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JUDUL : PERMEABILITY AND SELECTIVITY STUDY OF POLYSUFONE MEMBRANE FOR GAS SEPARATION

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Signature : ....

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Date : 24 April 2009

PERMEABILITY AND SELECTIVITY STUDY OF POLYSULFONE MEMBRANE FOR GAS SEPARATION

FARHANA BINTI HASBULLAH

A thesis submitted in fulfillment of the requirements for the award of the Degree of Chemical Engineering (Gas Technology)

FACULTY OF CHEMICAL AND NATURAL RESOURCES ENGINEERING
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APRIL 2009

I declare that this thesis entitled "Permeabitily and Selectivity of Polysulfone Membrane for Gas Separation" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Date : April 18th, 2009

To my beloved parents,siblings and friends.

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Bismillihirrahmanirrahim..

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ABSTRACT

Polysulfone (PSU) membrane is one of the economical and potential membranes to be used in gas separation process. Polysulfone flat sheet membrane were fabricated from 22.0 wt% polysulfone, 31.8 wt% N,N-dimethylformamide, 31.8 wt% tetrahydofuran and 14.4 wt% ethanol using dry/wet phase inversion process. Eight different samples were tested. The permeability of the membranes were studied using the gas permeation unit with pressure of 1.5-2.5 bar and were tested with CO_2, CH_4, N_2 and also O_2. Among all these eight types of membrane tested, several show that the behavior of polysulfone membrane to permeate CO_2 relies on the treatment that the membranes undergo and the temperature of the coagulation bath. Thus, the most excellent value of permeability for CO_2 among eight types of membranes tested was 4.98×10^{-3} $cm^3/cm^2.s.cmHg$ which was PSU membrane immersed in a 4°C coagulation bath and treated with polydimethylsiloxane (PDMS) as a coating agent with the selectivity value of 1.36.From the data and result collected it has been proven that temperature of coagulation bath and also the coating agent for membrane treatment play a major role in affecting PSU membrane permeability and selectivity as a whole.

ABSTRAK

Membran polisulfona (PSU) adalah salah satu membran yang ekonomikal dan berpotensi untuk digunakan dalam proses pemisahan gas. Kepingan nipis membrane polisulfona telah difabrikasi dari 22.0 %berat polimer polisulfona, 31.8 % berat N,N-dimetilformamida (DMF), 31.8 % berat tetrahidofuran dan juga 14.4 % berat etanol menggunakan fasa proses balikan kering/basah. Lapan jenis sampel telah diuji. Kadar kebolehtelapan membran telah diuji dengan menggunakan set unit 'Gas Permeation' dengan tekanan 1.5 hingga 2.5 bar. Kajian ini telah menggunakan variasi gas seperti CO_2, CH_4, N_2 dan juga O_2. Antara kesemua lapan jenis membran yang telah diuji menunjukkan ciri-ciri membran polisulfona menyerap partikel-partikel gas bergantung dengan rawatan yang telah membran itu lalui. Ujian ini juga telah menunjukkan pengaruh suhu rendaman koagulasi bagi membran juga memainkan peranan terhadap kadar serapan partikel CO_2 yang menembusinya. Hasil eksperimen yang telah dikumpul telah menunjukkan data yang terbaik. Nilai kadar serapan partikel CO_2 yang menembusi membran polisulfona yang terbaik adalah 4.98 x 10^{-3} cm^3/cm^2.s.cm Hg dengan nilai pemilihan 1.36 iaitu membran polisulfona yang telah direndam di dalam rendaman yang bersuhu 4°C dan dirawat dengan polidimetilsiloksen (PDMS) sebagai agen salutan.Dari semua pengumpulan data, adalah disimpulkan bahawa suhu rendaman koagulasi serta jenis rawatan agen salutan yang dilakukan ke atas membran polisulfona mempengaruhi kadar serapan partikel dan juga pemilihan gas untuk pemisahan gas secara keseluruhan.

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Å - Angstrom

P - Constant of Permeation

l - Thickness of Membrane

µ - micro

MPa - Mega Pascal

kPa - kilopascal

cm - centimeter

J - The rate of transfer or flux ($g/cm^2 \bullet s$)

D - diffusion coefficient of the gas in the polymer (cm^2/s)

S - Solubility

Δp - Difference of CO_2 and permeate low pressure between flow in phase and the filtrate, and l is the thickness of membrane

P_{CO2} - Permeability of CO_2

D - Diffusivity

Ω - Selectivity

ΔP - Trans Membrane Pressure

Q - Flow rate of supplied gas (cm^3/s)

A - Area of the membrane (cm^2)

P_x - Permeability of x gas

r - pore radius

T - Temperature

m - Molecular Mass

ε – Porosity of the membrane

ℓ - Pore length

p_ℓ - Absolute pressure of the gas species at the beginning of the pore

p_o - Absolute pressure of the gas species at the end of the pore

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Hydrogen sulfide, H_2S and carbon dioxide, CO_2 are the main acid gases which have to be removed from natural gas. The specifications on acid gas contents are imposed by safety requirements, transport requirements and distribution specifications. The cause of corrosion in natural gas pipelines are primarily of the existence of mainly both hydrogen sulfide and carbon dioxide. Acid gas removal is a very important step taken to prevent any corrosion and erosion that will cost highly in the future in term of three factors which are safety, distribution and natural gas quality.

As established today, there are many ways that can be implemented to remove acid gases from natural gas. Hydrogen sulfide and carbon dioxide both can be removed by processes based on chemical solvents i.e. Amine scrubbing; adsorption, gas permeation, fractionation and sweetening of liquid fraction. All of these conventional methods are applicable as cost, easily installed and various factors in concerned.

Gas permeation using membrane is already applied industrially to remove carbon dioxide from natural gas (Meyer and Cooley, 1990). In industrial application so far, these technology have only been used for small capacities. This membrane technology offers the advantages of reducing CO_2 subsistence and reduces methane loss in natural gas. Gas permeation membranes are usually made with vitreous polymers that exhibit good diffusion selectivity (derivatives of cellulose acetate, polyethersulfones, polyimides, polyamides) (Alexandre Rojey, 1997).

In the early years of membrane technology, there were a lot of limitations for the membrane to perform at its high performance. The selectivity was very low and the permeation flux was very poor. These problems occurred due to the fact that the membranes had to be relatively thick in order to avoid holes and defect. In the upgraded technology, membrane are created very thin that increased the permeation fluxes thousand of time higher that the previous technology.

Carbon dioxide removal from natural gas has been performed with the usage of polysulfone membranes. Advance researches were made to comply with the requirement of having high permeated flux and also selectivity towards acid gas separation. Due to rarity of polysulfone membrane usage in removing acid gases, it is one of the challenges to produce a high quality membrane that fulfill the necessities of selectivity and high permeated flux en route for a better implication in separating acid gases.

Thus, this study sum up the growth and development of polysulfone membrane in used of separation not only carbon dioxide, CO_2 but various gases that would be a parameter of comparison within the experimentation.

1.2 Problem Statement

As the development of natural gas usage, the concern of maintaining the plant, distribution pipelines and the instrumentation of conducting a natural gas plant from any hazardous condition is rapidly taking into consideration. The existent of carbon dioxide, CO_2 and other acid gases in the natural gas components can affect the quality of the gas itself and it can cause major corrosion in the instrumentation and also pipelines. Membrane technology is one of the ways to prevent corrosion to happen in the oil and gas industry.

1.3 Objective of Study

The objective of this study was to develop the preparation of polysulfone membrane for the usage of the study.

1.4 Scope of Study

Scope of this research was to prepare polysulfone membranes for the usage of the permeating several gases. The study of permeability and selectivity of polysulfone membranes were tested by using different gases such as N_2, CH_4, O_2, and CO_2.By doing this, the study indicates the permeability and the selectivity at different coagulation bath temperature. Furthermore, the membrane was coated using various coating agent such as polydimethylsiloxane(PDMS), bromine(Br_2) and iodine(I_2) to see the effect towards the study of its permeability and selectivity.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Definition

The origin of the word 'membrane' is from the Latin word 'membrana' which means skin of body. Membrane can be defined as a flexible enclosing or separating tissue forming a plane or film and separating two environments (usually in a plant or animal). It is also known as a mechanical, thin, flat flexible part that can deform or vibrate when excited by an external force (Rundell, 2003).

A membrane is a permeable or semi-permeable phase, often a thin polymeric solid, which restricts the motion of certain species. This added phase is essentially a barrier between the feed stream for separation and one product stream. The performance of a membrane is defined in terms of two simple factors, flux and selectivity, defined as:

> *Flux or permeation rate; the volumetric (mass or molar) flowrate of fluid passing through the membrane per unit area of the membrane per unit time.*
>
> *Selectivity; for solutes and particulates in liquids and gases; retention is the fraction of solute in the feed retained by the membrane*

Selectivity; for mixture of miscible liquids and gases; Separation factor is the ratio of the concentration in the permeate divided by that in the feed fro two components (Scott and Hughes, 1996).

The particle which is bigger than the other particle in a solution will be blocked and the smaller particle will pass through the membrane which is called permeates. The bigger particle which is blocked by the membrane is called rejection or retentate. The basic principle of membrane separation process is shown in Figure 2.1.

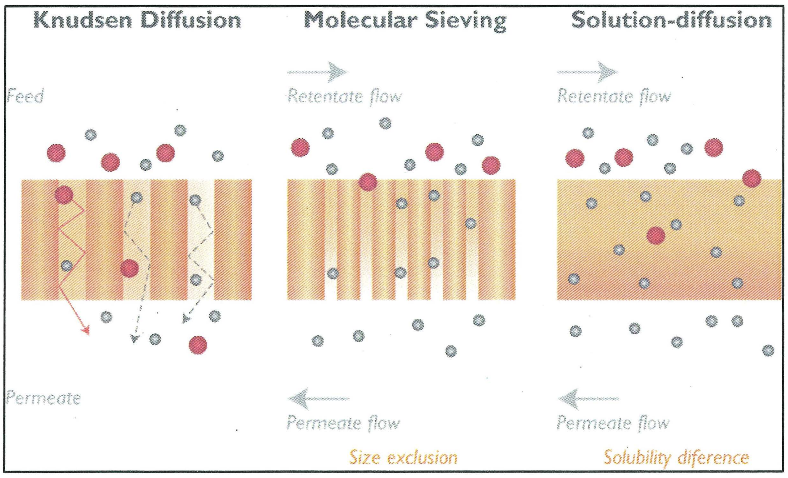

Figure 2.1 The Principle of Membrane Separation (Yompulskii, 2008).

