit	442.52 g/mol
Repeat Unit	

3.1.2   1-Methyl-2-Pyrrolidone (NMP)

1-methyl-2-pyrrolidone (NMP) is the solvent. NMP is chosen as the solvent used since it has a high solvent power for polymer, low toxicity and completely miscible with water, alcohols and organic acids. Table 3.2 shows the properties of NMP.

Table 3.2: Properties of NMP

Properties	Value
Molecular formula	C_5H_9NO
Molar mass	99.13 g/mol
Melting point	-24°C
Boiling point	202-204°C

3.1.3   Physical Properties of Non-Solvent Additives and Coagulation Bath

The non solvent additives use in this study is distilled water while tab water is used as the coagulation bath medium. Table 3.3 below shows the properties of non solvent additive and coagulation bath medium.

Table 3.3: The physical properties of non solvent additive and coagulation bath

Component	Molecular weight (g/mol)	Boiling Point (°C)	Melting Point (°C)	Density (kg/m³)
Non-solvent additives				
Distilled water	18.02	100	0	998
Coagulation bath				
Tab water	18.02	100	0	998

3.2   RESEARCH DESIGN
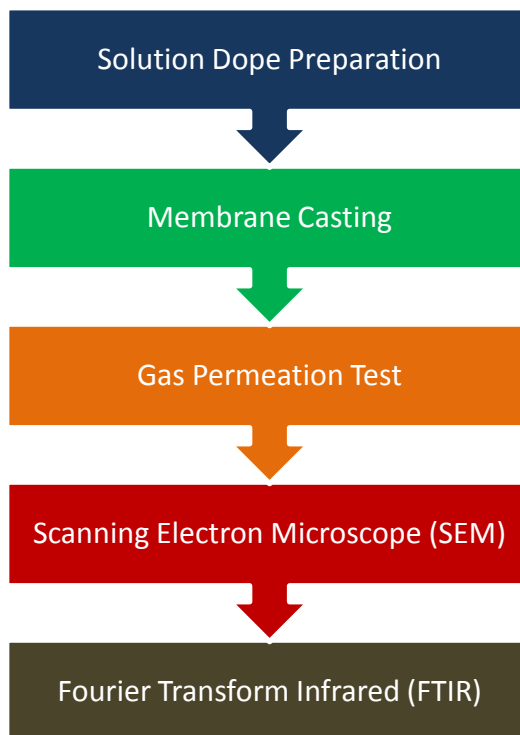
Figure 3.1: Research Design

3.3   SOLUTION DOPE PREPARATION

Polymer is dried first at least 4 hours in a vacuum oven at a temperature of 150°C in order to removed all absorbed water vapor. Next, the polymer is dissolved in NMP, and distilled water. The solution is heated at 40-60°C and is stirred about 4 to 6 hours to achieve complete homogeneity. Finally, the solution is kept in a storage bottle. Apparatus for preparing the casting solution is shown in Figure 3.2.

Figure 3.2: Apparatus for preparing the casting solution (Ismail *et al*., 2004)

3.3   MEMBRANE CASTING

Asymmetric polysulfone membranes were prepared according to the dry wet phase inversion separation using casting knife. The procedures involve four different steps:

    I.   Casting of homogenous casting solution

    II.   Evaporation of solvent

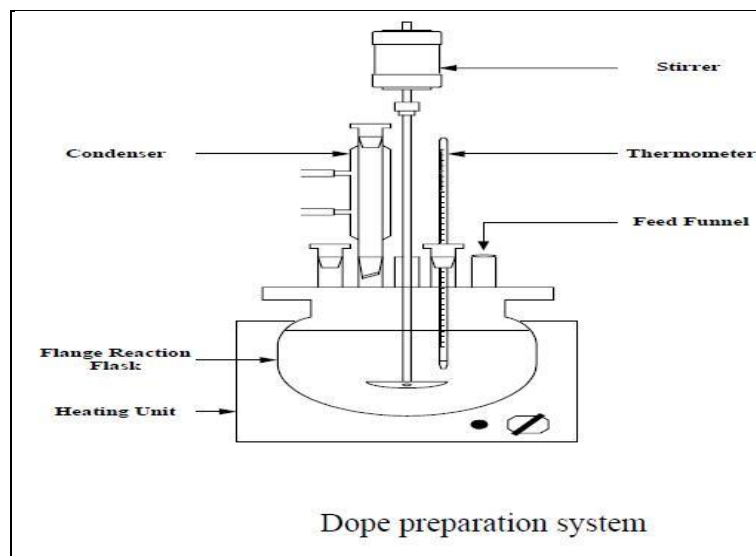   III.   Immersion in a nonsolvent bath

    IV.   Washing and drying of the membrane

The membrane casting process conducted at 30°C (at room temperature). A small amount of casting solution was poured onto a glass plate with casting knife gap setting of 150µm. the glass plate together with membrane was then immersed into the coagulation bath with water as coagulation medium. Then, the membranes were transferred to a water bath for 1 day before washed with methanol for 1 day. Finally, membranes were dried for at least 48 hr at room temperature to remove any residual organic compounds.

3.4   GAS PERMEATION TEST

The pressure normalized fluxes of the membranes is determined by using pure oxygen and nitrogen gases. Membrane is cut into circular disc of 13.5cm² in area. This experiment is carried out at ambient temperature (30°C) at pressure drop 1, 3 and 5 bar. Rate of gas permeation is measured by using a soap buble flow meter. The pressure – normalized flux, $(P/\ell)i$ of pure gases such as oxygen and nitrogen is calculated by :

$$(P/\ell)i = Qi/\Delta piA \qquad\qquad (3.1)$$

Where $(P/\ell)i$ is pressure normalized flux for the gas i (permeability coefficient divided by effective skin thickness) (cm³(STP)/cm².s.cmHg), Qi is the volumetric flow rate of gas i (cm³/s) at STP, Δpi is the membrane pressure drop (cmHg), and A is the membrane surfaces area(cm²). the unit is GPU. Membrane selectivity, αij with respect to any gases, I and j, is the ratio of pressure normalized fluxes.