2.2 The Concept of Membrane Separation

Membranes separations are in competition with physical methods of separation such as selective adsorption, absorption, solvent extraction, distillation, crystallization, cryogenic gas separation etc. The feature which distinguishes membrane separations from other separation techniques is provision of another phase, the membrane. This phase, solid, liquid or gaseous, introduces an interface(s) between the two bulk phases involved in the separation and can give advantages of efficiency and selectivity. The membrane can be neutral or charged and porous or non-porous and act as a permselective barrier.

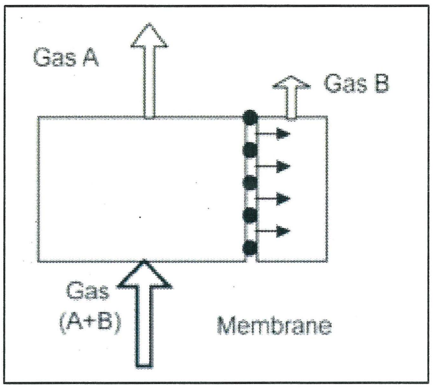

Figure 2.2: Flow in a Membrane Separator.

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 kinetically driven, by the application of their mechanical, chemical or electrical work. Table 2.1 lists the more industrially important membrane processes under these headings, together with the general classification of membranes used (Scott, 1996).

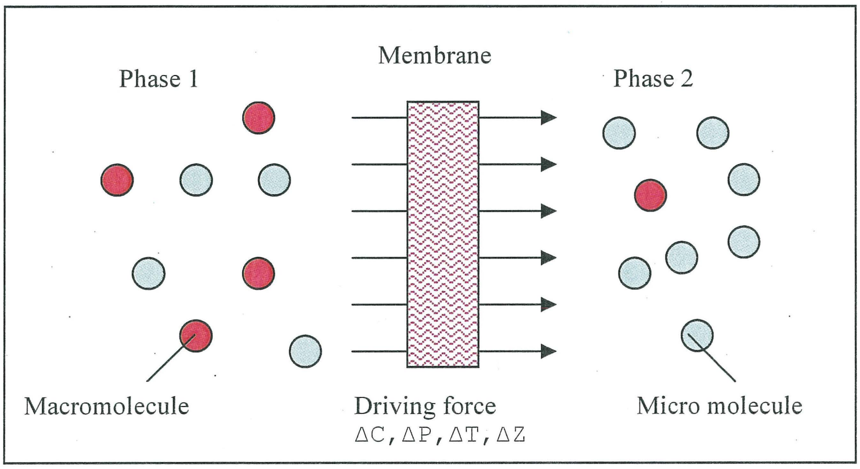

Figure 2.3: Schematic Representation of a Two-Phase System Separated by a Membrane

Table 2.1 Classification of Driving Force According to Membrane Separation Processes (Matsuura, 1994)

Type of driving force	Classification of the process
Pressure	a) Reverse Osmosis b) Ultrafiltration c) Microfiltration d) Membrane gas separation e) Pervaporation
Temperature	a) Membrane Distillation
Concentration Gradient	a) Dialysis b) Membrane Extraction
Electric Potential	a) Electro Dialysis

2.3 Types of Membranes

For gas separation, the selectivity and permeability of the membrane material determines the efficiency of the gas separation process. Porosity is an important characteristic of such membranes. Based on flux density and selectivity, membranes can be classified broadly into three: (a) porous, (b) non-porous and (c) asymmetric.

2.3.1 Porous Membranes

A porous membrane is a rigid, highly voided structure with randomly distributed inter-connected pores. The separation of materials by porous membranes is mainly a function of the permeate character and membrane properties like the molecular size of the membrane polymer, pore size and pore size distribution. Porous membranes for gas separation can exhibit very high levels of flux but provide for low separation and low selectivity (Pandey, 2001).

2.3.2 Non-porous Membranes

Non-porous or dense membranes provide high selectivity or separation of gases from their mixtures but the rates of transport of the gases usually low. An important property of non-porous dense membranes is that even permeants of similar sizes may be separated if their solubility in the membrane differs significantly (Chauhan, 2001).

2.3.3 Asymmetric Membranes

Asymmetric membranes consists of two structurally distinct layers, one of which is a thin, dense selective skin or barrier layer and the other a thick, porous matrix substructure layer whose main function is to provide a physical support for the thin skin (Pandey, 2001).

2.4 Membrane Modules

Membrane module can be defined as housing of membrane in a suitable device. There are 4 major types of module normally used in membrane separation processes which are plate and frame, spiral wound, tubular and also hollow fibre.

2.4.1 Plate and Frame Membrane Modules

Flat membranes were mainly used in experiments to characterize the permeability of the membrane. The modules were easy to fabricate, used and the areas of the membranes are well defined. In some cases modules were stacked together like a multilayer sandwich or plate-and-frame filter press as shown as Figure 2.4 below. (Geankoplis, 2003)

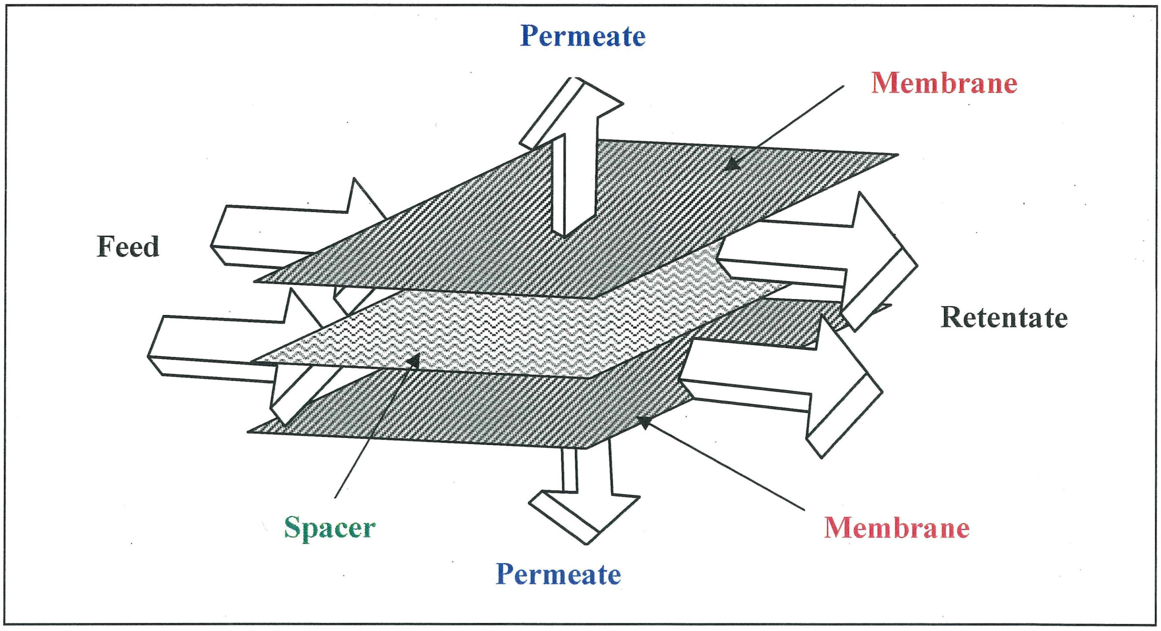

Figure 2.4: Plate and Frame Membrane Module (Geankoplis, 2003).

2.4.2 Spiral Wound Membrane Module

In the spiral wound arrangement, two flat sheets of membrane with a permeate spacer in between were glued along three or their sides to form an envelope (or leaf, as it is called in membrane industry) that was open at one end. Many of these envelopes were separated by feed spacers and wrapped around a permeate tube with their open ends facing the permeate tube (Dortmundt *et al*, 1999).

The spiral wound element is located inside a metal shell. The feed gas enters at the left end of the shell, enters the feed channel, and flows through this channel in the axial direction of the spiral to the right end of the assembly (Figure 2.4.1). Then the exit residue gas leaves the shell at this point. The feed stream, which is in the feed channel, permeates perpendicularly through the membrane (Geankoplis, 2003).

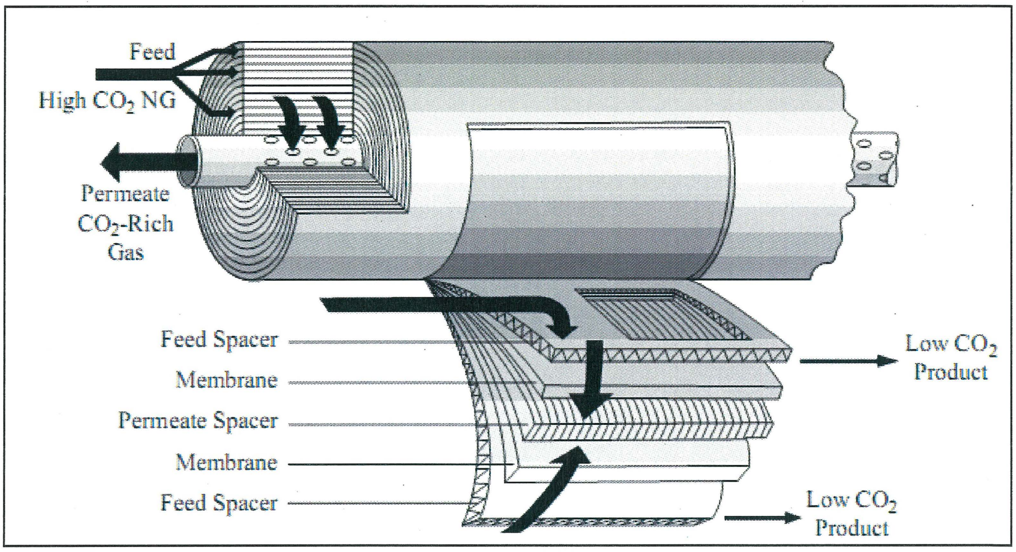

Figure 2.5: Spiral Wound Module (Dortmund *et al*, 1999).

2.4.3 Tubular Membrane Module

An ultra-filtration and reverse osmosis module comprising a tubular casing having a plurality of tubular membrane assemblies spaced therein by spacing plates, in stepped end portions of the casing bore, and held therein by sealing plates clamped to flanges on the ends of the casing. The tubular membrane assemblies are sealed around bores in the spacing plates and boxes in the sealing plates by "O"-rings and are held against collapse by sleeves in the ends of the tubular membrane assemblies (Thayer *et al*, 1984).

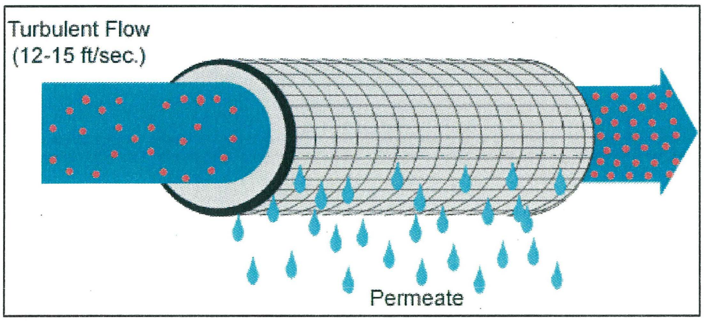

Figure 2.6: Tubular Membrane Module

2.4.4 Hollow-fibre Membrane Module

The membranes were in the shape of very small mall diameter hollow fibres. The inside diameter of the fibres is in the range of 100-500µm and the outside 200-1000µm, with the length up to 3-5m. The module resembles a shell and tube heat exchanger. Thousands of fine tubes were bound together at each end into a tube sheet that was surrounded by a metal shell having a diameter if 0.1-0.2m, so that the membrane area per unit volume is up to 10 000m^2/m^3, as is Figure 2.7(Geankoplis, 2003)

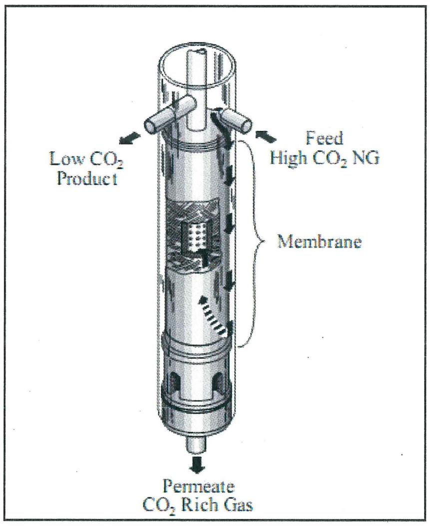

Figure 2.7: Hollow Fibre Membrane Module (Dortmundt *et al*, 1999).

2.5 Advantages of Membrane Technology

There were several advantages of the membrane technology. It can lower the capital cost, lower the operating cost, deferred capital investment, environmental friendly and it is also operational simplicity with high reliability.

2.5.1. Lower Capital Cost

Membrane systems were skid mounted, except for the larger pre-treatment vessels, and so the scope, cost, and time taken for site preparation were minimal. Therefore, installation costs were 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 (Dortmundt *et al*, 1999).

2.5.2 Lower Operating Cost

The only major operating cost for single-stage membrane systems was membrane replacement. This cost was significantly lower than the solvent replacement and energy costs associated with traditional technologies. The improvements in membrane and pre-treatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors were usually comparable to those for traditional technologies (Dortmundt *et al*, 1999).

2.5.3 Deferred Capital Investment

Often, contracted sales-gas flow rates increase overtime, as more wells were 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 was 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 *et al*, 1999).

2.5.4 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 pre-treatment system that could cause downtime, such as filter coalescers, were 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 was 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 *et al*, 1999).

2.5.1.5 Environmentally Friendly

Membrane systems do not involve the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or reinjected into the well. Items that do need disposal, such as spent membrane elements, can be incinerated (Dortmundt *et al*, 1999).

2.6 Types of Gas Separation Membranes

There are various types of gas separation membranes used to separate gases according to its properties. The three general types of gas separation membrane are polymeric, metal, ceramic and zeolite membrane.

2.6.1 Polymeric Membrane

Polymeric Membranes have a range of applications due to their filtration capabilities, including on micro and nano scales. This is further assisted by the physical structure/shape providing a large surface area relative to the volume of material.

Perhaps the most prominent application is in the Proton Exchange Membrane Fuel Cells which help convert chemical energy into electrical energy without the process of combustion. This technology is expected to overhaul the way in which vehicles are powered and/or fuelled (Raptra, 2005).

2.6.2 Metal Membrane

Dense metal membranes are a well-developed technology for the production of high-purity hydrogen. The physical mechanism of hydrogen transport across metal films—dissociation of molecular hydrogen, diffusion of interstitial atomic hydrogen, and subsequent recombinative desorption of molecular hydrogen—means that metal membranes can have extremely high selectivities for hydrogen transport relative to other gases. We describe current experimental and theoretical trends in the development of metal alloy membranes for hydrogen purification in practical, chemically robust processes (Sholl and Ma, 2006).

2.6.3 Ceramic and Zeolite Membrane

Ceramic and zeolite based membranes have begun to be used for commercial separations. These membranes are all multilayer composite structures formed by coating a thin selective ceramic or zeolite layer onto a microporous ceramic support. Extraordinarily high selectivities have been reported for these membranes, and their ceramic nature allows high temperatures, so fluxes are high. These advantages are however, offset by the costs of the membrane modules (Baker, 2004).

2.7 Types of Membrane Preparation

Membrane used in gas separation can be form in several ways of preparation. One of the most known techniques of making asymmetric polymer membrane was phase inversion separation. This technique can be discrete into four different techniques which were thermal precipitation, air casting of dope solution, precipitation from the vapor phase and immersion precipitation.

Among these techniques, immersion precipitation was widely used to produce commercial gas separation membranes and other membrane based separation. Immersion precipitation technique can be further divided into three categories namely wet, dry and dry/wet phase inversion technique.

2.7.1 Air Casting of Dope Solution

Air casting was the oldest technique of forming membranes. A distinguishing feature of air casting, which was also sometimes referred to as a "dry process", was known as evaporation of a volatile solvent in a controlled atmosphere. Evaporation causes gradual reduction in the solvent/nonsolvent ratio. (Leos J. Zeman *et al,* 1996)

2.7.2 Immersion Precipitation

Isothermal immersion-precipitation was a process widely used to synthesize porous polymeric membranes. In this process, a dope composed of polymer, solvent and additives was immersed in a nonsolvent coagulation bath to induce precipitation by means of liquid-liquid demixing and/or crystallization. In fact, for membranes synthesized from crystalline polymers, various studies have pointed out that the structure of the formed membrane was dictated by the sequence of these phase separation events. The formed membranes often exhibit characteristics from both types of phase separations (Lin *et al,* 2002).

2.7.3 Thermal Precipitation

In thermal precipitation technique, the polymer was dissolved in a solvent at high (vs low) temperature and was spun in a spinneret or was extruded. In the preparation of hollow fiber membranes, the fiber lumen is generally filled with a gas through the inner concentric needle to prevent its mechanical collapse (Barbucci, 2002).

2.7.4 Precipitation from the Vapor Phase

In the precipitation from the vapor phase process, phase separation of the polymer solution was induced by penetration of nonsolvent vapor in the solution (Ismail *et al,* 2002).

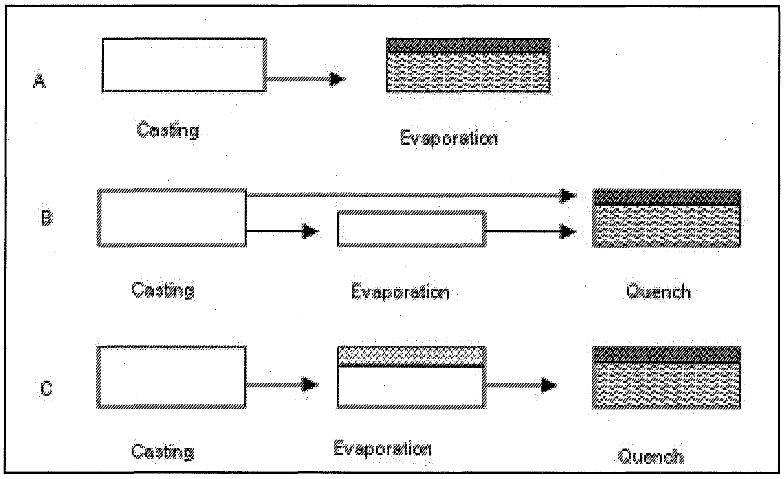

Figure 2.8: Schematic Representations of Immersion Precipitation Phase Inversion Processes: (A) dry, (B) wet, (C) dry/wet (Ismail, 2003).

2.8 Membrane Preparation Methods

In the preparation of membrane, it is crucial to know what type of membrane that will be produced. Basically, the steps and methods were membrane casting. To produce a defect-free membrane, membrane coating were done to the membranes.

2.8.1 Asymmetric Polysulfone Membrane Casting

There were various ways of preparing polysulfone membrane that can be use for gas separation membrane. Most of the previous studies tested that the method that was often used was immersion precipitation phase inversion dry/wet processes. The solution prepared in this method was to produce a membrane consisting of an extremely thin nonporous layer mounted on a much thicker and highly porous layer of the same material. This membrane structure was referred to as asymmetric, as opposed to a homogenous structure, where membrane porosity is more-or-less uniform throughout. An example of an asymmetric membrane is shown in Figure 2.9

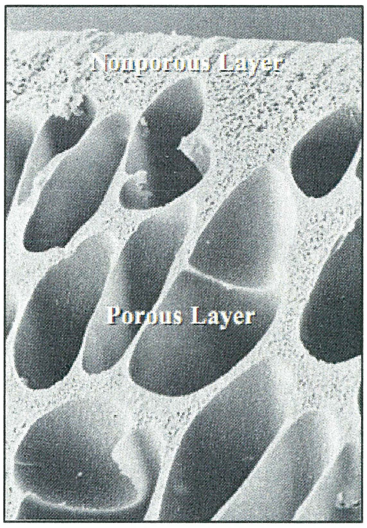

Figure 2.9: Asymmetric Membrane Structure (Dortmundt *et al*, 1999)

(Lai *et al*, 2002) studied by using a casting solution consist of 22.0 wt.% polysulfone (polymer), 31.8 wt.% N,N-dimethylacetamide (less volatile solvent), 31.8 wt.% tetrahydrofuran (more volatile solvent), and 14.4 wt.% ethanol (nonsolvent).

An optimized four multi-component dope solution was used: 22% (w/w) polysulfone; 31.8% (w/w) DMAc; 31.8% (w/w) THF; and 14.4% (w/w) ethanol. Water was used in the coagulation bath. The solutions were mixed in a round bottom reaction vessel stirred by motor driven stirrer under temperature of 60°C for 8- 10 h until the polymeric solution become homogeneous. The homogeneous solution will be placed in an ultrasonic water bath to remove the particles and gas bubbles that may exist in the casting solution dope prior membrane casting process (Lai, 2002).