$$\alpha ij = (P/\ell)i\ /(P/\ell)j \qquad\qquad (3.2)$$
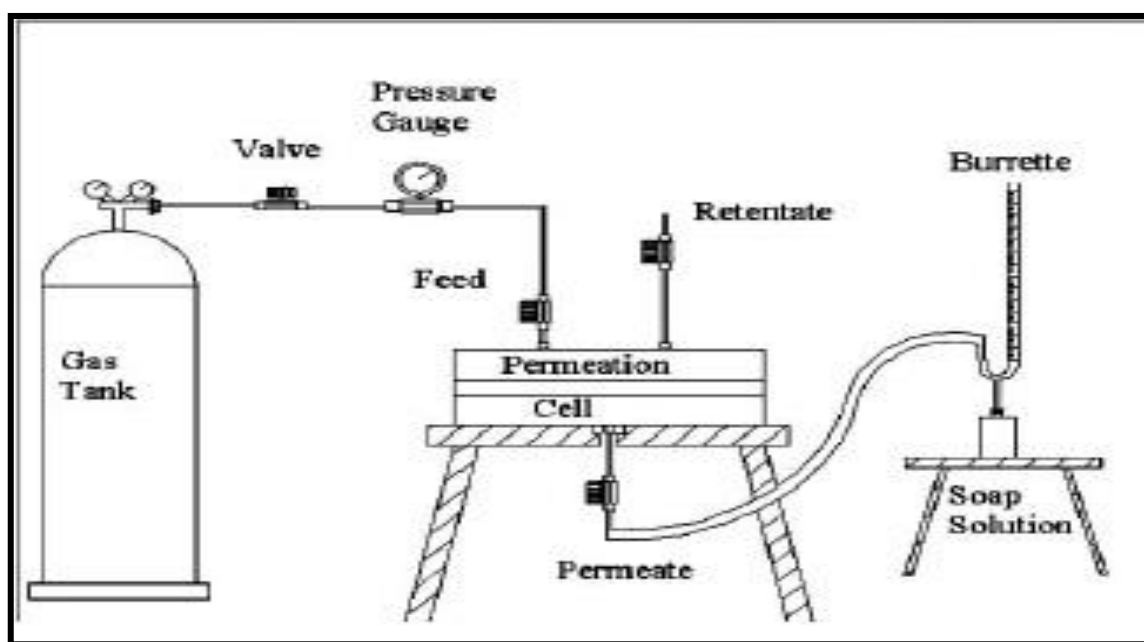
Figure 3.2: Schematic diagram for gas permeation test

3.5   MEMBRANE CHARACTERIZATION

3.5.1   Scanning Electron Microscope

Membrane morphology is examined by using scanning electron microscope (SEM) method. A small piece of the tested membrane is cut and conditioned in liquid nitrogen to leave an underformed structure and mounted on sample stubs. The morphologies is then view with SEM with 20kV under magnifying ranging from 300X to 10000X.

3.5.2   Fourier Transform Infrared (FTIR)

FTIR was performed in order to study the chemical structure of organic molecules and potential structural changes that occur as a membrane chemical treatment.

CHAPTER 4

RESULTS AND DISCUSSIONS

Polysulfone Asymmetric Membranes were prepared by a dry/wet phase inversion process from casting solutions containing of polysulfone, 1-methyl-2-pyrrolidone (NMP) and water as non-solvent additive. As mentioned previously, three dope solution of different polymer concentration were made to cast the membrane. The compositions were labelled as PSU1, PSU2 and PSU3 based on the different weight of polymer as listed in table 4.1 below.

Table 4.1: Composition for dope solution preparation

Component	Solution composition (wt %)		
	PSU1	**PSU2**	**PSU3**
Polymer Polysulfone	20	25	30
Solvent 1-methyl-2-pyrrolidone (NMP)	75	70	65
Nonsolvent Water	5	5	5

Dope formulation: 20 wt% PSU, 75 wt% NMP, 5 wt% H_2O

Type of gas applied: 1,2,3 Bar

Volume changes: 10 cm^3

Membrane area: 12.568 cm^2

Table 4.1: Pressure Normalized Flux and Selectivity of 20 wt% Polysulfone concentration

Pressure (bar)	Membrane	Pressure Normalized Flux of CO_2 (GPU)	Pressure Normalized Flux of CH_4 (GPU)	Average Pressure Normalized Flux of CO_2 (GPU)	Average Pressure Normalized Flux of CH_4 (GPU)	Selectivity
	1	86.210	56.431			
	2	65.174	50.906			
1	3	102.490	48.844	85.958	52.06	1.65
	1	98.231	88.178			
	2	86.111	59.301			
2	3	83.897	52.702	89.413	66.727	1.340
	1	112.383	90.203			
	2	123.074	110.114			
3	3	129.694	99.431	121.717	99.916	1.22

Dope formulation: 25 wt% PSU, 70 wt% NMP, 5 wt% H_2O

Type of gas applied: 1,2,3 Bar

Volume changes: 10 cm^3

Membrane area: 12.568 cm^2

Table 4.2: Pressure Normalized Flux and Selectivity of 25 wt% polysulfone concentration

Pressure (bar)	Membrane	Pressure Normalized Flux of CO_2 (GPU)	Pressure Normalized Flux of CH_4 (GPU)	Average Pressure Normalized Flux of CO_2 (GPU)	Average Pressure Normalized Flux of CH_4 (GPU)	Selectivity
	1	71.468	34.222			
	2	67.330	38.974			
1	3	62.535	58.743	67.111	43.980	1.53
	1	88.408	60.000			
	2	74.294	37.567			
2	3	89.301	70.214	84.001	55.927	1.50
	1	99.615	70.213			
	2	112.600	70.770			
3	3	87.533	67.454	99.916	69.479	1.44

Dope formulation: 30 wt% PSU, 65 wt% NMP, 5 wt% H_2O

Type of gas applied: 1,2,3 Bar

Volume changes: 10 cm^3

Membrane area: 12.568 cm^2

Table 4.3: Pressure Normalized Flux and permeability of 30 wt% polysulfone concentration.

Pressure (bar)	Membrane	Pressure Normalized Flux of CO_2 (GPU)	Pressure Normalized Flux of CH_4 (GPU)	Average Pressure Normalized Flux of CO2 (GPU)	Average Pressure Normalized Flux of CH4 (GPU)	Selectivity
	1	53.018	17.550			
	2	35.517	17.720			
1	3	35.351	19.635	41.296	18.302	2.619
	1	55.254	17.658			
	2	47.361	14.883			
2	3	44.953	26.522	49.19	19.688	2.499
	1	50.956	25.223			
	2	54.072	23.894			
3	3	69.476	27.244	58.168	25.454	2.285