Asymmetric flat sheet membranes were prepared according to dry/wet phase separation process. The polymer solution was cast on a clean glass plate using a unique pneumatically-controlled membrane casting system as shown in Fig. 2.10. The casting knife consists of a steel blade, which rested onto two runners, arranged to form a precise gap between the blade and glass plate. Polymer solution was spread by casting knife with a slit height of 150 mm across the glass plate (Ismail *et al*, 2003).

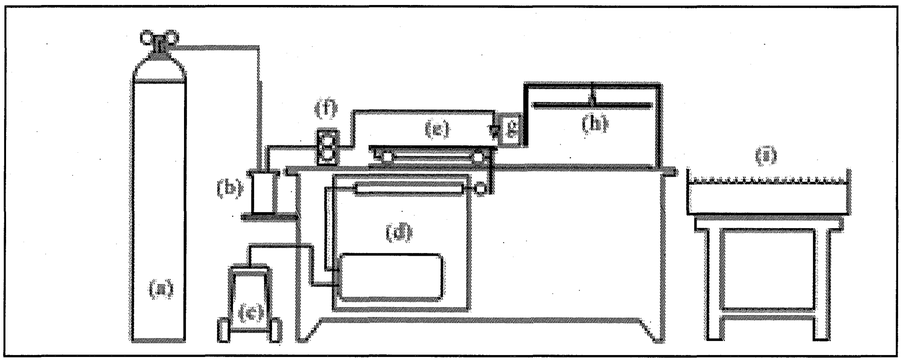

Figure 2.10: Pneumatically-Controlled Flat Sheet Membrane Casting System (a) Nitrogen gas tank; (b) solution dope reservoir; (c) air compressor;(d)pneumatic system; (e) trolley and glass plate; (f) gear pump; (g) casting knife; (h) evaporation chamber;(i) coagulant bath (Abdul Rahman,2003)

The casting knife was used to spread an even polymer solution across a glass plate. Depending on the desired final film thickness, casting knife with slit heights ranging from 150 to 250 μm was used. In this work, partial evaporation was carried out by forcing nitrogen gas stream across the cast membrane to induce phase separation in the outermost region of the cast membrane (dry-phase inversion) before immersion into a coagulation bath. The initially clear, nascent membranes became turbid instantaneously at the onset of the blowing process. After the dry-phase inversion, the membranes are immersed in the coagulation bath for at least 12 hr and the ultimate bulk membrane structure is formed. Finally, the resulting membranes were then removed from the quench bath and transferred to methanol as a solvent exchange before being air dried at room temperature (Wong, 2003).

Once cast, the nascent membranes were immediately immersed in a pure water coagulation bath at 4 ℃ for 10 min. The membranes were then air-dried for 1 day at room temperature before being finally dried under vacuum at 70°C for 2hr (Shilton *et al*, 1996).

2.8.2 Membrane Coating

2.8.2.1 Polysulfone Membrane Treated by Elastomeric Silicone Polymer

The membrane sheets were coated with a highly permeable elastomeric silicone polymer. The coating was applied by dipping the sheets into a 3%w/w solution of the silicone in hexane for 15 min. After coating, the membranes were placed in an oven at 60°C for 2 hours to allow curing (Shilton *et al*, 1996).

The difference between methods done by Shilton compared to Ismail was the coated membrane was applied by flooding the membrane skin layer surface with 3% w/w solution of the silicone in n-hexane for 15 min. After done coating, the membranes were placed in an oven at 60°C for 4 hours to allow curing prior the gas permeation testing (Ismail, 2003).

2.8.2.2 Polysulfone Membrane Treated With Molecular Bromine

Melt-extruded polysulfone films (5 mil or 125µm in nominal thickness), were treated with an aqueous solution of Br_2 at pH 2 for 24 hr. Bromine water, was purchased from Aldrich Chemical Company. At neutral pH, the equilibrium in bromine water was shifted to bromate and bromide ions. At lower pH, achieved in this study through the addition of sulfuric acid, molecular bromine is favored and the aqueous solution develops a deep color. Upon removal from the bromine solution, the films were washed in distilled water to remove any Br_2 that does not form charge-transfer complexes with the polymer. Once treated in this fashion, the films were dried in a vacuum oven for 24 h at room temperature to remove water and any residual, reversibly-sorbed Br_2. This treatment process resulted in a 20% increase in the thickness of the base film (Barbari, 1995).

2.9 Gas Permeation

The flow of a separation operation by gas permeation was showed in Figure 2.11

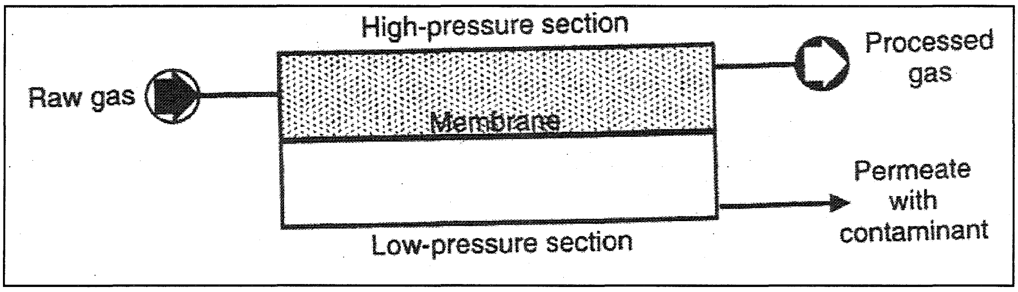

Figure 2.11: Gas Permeation (Durand *et al*, 1997).

The movement of gases through porous structures is fairly well understood. The theory was used in heterogeneous catalysis and adsorption. In this chapter we consider the transport coefficients of gases in structures consisting of either parallel cylindrical pores, or a random packing of equal-sized spheres (Durand *et al*, 1997).

2.10 Gas Permeation Test

In testing the permeation rate for various gases differs for each gases that were tested. According to Lie *et al*, most of the permeation test were run at 30°C and were feed at 2 bar.

Single gases were tested at 30°C and a feed pressure of 2 bar (permeate side evacuated) in a standard pressure-rise setup. The order of testing was always N_2, H_2, CH_4, O_2, CO_2, and finally N_2 again to measure any degree of aging (productivity loss) (Lie *et al*, 2006).

According to A.F Ismail et al, the gas permeation test for CO_2 and CH_4 was carried out at room temperature at 1 bar feed pressure. The test was run after a period of equilibration of 10 min. Stainless steel and double-walled permeation cells were used for the gas permeation tests (Ismail, 2003).

The gas permeation of the membranes was evaluated by fixing a sample into a permeation chamber, pressurizing one side and the measuring the resulting gas transmission rate. The test gases used were pure carbon dioxide and methane. The pressure difference across the membranes modules in the test was 1 bar (Shilton *et al,* 1996).

Tanaka runs a pure (single-component) gas permeation experiment using a vacuum time-lag method to measure permeability coefficient. The efficient membrane area was 18cm^2. The research was carried out at 35°C and upstream pressure of 1 atm with the downstream pressure of less than 0.7cmHg. (Tanaka *et al*, 2006).

The pressure-normalized fluxes of the membranes were determined by a variable volume method using pure oxygen, nitrogen, carbon dioxide and methane at room temperature, 29°C using an upstream pressure of 1 bar. (Ismail *et al*, 2003)

2.11 Design Equations

The simplest model used to explain and predict gas permeation through non-porous polymers is the solution-diffusion model. In this model it was assumed that the gas at the high-pressure side of the membrane dissolves in the polymer and diffuses down a concentration gradient to the low pressure side, where the gas was desorbed. It was further assumed that sorption and desorption at the interfaces was fast compared to the diffusion rate in the polymer. The gas phase on the high and low pressure side was in equilibrium with the polymer interface. The combination of Henry's Law (solubility) and Fick's Law leads to

$$J = \frac{P \times \Delta p}{l} \tag{2.1}$$

where D is the diffusion coefficient of the gas in the polymer, S is the gas solubility, Δp is the pressure difference between the high and low pressure side, l is the membrane thickness and P is the permeability coefficient. According to Knudsen diffusion given by Equation (4)

$$j = \frac{4r\varepsilon}{3} \cdot \left(\frac{2RT}{\pi m}\right)^{1/2} \cdot \frac{p_o - p_\ell}{\ell \cdot RT} \tag{2.2}$$

where m is the molecular weight of the gas, j is the flux in gmol/cm$^2 \cdot$ s, ε is the porosity of the membrane, r is the pore radius, ℓ is the pore length and p_o and p_ℓ are the absolute pressures of the gas species at the beginning of the pore and at the end (Baker, 2004).

2.12 Research Done by Other Researcher

The research findings in membranes for gas separation by various researchers are shown in Table 2.2.

Table 2.2 Researches done in Membrane for Gas Separation.

Researcher	**Membrane/gas properties**	**Result & Findings**
Shilton *et al*,1997	Treated and untreated polysulfone and polyacrylonitrile with effect shear rate for gas separation.	PCO_2=11.03x10^4 $cm^3s^{-1}c^{-2}cmHg^{-1}$ for coated polycrilonitrile. α=6.30 (coated polysulfone) for CO_2/CH_4
Costa *et al*, 1998	MTES membrane coated with alpha alumina.	PCO_2=36.7 GPU, α= 16.68
Ismail *et al*, 1998	Polysulfone hollow fiber for CO_2/CH_4 gas separation	Pure water in the bore :(Low shear) Uncoated PCO_2=60.5, α=1.49; Coated PCO_2=36.13, α=6.41. (High shear)Uncoated PCO_2 =77.7,α=1.84;Coated PCO_2=46.77, α=28.73 Reduced activity in the bore: (Low shear) Uncoated PCO_2=17.5, α=6.35; Coated PCO_2=15.03, α=40.83. (High shear)Uncoated PCO_2=40.97,α=4.06;Coated PCO_2 =28.93, α=65.8
Ng *et al*, 2000	Polysulfone	Uncoated PO_2=13.60, PN_2=2.88, α=4.78 for O_2/N_2; Coated PO_2 =9.08, PN_2=1.48, α=6.38 for O_2/N_2
Ismail *et al*, 2002	Polysulfone for performance of membrane-assisted lead acid battery	The higher the polymer concentration in the casting solution, the thicker the membrane and the deeper the polymer matrixes. Therefore permeability will be lower every time the polymer concentration is increased. The membrane thickness must be reduced to give a higher permeability.
Ismail *et al*, 2006	Treated and untreated asymmetric polysulfone hollow fiber membrane in series and cascade module configurations for	For three-stage series configuration, the pressure-normalized flux of CO_2 was in the range of 7–10 GPU with CO_2/CH_4 selectivity of about 13–19. For cascades configuration, the

	CO_2/CH_4 gas separation system	pressure-normalized flux of CO_2 was in the range of 1.3–1.7 GPU with CO_2/CH_4 selectivity in the range of 20–45.
Tanaka *et al*, 2006	Sulfonated polyamide membranes for gas separation.	Introduction of sulfonic acid groups decreased gas permeability and increased gas selectivity for CO_2/CH_4
Sridhar *et al*, 2007	Polysulfone for gas permeation	$PCO_2 = 15.2$ GPU $PH_2S = 51.6$ GPU and $\alpha=14.4$ for CO_2/CH_4 and $\alpha= 49.1$ for H_2S/CH_4
Scoles *et al*, 2007	Polysulfone	$PCO_2 =4.46$ GPU, $PN_2 =0.18$, $\alpha=24.8$ for CO_2/N_2
Torres-Trueba *et al,*2008	Integrally skinned asymmetric polysulfone for gas separation.	Thickness of dense membrane: 26.16μm,$PO_2= 0.0532$,$PN_2=0.00987$, $\alpha=5.39$ for O_2/N_2
Ahn *et al,*2008	Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation	$PCO_2 =6.3$, $PCH_4 =0.22$, $\alpha=29$ for CO_2/CH_4 $PO_2 = 1.4$, $PN_2 =0.24$, $\alpha=5.6$ for O_2/N_2

The research that was done by Ahn in 2008 using polysulfone polymer that was mixed with silica nanoparticle formed mixed-matrix membranes. The gas used was CO_2, CH_4, O_2 and N_2. The tests were done to examine the separation between CO_2/CH_4 and O_2/N_2. It was proved that by using polysulfone/silica nanoparticle mixed matrix membranes, the value of permeability and selectivity for CO_2 was higher.

2.11.1 Design of Equation for Permeability Test

It was given that to calculate the permeance of the gases that were passing through the membrane, P, permeability is define from the equation below;

$$Permeability, P = \frac{Q}{AP} \tag{2.3}$$

where;

Q= Flow rate of supplied gas (cm^3/s)

A= Area of the membrane (cm^2)

P= Trans membrane pressure (bar)

2.11.2 Design of Equation for Selectivity

Selectivity for the gases that were tested through the membrane can be calculated using Equation (2.3);

$$Selectivity, \Omega = \frac{P_x}{P_{CH_4}} \tag{2.4}$$

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CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Polysulfone

Polysulfone is one of the well known family members of the thermoplastic polymer. This type of polymer is also well known for its toughness and stability at high temperature. Polysulfone contains the subunit aryl-SO_2-aryl, the defining feature of which is the sulfone group. Figure 3.1 shows the structure of polysulfone.

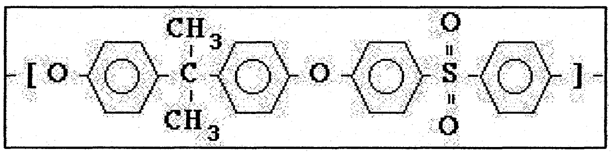

Figure 3.1: Structure of Polysulfone

Polysulfone is not resistant to low-polar organic solvents (eg. ketones and chlorinated hydrocarbons), and aromatic hydrocarbons. It is also stable in aqueous acids and bases and many non-polar solvents; however it is soluble in dichloromethane and methylpyrrolidone. Table 3.1 shows the table of properties for polysulfone.

Polysulfone was selected for the membrane material because of the characteristic and criteria of a good separation medium for gas separation. Polysulfone is well known as an ultrafiltration membrane. In this research, it was an experiment of familiarized polysulfone character for gas permeation. A great advantage of polysulfone properties is that it's resistance in extreme pH conditions as well as its thermal stability. Polysulfone are soluble in chloroform and dimethylformamide, and are easily applied in conventional phase-inversion processes. In this research, the use of solvent for dissolving polysulfone resins are N,N-dimethylformamide and tetrahydrofuran.

Table 3.1 Table of Properties for Polysulfone

Properties	**Values**
Density	1.24 – 1.25 g/cc
Water Absorption	0.2 – 0.8%
Tensile Strength, Ultimate	70-76 MPa
Tensile Strength, Yield	69-80 MPa
Shear Strenght	62 MPa
Specific Heat Capacity	1.2 J/g°C
Thermal Conductivity	0.12-0.26 W/mK
Maximum Services Temperature, Air	149-180°C
Glass Temperature	188-190 °C
Oxygen Index	30-32%
Retaining properties	−100 °C until +150 °C
pH range	2-13

3.1.2 N,N-dimethylformamide

Dimethylformamide is the organic compound with the formula $(CH_3)_2NC(O)H$. Commonly abbreviated DMF, this colourless liquid is miscible with water and the majority of organic liquids. DMF is a common solvent for chemical reactions. Pure DMF is odorless whereas technical grade or degraded DMF often has a fishy smell due to impurity of dimethylamine. The chemical properties were stated in Table 3.2. Its name is derived from the fact that it is a derivative of formamide, the amide offormic acid. DMF is a polar (hydrophilic) aprotic solvent with a high boiling point. Figure 3.2 showed the structure of N,N-dimethylformamide.

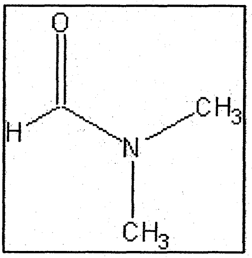

Figure 3.2: Structure of N,N-dimethylformamide

Table 3.2: The Chemical Properties of N,N-dimethylformamide

Chemical Properties	Values
IUPAC Name	N,N-dimethylmethanamide
Other Names	DMF, dimethylformide, N,N-dimethylformide, DMFA
Molecular Formula	C_3H_7NO
Appearance	Clear liquid
Molar Mass	73.09 g/mol
Boiling point (760 mmHg)	153 °C
Melting point (760 mmHg)	-61 °C
Flash point	58 °C

3.1.3 Tetrahydrofuran

Tetrahydrofuran, also known as THF, is a heterocyclic organic compound with the formula $(CH_2)_4O$). It is a colourless low-viscosity liquid with a smell similar to diethyl ether. It is one of the most polar ethers. THF is the fully hydrogenated analog of the aromatic compound furan. The Figure 3.3 shows the structure of tetrahydrofuran and Table 3.3 shows its chemical properties.

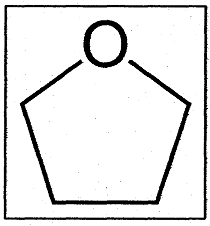

Figure 3.3: Structure of Tetrahydrofuran

THF is an aprotic solvent with a dielectric constant of 7.6. It is a moderately polar, aprotic solvent that dissolves a wide range of nonpolar and polar compounds.

For example, it can be used to dissolve rubber prior to determining its molecular mass using gel permeation chromatography.

Table 3.3: Chemical Properties of Tetrahydrofuran

Chemical Properties	Values
Synonyms	1,4-Epoxybutane; cyclotetramethylene oxide; hydrofuran; oxacyclopentane; tetramethylene oxide; THF.
Appearance and odor	Tetrahydrofuran is a colorless, mobile liquid with a faintly fruity, ether-like odor.
Molecular weight	72.12g/mol
Boiling point	66°C
Specific gravity (water = 1)	0.88 at 20 °C
Melting point	-108.4 °C
Solubility	Soluble in water; miscible with alcohols, ethers, ketones, esters, and hydrocarbons.
Flash point	-14 °C

3.1.4 Ethanol

Ethanol, also called ethyl alcohol, pure alcohol, grain alcohol, or drinking alcohol, is a volatile, flammable, colorless liquid. Ethanol is a straight-chain alcohol, and its molecular formula is C_2H_5OH. Ethanol is often abbreviated as EtOH, using the common organic chemistry notation of representing the ethyl group (C_2H_5) with Et. Ethanol is a versatile solvent, miscible with water and with many organic solvents, including acetic acid, acetone, benzene, carbon tetrachloride, chloroform, diethyl ether,ethylene glycol, glycerol, nitromethane, pyridine, and toluene. It is also miscible with light aliphatic hydrocarbons, such as pentane and hexane, and with aliphatic chlorides such as trichloroethane and tetrachloroethylene. Figure 3.4 shows the chemical structure of ethanol and Table 3.4 is the chemical properties of ethanol.

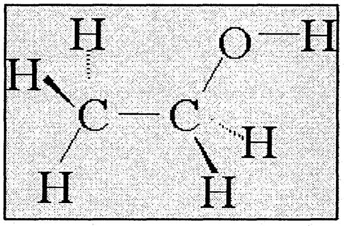

Figure 3.4: Structure of Methanol

Table 3.4: Physical and Chemical Properties of Methanol

Chemical/ Physical Properties	**Values**
Appearance	Clear, colorless liquid.
Solubility	Fully miscible.
% Volatile by volumes at 21°C	100
Boiling point	78.4 °C
Melting point	−114.3°C
Evaporation Rate (BuAc=1)	5.9

3.1.5 Methanol

Methanol, also known as methyl alcohol, carbinol, wood alcohol, wood naphtha or wood spirits, is a chemical compound with chemical formula CH_3OH (often abbreviated MeOH). It is the simplest alcohol, and is a light, volatile, colourless, flammable, poisonous liquid with a distinctive odor that is somewhat milder and sweeter than ethanol (ethyl alcohol). Figure 3.4 shows the chemical structure of methanol.

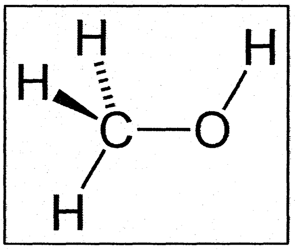

Figure 3.5: Structure of Methanol

At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethyl alcohol. A methanol flame is almost colorless, causing an additional safety hazard around open methanol flames. Table 3.5 shows the chemical and physical properties of methanol.