4.1 EFFECT OF POLYSULFONE CONCENTRATION ON GAS SEPARATION PERFORMANCE

Each and every type of the cast membranes was tested for its permeation of pure carbon dioxide, CO_2 and methane, CH_4 gases. Table 4.1, 4.2 and 4.3 shows the results for the pressure normalized flux and selectivity of membrane for different type of polymer concentration which is 20 wt%, 25 wt% and 30 wt%. The value of pressure normalized flux and selectivity is calculated based on the formula as mention in equation 4.1 in chapter four. All membranes showed different standard of performances, with higher permeabilities for lower polymer concentrations and vice versa.
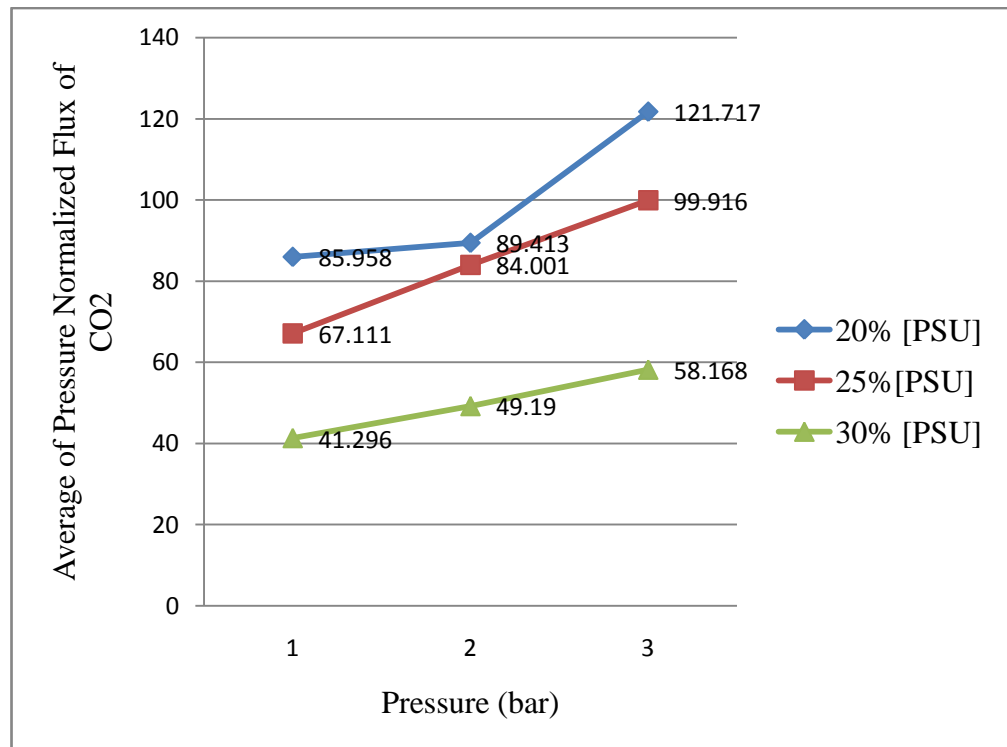

Figure 4.1: Graph of average pressure normalized flux (GPU) of CO_2 versus pressure (bar) at different type of concentration
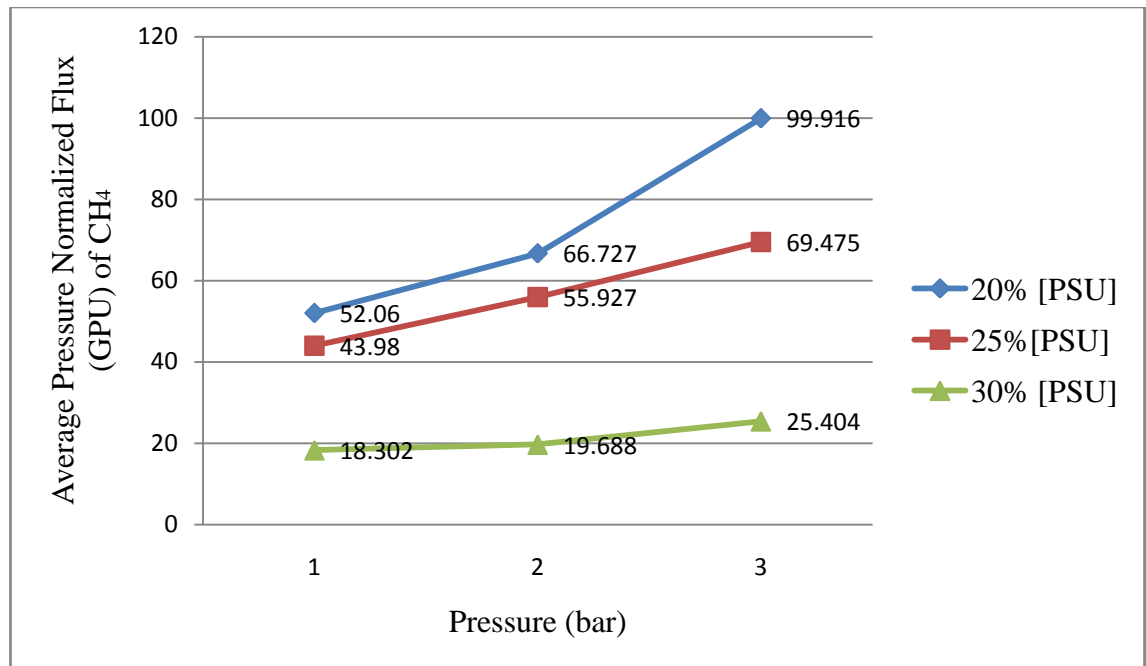
Figure 4.2: Graph of average pressure normalized flux (GPU) of CH_4 versus pressure (bar) at different type of polysulfone concentration

Figure 4.1 and 4.2 shows the effect of different formulations by varying the polymer concentration on pressure normalized flux at three different pressures for both CO_2 and CH_4 gases. Based on the experimental results, the average of pressure normalized flux of carbon dioxide, CO_2 of the three membranes was decreased from 85.958 GPU at 20 wt% polymer concentration to 41.296 GPU at 30 wt% polymer concentration at 1 bar, but 89.413 GPU at 20 wt% polymer concentration to 49.19 GPU at 30 wt% polymer concentration at 2 bar and 121.717 GPU at 20 wt% polymer concentration to 58.168 GPU at 30 wt% polymer concentration at 3 bar. While for the methane, CH_4 gas, the average of pressure normalized flux of the three membranes was decreased from 52.06 GPU at 20 wt% polymer concentration to 18.302 GPU at 30 wt% polymer concentration at 1 bar, but 66.727 GPU at 20 wt% polymer concentration to 19.688 GPU at 30 wt% polymer concentration at 2 bar and 99.916 GPU at 20 wt% polymer concentration to 25.454 GPU at 30 wt% polymer concentration at 3 bar