Table 3.5: Physical and Chemical Properties of Methanol

Chemical/ Physical Properties	**Values**
Appearance	Clear, colorless liquid.
Solubility	Miscible in water.
Specific Gravity	0.8
% Volatile by volumes at 21°C	100
Boiling point	64.5°C
Melting point	-98°C
Evaporation Rate (BuAc=1)	5.9

3.1.6 N-Hexane

Hexane is an alkane hydrocarbon with the chemical formula $CH_3(CH_2)_4CH_3$. The "hex" prefix refers to its six carbons, while the "ane" ending indicates that its carbons are connected by single bonds. Hexane isomers are largely unreactive, and are frequently used as an inert solvent in organic reactions because they are very non-polar. Figure 3.5 shows the chemical structure of hexane.

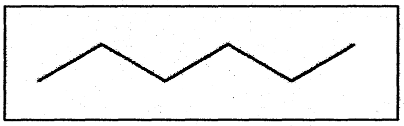

Figure 3.6: The Basic Chemical Structure of Hexane

In laboratories, hexane is used to extract oil and grease from water and soil before determination by gravimetric analysis or gas chromatography. Table 3.6 showed the physical and chemical properties of n-Hexane.

Table 3.6: The Physical and Chemical Properties of n-Hexane

Physical properties	**Value**
Molecular formula	C_6H_{14}
Molar mass	86.18 g/mol
Appearance	Colorless liquid
Density	0.6548 g/ml, liquid
Melting point	−95 °C (178 K)
Boiling point	69 °C (342 K)
Solubility in water	Immiscible
Viscosity	0.294 cP at 25 °C
Flash point	−23.3 °C
Autoignition temperature	233.9 °C

3.1.7 Carbon dioxide, (CO_2)

Carbon dioxide is a molecule with the molecular formula CO_2. The linear molecule consists of a carbon atom that is doubly bonded to two oxygen atoms, O=C=O Although carbon dioxide mainly consists in the gaseous form, it also has a solid and a liquid form. It can only be solid when temperatures are below -78 °C. Liquid carbon dioxide mainly exists when carbon dioxide is dissolved in water. Carbon dioxide is only water-soluble, when pressure is maintained. After pressure drops it will try to escape to air, leaving a mass of air-bubbles in the water. Table 3.7 showed the properties of carbon dioxides.

Table 3.7: Physical Properties of Carbon Dioxide

Properties	**Values**
Molecular weight	44.01g/mol
Specific gravity	1.53 at 21°C
Critical density	468kg/m^3
Concentration in air	370.3 x 10^7 ppm
Water solubility	0.9 vol/vol qt 20 °C

3.1.9 Methane, (CH_4)

Methane is a colourless, odourless gas which is lighter than air. It is formed by the decomposition of organic carbons under anaerobic conditions and is commonly found in or near swamps and wetland areas, peat deposits, woodwastes such as hogfuel, or in the area of old landfills. Figure 3.9 showed the chemical structure of methane.

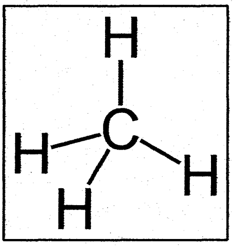

Figure 3.7: The Chemical Structure of Methane

Methane burns in air with a blue flame. We have seen earlier that in sufficient amount of oxygen, methane burns to give carbon dioxide and water. In insufficient oxygen it gives out carbon monoxide. Methane produces a good amount of heat when it undergoes combustion. This is the reason why it is used as fuel. Methane is quite unreactive, except with fluorine, chlorine, etc. With these it undergoes substitution reactions. Table 3.9 showed the properties of methane.

Table 3.9: Properties of Methane

Properties	**Units**
Molecular weight	16.043 g/mol
Melting point	-182.5 °C
Boiling point (1.013 bar)	-161.6 °C
Critical temperature	-82.7 °C
Critical pressure	45.96 bar
Gas density (1.013 bar at boiling point)	1.819 kg/m^3
Autoignition temperature	595 °C

3.1.10 Oxygen, (O_2)

Oxygen is an active, life-sustaining component of the atmosphere; making up 20.94% by volume or 23% by weight of the air we breathe. The word originated from the Greek word oxys and genes meaning sharp or acid and born respectively. Combining these Greek words together forms oxy genes that mean acid forming.

Oxygen can exist in a number of physical forms. The most commonly found state of oxygen is the diatomic form and the triplet state. The diatomic form is molecular oxygen and the triplet state of commonly called ozone. Ozone (O_3), a highly active compound with a name derived from the Greek word for 'I smell', is formed by the action of an electrical discharge or ultraviolet light on oxygen. It exists in all three forms- solid, liquid and gases. The liquid and solid forms are a pale blue color and are strongly paramagnetic. Liquid oxygen is potentially hazardous about flames and sparks as it will greatly accelerate combustion. Nine isotopes of oxygen are known and natural oxygen is a mixture of three isotopes. Table 3.10 showed the properties of oxygen.

Table 3.10: The Properties of Oxygen

Properties	**Values**
Atomic Number	8
Atomic Radius	74 pm
Ionic Radius	140 (O^{2-})
Physical properties	Colorless, odorless, and tasteless.
Boiling point	-183
Meltind Point	-218.4
Electronegativity	3.4
Heat of vaporization	3.4099 kj/mol
Heat of fusion	0.22259 kj/mol

3.1.11 Bromine, (Br_2)

Bromine is a chemical element with the symbol Br and atomic number 35. A halogen element, bromine is a red volatile liquid at standard room temperature that is intermediate in reactivity between chlorine and iodine. Bromine vapours are corrosive and toxic.

Bromine is the only liquid nonmetallic element at room temperature (the other is Mercury) and one of only six elements on the periodic table that are liquid at or close to room temperature. The pure chemical element has the physical form of a diatomic molecule, Br_2. It is a dense, mobile, reddish-brown liquid, that evaporates easily at standard temperature and pressures to give a red vapor (its color resembles nitrogen dioxide) that has a strong disagreeable odor resembling that of chlorine. Bromine is a halogen, and is less reactive than chlorine and more reactive than iodine. Bromine is slightly soluble in water, and highly soluble in carbon disulfide, aliphatic alcohols (such as methanol), and acetic acid. It bonds easily with many elements and has a strong bleaching action. Table 3.11 shows the properties of bromine.

Table 3.11: Table of Properties for Bromine.

Properties	**Values**
Phase	Liquid
Density	3.1028 $g \cdot cm^{-3}$
Melting point	265.8K (-7.2°C, 19°F)
Boiling point	332.0K (58.8°C, 137.8°F)
Critical point	588 K, 10.34 MPa
Heat of fusion	10.571 $kJ \cdot mol^{-1}$
Heat of vaporization	29.96 $kJ \cdot mol^{-1}$
Specific heat capacity	75.69 $J \cdot mol^{-1} \cdot K^{-1}$at 25°C

3.1.12 Polydimethylsiloxane, (PDMS)

Polydimethylsiloxane (PDMS) is the most widely used silicon-based organic polymer, and is particularly known for its unusual rheological (or flow) properties. Its applications range from contact lenses and medical devices to elastomers, in shampoos (as dimethicone makes hair shiny and slippery), caulking, lubricating oils and heat resistant tiles. PDMS is optically clear, and is generally considered to be inert, non-toxic and non-flammable. It is occasionally called dimethicone and is one of several types of silicone oil (polymerized siloxane). The Figure 3.8 shows the chemical bond of PDMS and the Table 3.12 shows the properties PDMS.

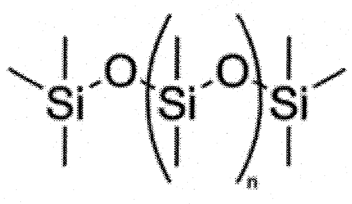

Figure 3.8: The Chemical Structure of Polydimethylsiloxane

Table 3.12: The Properties of Polydiemthylsiloxane

Properties	**Units**
Molecular formula	$(C_2H_6OSi)_n$
Density	965 kg m^{-3}
Melting point	N/A (vitrifies)
Boiling point	below about 200 °C

3.1.13 Iodine, (I_2)

Iodine is a chemical element that has the symbol I and atomic number 53. Naturally-occurring iodine is a single isotope with 74 neutrons. Chemically, iodine is the second least reactive of the halogens, and the second most electropositive halogen; trailing behind astatine in both of these categories. However, the element does not occur in the free state in nature. As with all other halogens, when freed from its compounds iodine forms diatomic molecules (I_2). Table 3.13 showed the physical properties of iodine.

Table 3.13: Physical Properties of Iodine

Properities	**Values**
Phase	solid
Density (near r.t.)	4.933 □g·cm^{-3}
Melting point	113.7□°C
Boiling point	184.3□°C
Triple point	12.1×10^{3}□Pa
Critical point	11.7 MPa
Heat of fusion	(I_2) 15.52 □kJ·mol^{-1}
Heat of vaporization	(I_2) 41.57 □kJ·mol^{-1}
Specific heat capacity	(25□°C) (I_2) 54.44 □J·mol^{-1}·K^{-}

3.2 Research Deisgn

The flowchart of polysulfone membrane preparation and testing were as shown in Figure 3.9.

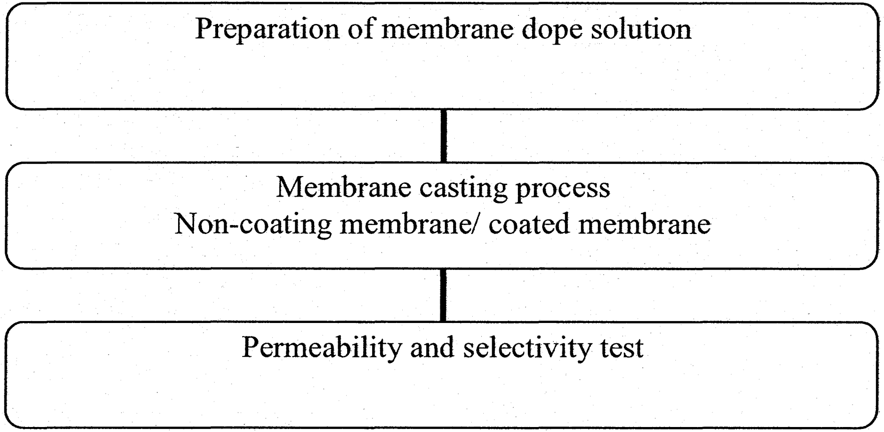

Figure 3.9: Flowchart of Membrane Preparation and Testing

3.3 Membrane Solution/Dope Solution Separation

The polysulfone polymer or resin was first dried for at least 24 hours in an oven at temperature about 140°C before being used for solution making. Drying was done for removing any absorbed water vapor. N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) is the solvents for polysulfone membrane in the making of the dope solution. The ratio of polymer-solvent was 22 wt% polysulfone, 31.8 wt% DMP, 31.8 wt% THF and 14.4 wt% Ethanol as a non-solvent additive. A mixture of 220g of polysulfone with 318ml of DMF, 318ml of THF and 144ml of ethanol were mixed in a round bottom reaction vessel stirred by a motor driven stirrer heated at 50-60°C for 24 hours for homogeneity. The mixture was stirred at 460 to 500 rpm speed. After that, the dope solution was kept in a storage bottle and degassed using ultrasonic bath to remove traces gas bubbles.