As it is seen, even the pressure applied changes; the trend of the pressure normalized flux is still same (increase when pressure increase) as compared when the polymer concentration increased. It can be concluded that pressures give the significant effect in the value of pressure normalized flux of the gas. When the pressure applied is increase, the pressure normalized flux is also increased since the increase in pressure creates a greater driving force across the membrane. So, more gas are allow to permeate across the membrane and promote the high permeability of the membrane.
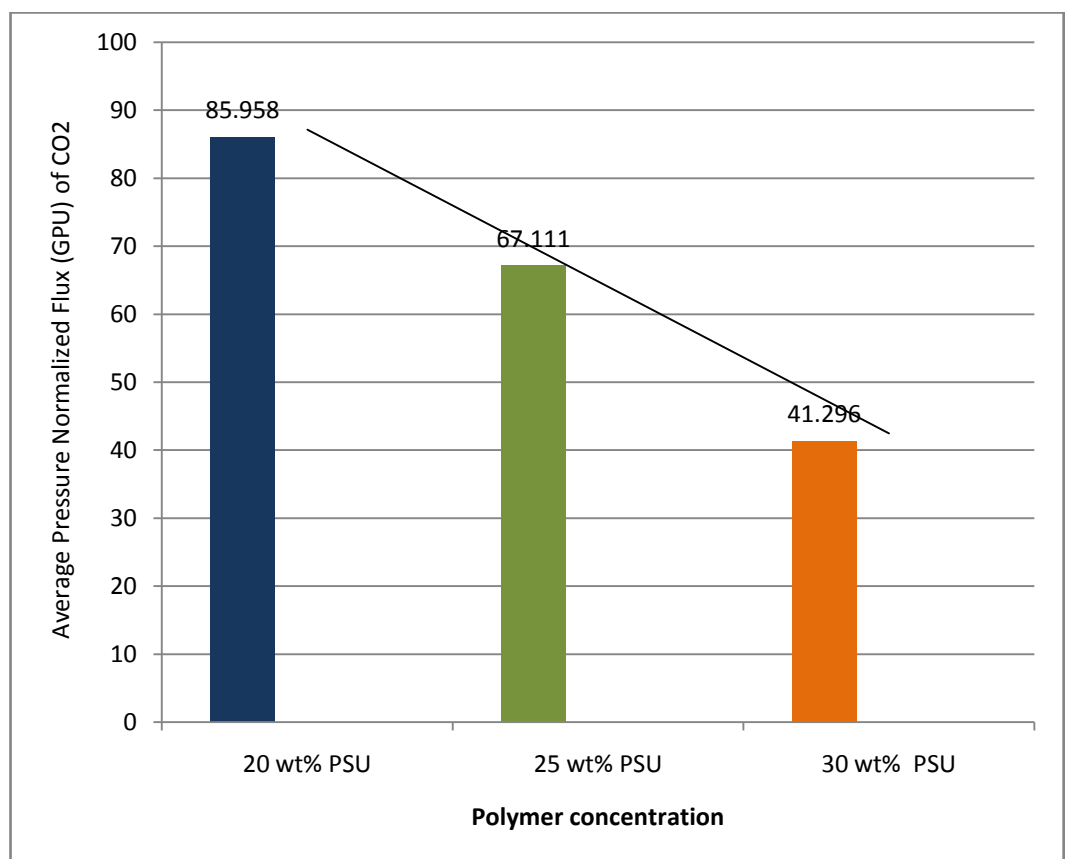

Figure 4.3 (a): Graph of average pressure normalized flux of CO_2 versus polysulfone concentration at 1 bar.
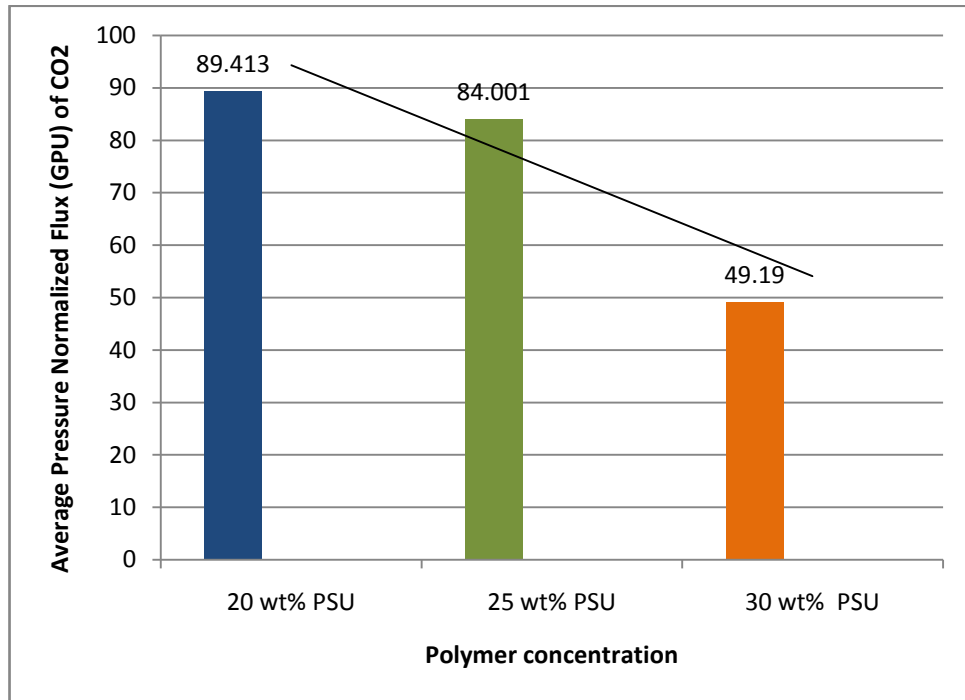
Figure 4.3 (b): Average pressure normalized flux (GPU) of CO_2 versus polymer concentration at 2 bar
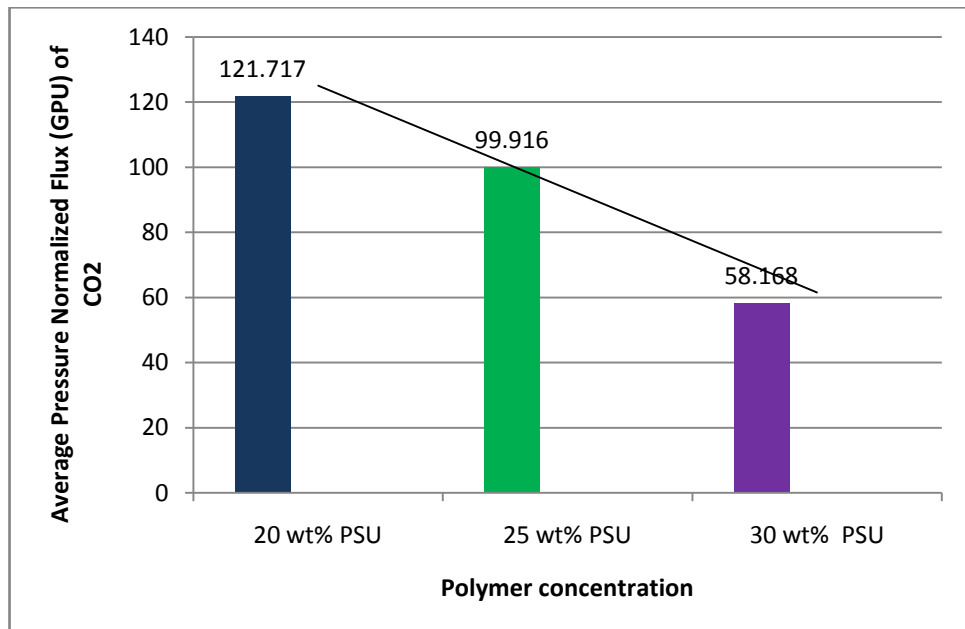

Figure 4.3 (c): Average pressure normalized flux (GPU) of CO2 versus polymer concentration at 3 bar

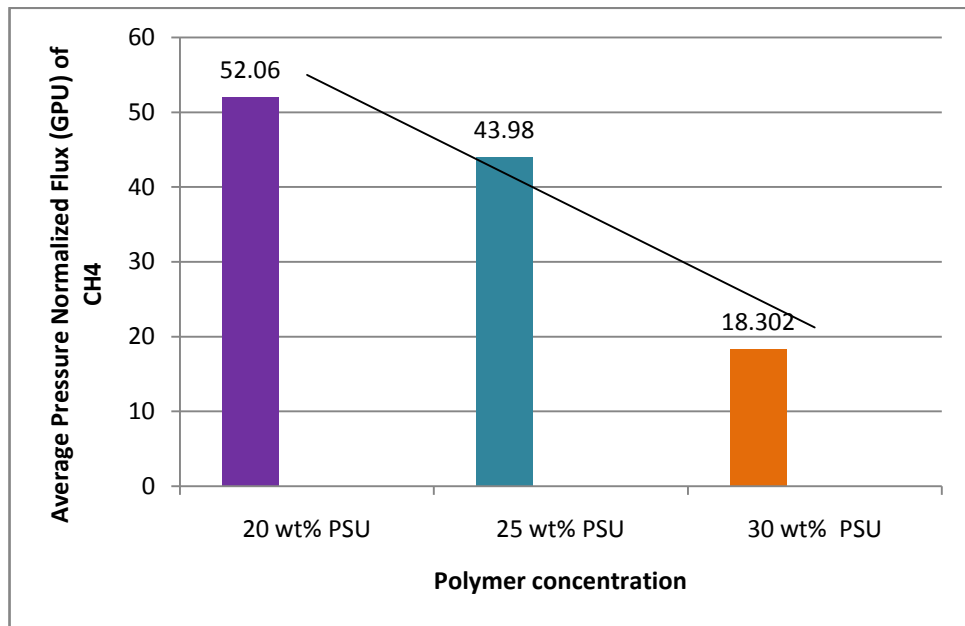**Figure 4.4 (a):** Graph of the average pressure normalized flux (GPU) of CH_4 versus polymer concentration (wt%) at 1 bar
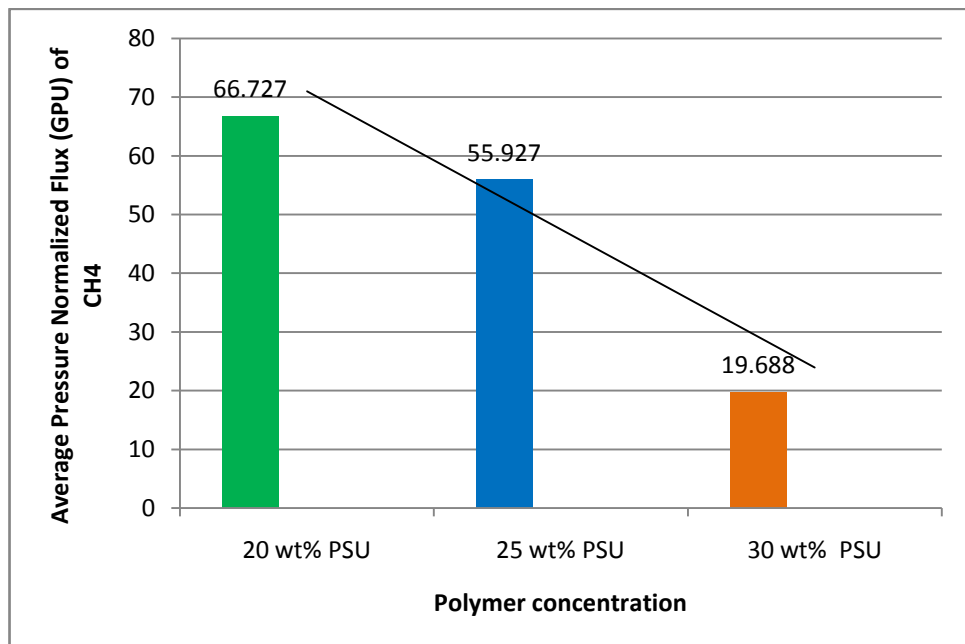

Figure 4.4 (b): Graph or average pressure normalized flux (GPU) of CH_4 versus polymer concentration (wt%) at 2 bar
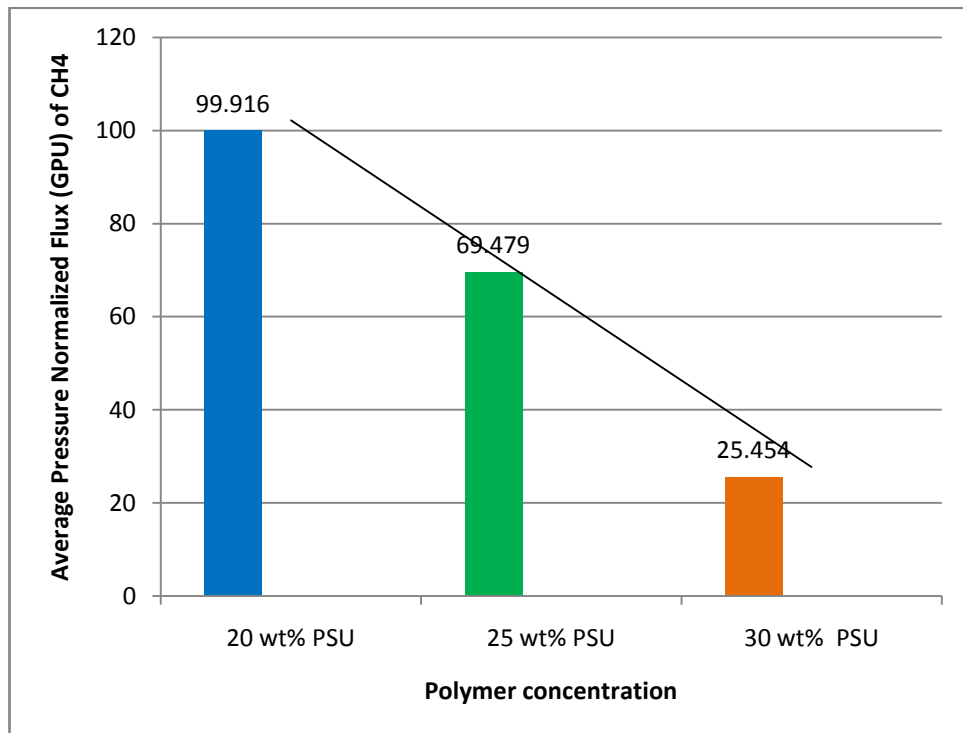
Figure 4.4 (c): Graph of the average pressure normalized flux (GPU) of CH4 versus polymer concentration (wt%) at 3 bar