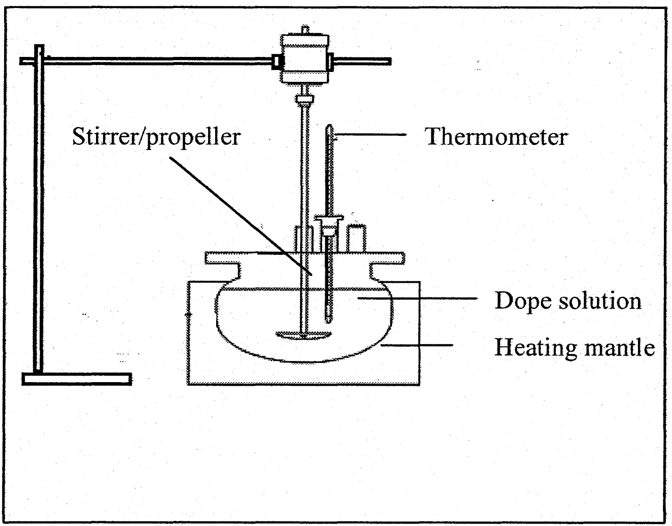

Figure 3.10: Instrument Setup for Dope Solution Preparation

3.4 Turbidity Test

Turbidity titration test was used to determine the cloud point or the equilibrium thermodynamic data on ternary system (polymer/ solvent/ nonsolvent additive). The titration is for indicates the first drop of the nonsolvent i.e distilled water that will result a 'cloudness' in the dope solution. Titration was carried out using an apparatus shown in Figure 3.11.

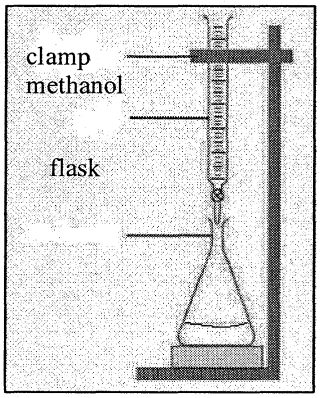

Figure 3.11: Apparatus Set Up for Turbidity Test

3.5 Membrane Casting Process

The dope solution was casted onto a clean glass plate at room temperature using a manual casting knife with a notch height of 100 to 200 µm. Figure 3.13 shows the apparatus used for membrane casting. Once cast, the flat sheet membrane was immersed immediately in a pure water coagulation bath at the two temperatures which was 27°C and 4°C until the membrane peeled off the glass plate. Figure 3.12 shows the steps of immersing the membrane in the water bath. The membranes were left immersed for 24 hours and then were immersed in 50 v/v% methanol for another 24 hours to allow the membrane for curing. After that, the membranes were air-dried for 1 day at room temperature.

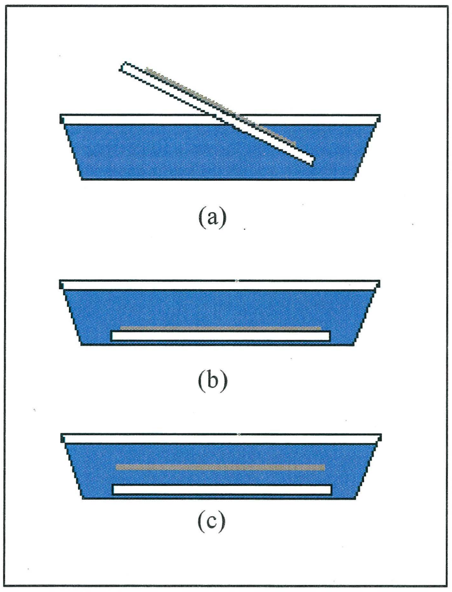

Figure 3.12: (a) Immersed the glass plate 45° from the water surface slowly. (b) The immersed membrane was left for about 10 minutes. (c) The membrane were left until it peeled off by itself

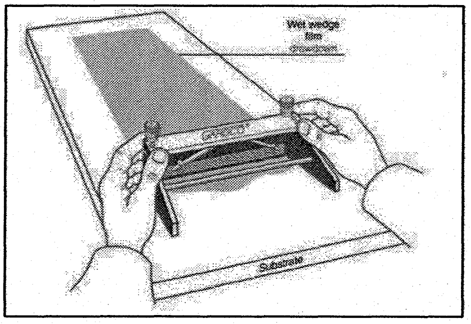

Figure 3.13: Membrane Casting Knife and Glass Plate

3.6 Treatment of Polysulfone Flat Sheet Membrane Preparation

The membranes were treated with three different coating agent which were PDMS, bromine and iodine. The preparation methods for three types of coating agent differs each other.

3.6.1 Treatment of Polysulfone Membrane with Polydimethylsiloxane.

The membrane sheets were coated with polydimethylsiloxane, a higly permeable elastromic silicone polymer. The coating was first prepared by adding 15ml of polydimethylsiloxane with 485ml of n-hexane. Then the coating of membrane was applied by flooding the flat sheet membrane into the solution for 15 min. After coating, the membranes were dried at room temperature to allow curing for 24 hours.

3.6.2 Treatment of Polysulfone Membrane with Molecular Bromine

Bromine water was prepared by mixing it with sulfuric acid to achieve pH 2 and as a result an aqueous solution with a light yellowish colour. Once done, the same application is applied to the membrane sheets. The membrane was deep in the solution for 24 hours. The treated membranes were washed with distilled water and then dry at room temperature. The membranes were all light yellow in colour after treated with Br_2.

3.6.3 Treatment of Polysulfone Membrane with Molecular Iodine

Iodine water was prepared by mixing it with sulfuric acid to achieve pH 2 and an aqueous solution with a deep orange colour was achieved. Once done, the same application is applied to the membrane sheets. The membranes were deep in the solution for 24 hours. The treated membranes were washed with distilled water and then dry at room temperature. The membranes were all deep orange in colour after the I_2 treatment.

3.7 Permeability Test

The flat sheet polysulfone membrane that has been casted either coated or non-coated, were then put in the permeation cell or permeation chamber for permeation test for various gases. The shining surface was faced down facing the inner chamber. The membrane sheets were cut according the size of the permeation chamber. The gases that were purged in the permeation cell were O_2, N_2, CO_2, and CH_4. The input pressure for the various gases is set from 1.5-2.0 bar. The experiment was carried out at room temperature. The permeate volumetric flow rate is measured using a soap bubble flow meter. Readings of the flow meter was taken for results of permeability test. Figure 3.14 shows the apparatus used to run the permeation test for the various gases.

Figure 3.14: Membrane Gas Permeation Unit

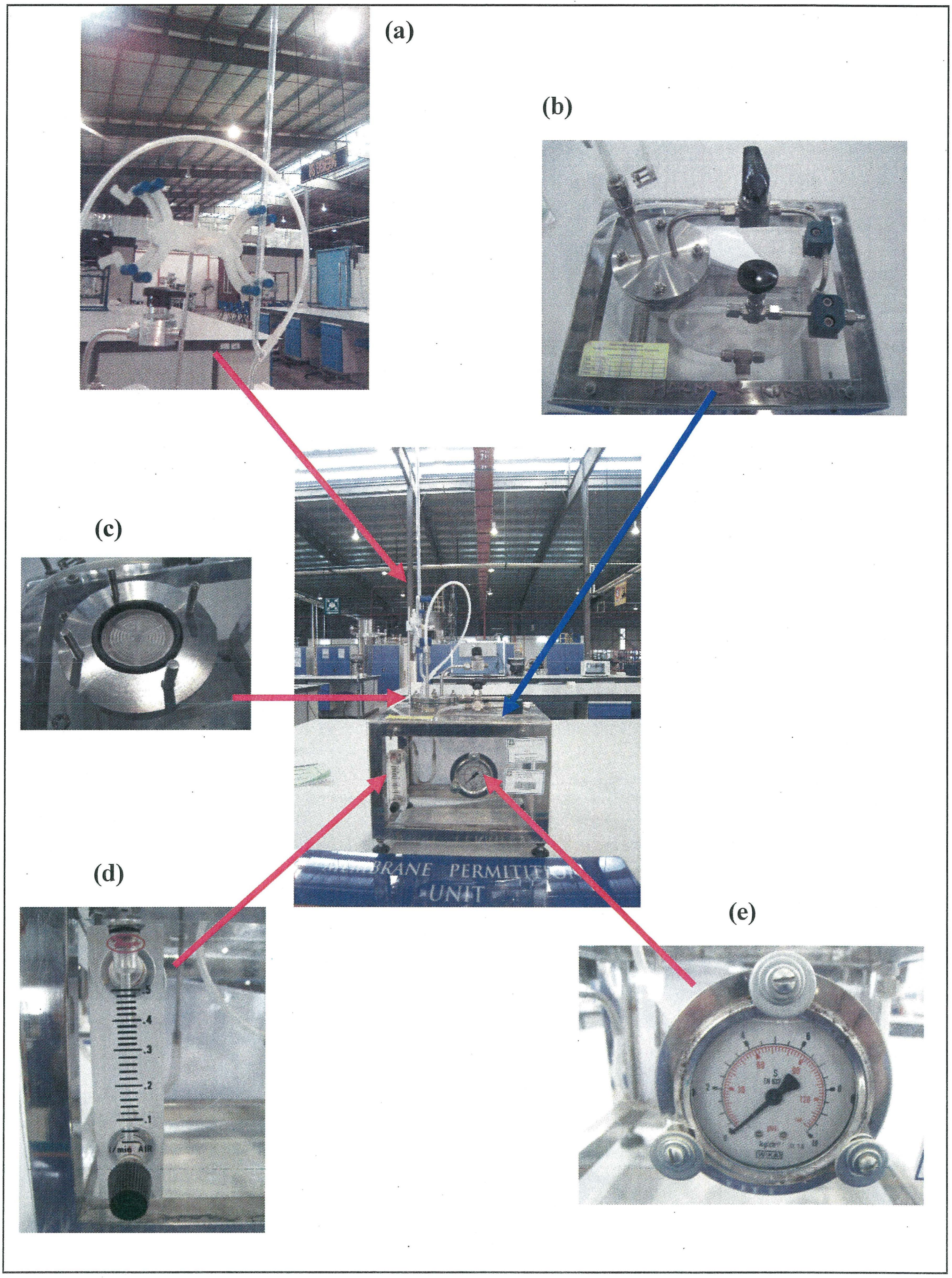

Figure 3.15: Gas permeation unit; (a) permeance gas meter; (b) Top view of the unit; (c) Permeating chamber; (d) volumetric flow meter; (e) pressure meter.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result and Discussion

From all the polysulfone membrane prepared and tested, the results were then classified into two categories. The permeability and selectivity of the various gases are affected by two of the parameters changed in the experiments.