Both figure 4.3 and figure 4.4 is the consequence from data from figure 4.1 and 4.2; shows the average pressure normalized flux versus polymer concentration for both carbon dioxide and methane gas. All the figures clearly show that the average pressure normalized flux decreased with increasing polymer concentration from 20 to 30 wt%.
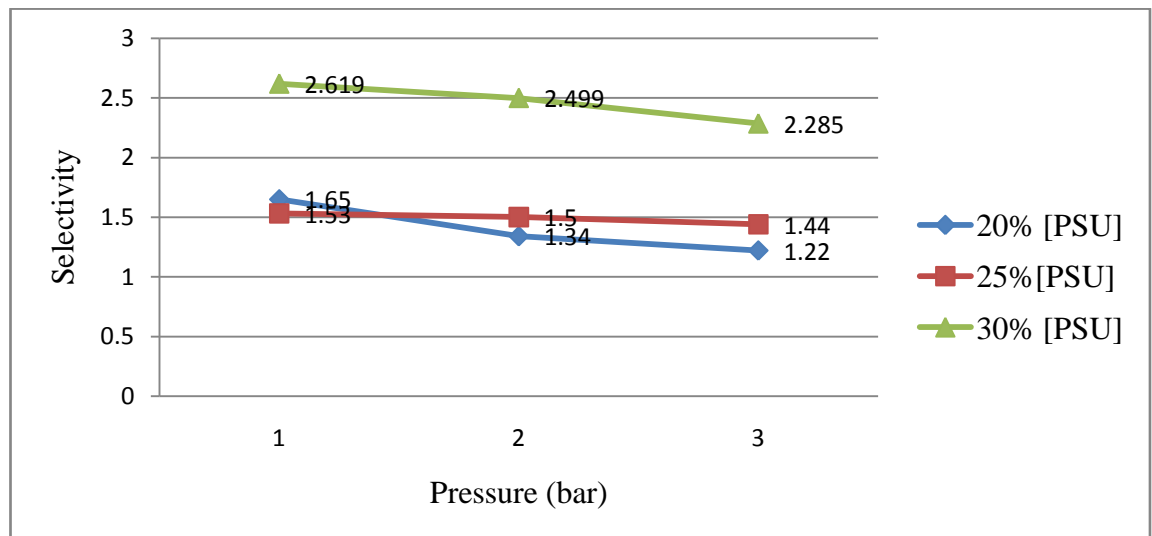

Figure 4.5: Graph of selectivity versus pressure (bar) at different type of polysulfone concentration.

Figure 4.5 shows the value of selectivity for CO_2/CH_4 gas separation for different type of polymer concentration at different pressure applied. The figure shows that the value of selectivity of the gas increased with the increasing of polymer concentration from 20 to 30 wt%. Based on the experimental results, the value of selectivity of the three membranes was increased from 1.65 at 20 wt% polymer concentration to 2.619 at 30 wt% polymer concentration at 1 bar, but 1.340 at 20 wt% polymer concentration to 2.499 at 30 wt% polymer concentration at 2 bar and 1.22 at 20 wt% polymer concentration to 2.285 at 30 wt% polymer concentration at 3 bar.

Increasing polymer concentration of casting solution will formed a denser and thicker skin layer, promoting more selective but less productive (pressure normalized flux) of membrane whereas dilute polymer solution will formed a thin and porous skin layer that lead to high permeability value but low degree of selectivity for gas separation. When the value of permeability is higher, less membrane area required for separation and the operating system cost will be lower while when the value of selectivity is higher, lower losses of hydrocarbon (methane) as carbon dioxide remove and this will results in higher volume of sailable gas product. Unfortunately, as the data shows above, the increasing of carbon dioxide permeability does not correspond to higher selectivity.

Polymer concentration has a strong correlation to viscosity and gives a big effluent to membrane performance. The increasing of polysulfone concentration will increased the viscosity of solution. The viscosity value is inversely proportional to the coagulation value. When the viscosity is increased, the coagulation value will reduced due to a stronger interaction of solvent and polymer and a greater interaction of non solvent and polymer that decreased the dissolving power of solvent for the polymer. Because of that, it will promote aggregation of polymer molecules through chain entanglement. These effects would decrease miscibility of the system and also will enlarge the demixing gap for phase separation leading to a rapid coagulation rate and instantaneous phase separation, especially for nascent skin layers that formed during the dry phase separation process.

Besides, when the viscosity of polymer concentration increase, it will hinder the diffusion exchange rate of the solvent (NMP) and non solvent (water) in sublayer, which slows the precipitation rate of a fast phase separation at the outer skin layer

supported by a closed cell sublayer was produced. In contrast, an asymmetric membrane with a thin and porous skin layer and open cell sublayer was prepared by a polymer solution with a lower concentration.

4.2   EFFECT OF POLYSULFONE CONCENTRATION ON MORPHOLOGY OF POLYSULFONE ASYMMETRIC MEMBRANE

The morphology of the prepared membranes at different compositions is examined using a high resolution scanning electron microscope (SEM).
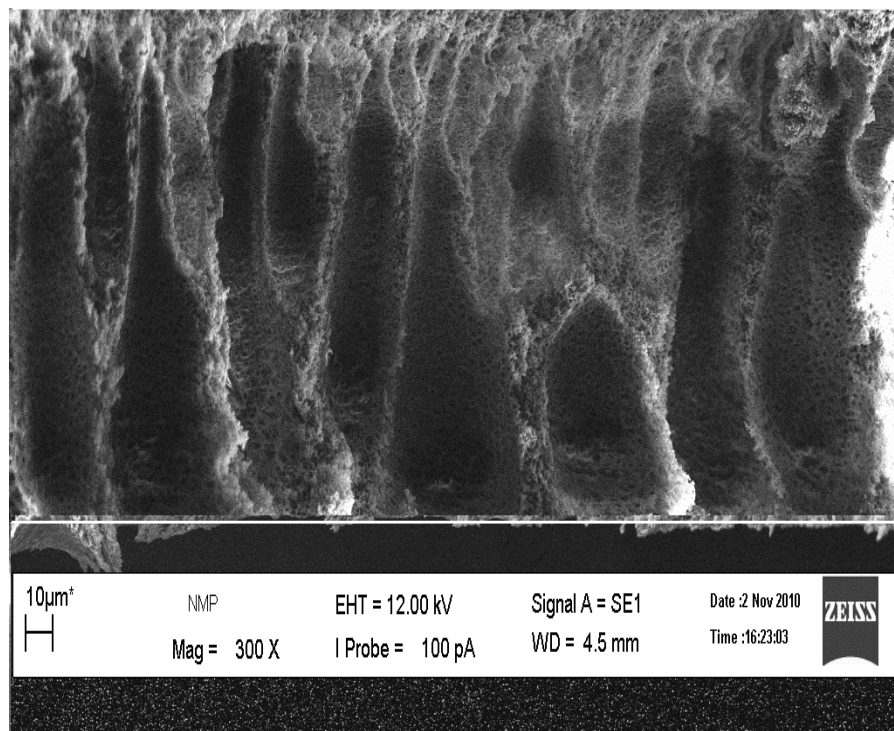
(a)
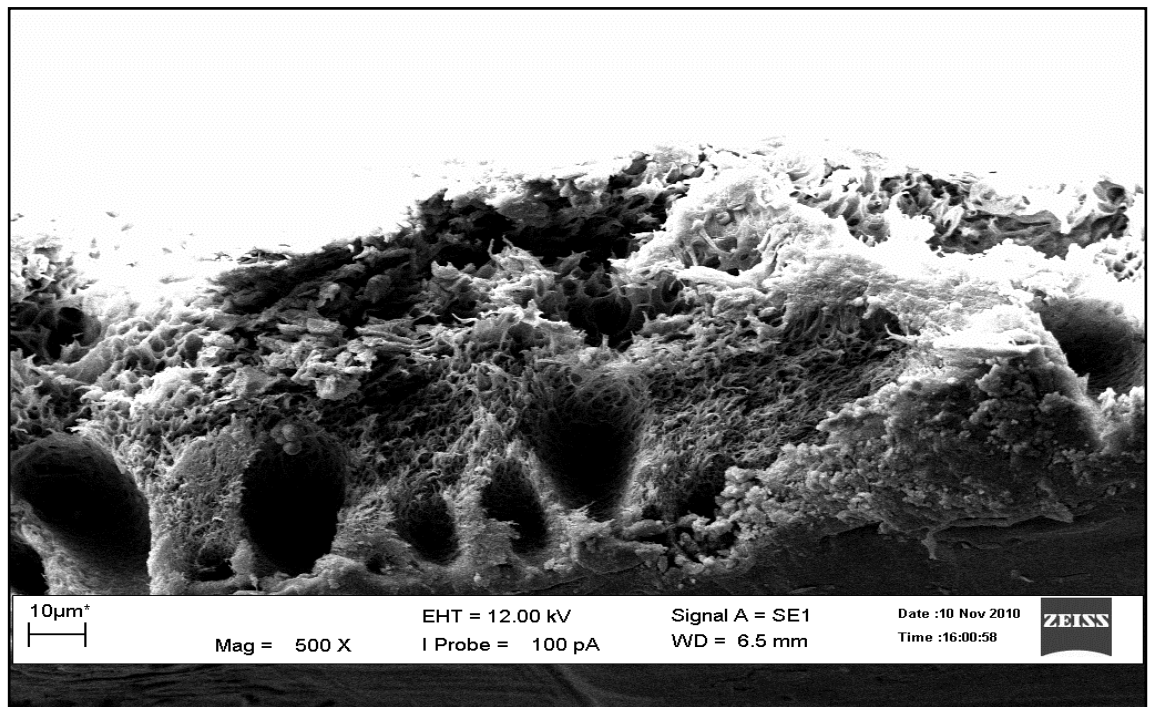
(b)
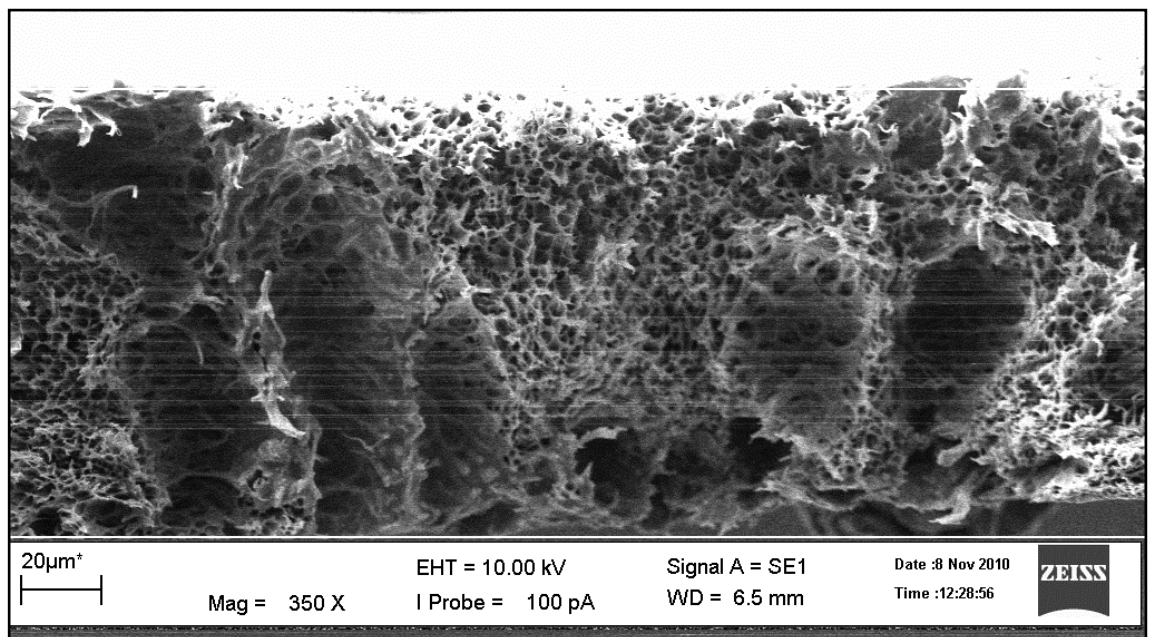
(c)

Figure 4.6: SEM of the cross section of the prepared polysulfone asymmetric membrane for CO_2/CH_4 gas separation: (a) M1 at 300 magnifications; (b) M2 at 1K magnifications; (c) M3 at 1K magnifications.

Figure 4.6 shows the morphology of the membrane for different type of polysulfone concentration.From figure 4.6 (a), at magnifications of 300x, it is seen that

the membranes formed are having asymmetric structure consisting of a dense top layer and a porous sublayer. The sublayer seems to have finger-like cavities as well as macrovoid structure. This phenomenon can be attributed to the fact that NMP as the solvent have high mutual affinity for water (used as nonsolvent during the phase inversion).

Figure 4.6 (b) shows that the solution containing 25 wt% polymer concentrations exhibits small finger like in the sublayer structure compare to figure 4.6 (a) that shows large finger like structure when the polymer concentration used is 20 wt%. The major part of the membrane containing 20 wt% polymer concentrations is covered by finger-like structure. Figure 4.6 (c) shows structure for the membrane containing 30 wt% polymer concentrations. The sublayer of this membrane is fully covered by the sponge like structure. From figure 4.6, it clearly shows that only small number of macrovoid appeared in the sublayer structure.

As illustrated, the cross-sectional membrane structures differ significantly depends on the polymer concentration used. Membranes that were prepared from casting solution with higher polymer concentrations exhibited a thicker skin layer with less macrovoid structure while membrane produced from casting solutions with lower polysulfone concentration showed a thinner skin layer with large voids throughout sublayer. From the comparison of morphology above, it is seen that membrane containing 30 wt% polymer concentration exhibits the characteristic of the good membranes in term of selectivity since the structure is dense and less macrovoid. While membrane with 20 wt% exhibits the lower performance in terms of selectivity since the structure consists of large macrovoid that promote high permeability of the gas.

4.3 EFFECT OF POLYMER CONCENTRATION ON THE CHARACTERISTIC OF ASYMMETRIC POLYSULFONE MEMBRANES FUNCTIONAL GROUP

The chemical structure of organic molecules has been analyzed by using fourier transform infrared (FTIR) technique. Figure 4.5 shows the organic molecules structure that can be recognized. By referring on table 4.5, it has been seen the present of O-H bond at wavelength 3604.09 cm^{-1}. Besides, at wavelength1428.38 cm_{-1}, it has been seen the present of aromatic C=C bond. The different in polymer concentration does not give the significant effect in the changes of functional group or chemical structure.
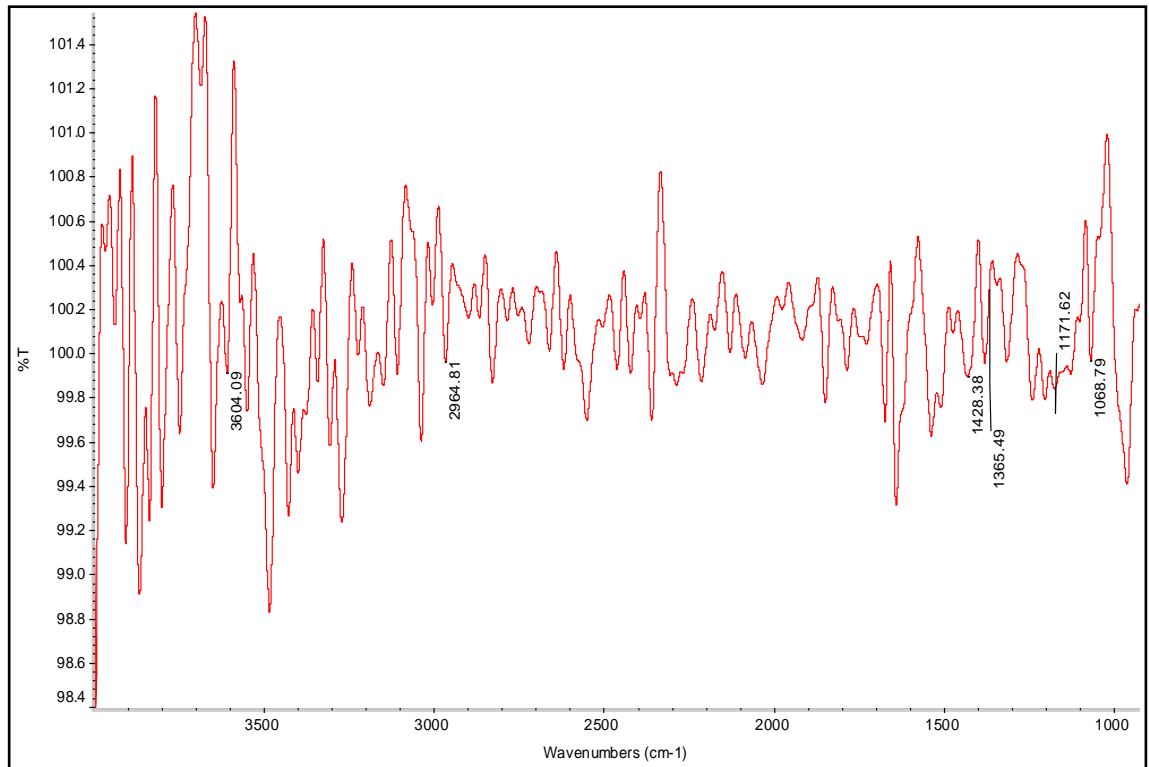

Figure 4.7: FTIR spectra of polysulfone asymmetric membrane

Table 4.5: Infrared assignments of Polysulfone

Frequency (cm^{-1})	Assignments
3600 3200	C-H stretching vibration
2980 2880	Asymmetric and C-H stretching vibration involve entire methyl group
1590 1485	Aromatic C=C stretching
1412	Asymmetric C-H bonding deformation of methyl group

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In this study, the asymmetric polysulfone membrane for CO_2/CH_4 gas separation has been produced. The different type of polymer concentration gives the significant effect to the performance asymmetric polysulfone membrane. When the concentration of polymer increased, the permeability of membrane decreased while the selectivity is increased. This resulting from the structure of membrane that becomes denser and thicker when the polymer concentration of casting solution increased, promoting in more selective membrane.

Membrane with 30 wt% polymer concentration exhibit the highest gas selectivity with the value of selectivity is 2.619 at 1 bar while membrane with 20 wt% polymer concentration gives the lowest value of selectivity which is 1.22 at 3 bar. The pressure applied also gives the significant effect to the performance of membranes whereas increasing the pressure applied will increased the pressure normalized flux of membrane since the driving force across membrane is increase when the pressure in increased.

For separation of CO_2/CH_4 gases, the membrane that exhibits highest selectivity value is needed since membrane with higher selectivity leads to more efficient separations, high recovery and lower power cost.

5.2 RECOMMENDATIONS

Based on the results and conclusions obtained from this study, the following recommendations are given for future work.

1. The parameter of the research should be varied (such as study type of solvent, type of drying membrane, type of coagulation bath) in order to develop the best performance of membrane.

2. The permeation test should be continued using gas mixture because mixed gas separation results difference from those test with pure gas only.

3. Instead of used casting knife in membrane casting procedure, the usage of pneumatically controlled casting machine is applicable in order to minimize error occurring during casting machine.

4. Characterization technique could be expanded to include Atomic Force Microscopy (AFM) to study the pore size and pore size distribution of the membrane, surface roughness and also macromolar nodules.

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