4.1.1 Temperature difference of coagulation water bath

Lowering the temperature of the coagulating system would result a smaller pores membrane and vice versa. The permeability of the gases would be affected directly, where as the smaller the pores, the membrane would perform better in permeating the gases that pass through the membrane. Table 4.1 showed the permeability and also the selectivity of gases at two different temperatures.

Table 4.1: Permeability and selectivity for uncoated polysulfone membrane immersed in 27°C and 4°C water bath

Temperature of Coagulant	**Uncoated**						
	CO_2		CH_4	N_2		O_2	
	P/ℓ	S, CO_2/CH_4	P/ℓ	P/ℓ	S, N_2/CH_4	P/ℓ	S, O_2/CH_4
27	13.83	0.62	22.27	21.77	0.98	18.26	0.82
	27.91	0.44	63.04	22.54	0.36	30.5	0.48
	33.77	1.15	29.46	23.24	0.79	19.57	0.66
Mean	**25.17**	**0.74**	**38.26**	**22.52**	**0.71**	**22.77**	**0.66**
4	13.72	0.85	16.11	10.13	0.63	11.03	0.68
	25.14	0.84	30.05	17.73	0.59	12.57	0.42
	13.68	0.62	22.03	12.09	0.55	12.21	0.55
Mean	**17.51**	**0.77**	**22.73**	**13.32**	**0.59**	**11.93**	**0.55**

**(P/l)GPU =measured in unit of* $cm^3/s.cm^2cmHg$*; GPU=1 x* 10^{-6} $cm^3/s.cm^2cmHg$*, S=Selectivity*

Polysulfone (PSU) membrane that was immersed in 4°C coagulant gave the highest permeability for CH_4 gas followed by CO_2, N_2, and O_2 respectively. At 4°C the permeability of CH_4, CO_2, O_2, and N_2 were 2.27 x 10^{-4}, 1.75 x 10^{-4}, 1.33 x 10^{-4}, and 1.19 x 10^{-4} $cm^3s^{-1}cm^{-2}cmHg$ respectively. At 27°C the permeability increased by ±30-40% where the permeability for CH_4 CO_2, O_2, and N_2 were 3.83 x 10^{-4}, 2.52 x 10^{-4}, 2.28 x 10^{-4}, and 2.25 x 10^{-4} $cm^3s^{-1}cm^{-2}cmHg$ respectively.

Smaller pore size can be achieved by lowering the temperature of coagulating bath. Asymmetric membrane has a dense non-porous top layer and open porous structure. Thus, adjusting the coagulating bath affected the membrane formation structure. Porous layer of the membrane can have an open-pore or closed-pore structure depending on the coagulation temperature. At higher temperature an open-pore structure was formed (Ohya *et al,* 1996). Rationally, small openings of the membrane's pores gave a smoother pathway for smaller molecular sized atoms. This scenario can be explained in Table 4.2 that showed the diverse range of molecular diameter of gases used.

Table 4.2: Molecular Diameter (Katz *et al,* 1959).

	Molecular Diameter (A)
Methane	3.35-3.88
Carbon Dioxide	3.996
Nitrogen	3.36-3.68
Oxygen	1.9-3.433

1 angstrom (A) =10^{-8}*cm*

From Table 4.2, it was clearly stated that molecular diameter of the gases itself also result a better permeation. CO_2 has the highest molecular diameter followed by CH_4, N_2 and O_2. Smaller diameter molecules tend to have low value of permeability because small molecules can pass through the small pores membranes. In other way of explaining, bigger molecules were trapped within the small pores resulting higher value of permeability. According to Knudsen's Equation (Eq 2.2), it can be expressed that flux of the membrane that was correlated with permeability can be affected with several parameters. From Eq 2.2, low membrane porosity and low pore radius can result a low flux value of the membrane simultaneously lower the permeability value.

The permeability plays an important role towards selectivity where as when lower permeability would result higher selectivity. It was proven that performance of membrane that were immersed in a lower temperature coagulating system were superior to the performance if membrane that were immersed in a higher temperature coagulating bath.

4.1.2 Effect of membrane treatment

The previous research showed that the treatment of membrane coating affect the permeability and selectivity of the membrane. The test was run with three types of coating which were polydimethylsiloxane (PDMS), bromine water (Br_2) and also iodine water (I_2). Table 4.3 showed the permeability and selectivity of gases for treated polysulfone membrane

Table 4.3: Permeability and selectivity for treated polysulfone membrane immersed in 27°C water bath

	Uncoated						
	CO_2		CH_4	N_2		O_2	
	P/ℓ	S, CO_2/CH_4	P/ℓ	P/ℓ	S,N_2/CH_4	P/ℓ	S,O_2/CH_4
1	13.83	0.62	22.27	21.77	0.98	18.26	0.82
2	27.91	0.44	63.04	22.54	0.36	30.5	0.48
2	33.77	1.15	29.46	23.24	0.79	19.57	0.66
Mean	**25.17**	**0.74**	**38.26**	**22.52**	**0.71**	**22.77**	**0.66**
	Coated with Br_2						
	CO_2		CH_4	N_2		O_2	
1	P/ℓ	S,CO_2/CH_4	P/ℓ	P/ℓ	S,N_2/CH_4	P/ℓ	S,O_2/CH_4
2	11.83	0.58	20.37	11.58	0.57	11.86	0.58
2	31.45	0.64	49.24	19.01	0.59	34.85	0.59
Mean	11.55	0.79	14.67	10.19	0.69	11.39	0.78
	18.28	**0.67**	**28.09**	**16.92**	**0.62**	**19.7**	**0.65**
	Coated with I_2						
	P/ℓ	S, CO_2/CH_4	P/ℓ	P/ℓ	S,N_2/CH_4	P/ℓ	S,O_2/CH_4
1	8.03	0.73	11	7.05	0.64	7	0.64
2	17.99	0.63	28.38	16.05	0.57	17.49	0.62
3	8.56	0.78	11.01	7.1	0.65	6.97	0.63
Mean	**17.29**	**0.71**	**25.2**	**15.1**	**0.62**	**15.73**	**0.63**
	Coated with PDMS						
	P/ℓ	S,CO_2/CH_4	P/ℓ	P/ℓ	S,N_2/CH_4	P/ℓ	S,O_2/CH_4
1	1158.31	0.61	1892.37	561.7	0.3	576.31	0.3
2	876.51	1.68	522	404.26	0.77	227.21	0.44
3	806.49	0.96	1357.2	648.28	0.48	651.99	0.48
Mean	**947.1**	**0.96**	**1257.19**	**538.05**	**0.52**	**485.17**	**0.41**

(P/l)GPU =measured in unit of $cm^3/s.cm^2cmHg$*; GPU=1 x* 10^{-6} $cm^3/s.cm^2cmHg$*, S=Selectivity*

PSU membrane that was treated with PDMS gave the highest permeability for CH_4 gas followed by CO_2, N_2, and O_2 respectively. The mean value of permeability for CH_4, CO_2, O_2, and N_2 were 12.5 x 10^{-3}, 9.47 x 10^{-3}, 5.38 x 10^{-3}, and 4.85 x 10^{-3} $cm^3s^{-1}cm^{-2}cmHg$ respectively.

By treating the membrane with coating agent, it gave an effect to the membrane performance. The PSU membrane treated with PDMS was superior compared to untreated PSU membrane. From Table 4.3, it can be showed that higher permeability can be achieved using PDMS as a coating agent. PDMS showed the highest gas permeability in rubbery polymers and had been considered as the most permeable polymer. PDMS character as a rubbery polymer is different than PSU which is a glassy polymer. In term of selectivity, PSU selectivity is dominantly diffusivity selectivity whereas PDMS selectivity is dominantly solubility selectivity (Tanabe, 1999). Permeability is the product of the diffusivity and solubility parameters, and characterizes a penetrant's ability to move across a membrane of given thickness under a given differential pressure drive force (Koros, 1991). The combination of PSU and PDMS as a coating agent showed the clash of different characters of polymer that produced a better performance membrane. PDMS acts as a coating agent where it closed up pores or defected area on the membrane resulting a better permeation to happen. It created a defect-free membrane compared to other coating agent.

On the other hand, Br_2 and I_2 had shown a different character as a coating agent. As halogens, both coating agent showed the permeability of PSU treated decreased compared to untreated PSU which increased the value of selectivity. Relatively small decreasing in CO_2 permeability indicated that the presence of Br_2 molecules in the polymer matrix affects the free volume distribution in a manner that influences the transport of CH_4 to a greater extent than the CO_2. It was evident that Br_2 treatment does improve the transport properties of PSU membranes (Barbari, 1995). The presence of I_2 in the polymer matrix affected the formation of membrane structure. From Table 4.3, clearly showed that coating PSU with I_2 gave a lower permeability and higher selectivity compared to coating PSU with Br_2. This explains that heavier halogens produced more free volume to the membrane.

4.1.3 Effect of Coagulation Temperature and Membrane Treatment

Both factors coagulation bath temperature and membrane treatment affected the membrane performance as a whole. By immersing PSU membrane in coagulation bath at lower temperature and then been treated in various coating agent gave a major impact towards PSU membrane's performance. Table 4.4 showed the permeability and selectivity for untreated and treated polysulfone membrane immersed in 4°C and 27°C water bath.

Table 4.4: Permeability and selectivity for untreated and treated polysulfone membrane immersed in 4°C and 27°C water bath

	CO_2		CH_4	N_2		O_2		**Coagulating Bath Temperature**
	P/ℓ	**S, CO_2/CH_4**	**P/ℓ**	**P/ℓ**	**S, N_2/CH_4**	**P/ℓ**	**S, O_2/CH_4**	
Uncoated	17.51	0.77	22.73	13.32	0.59	11.93	0.55	**4**
Coated with Br_2	28.09	0.7	42.72	27.27	0.66	21.56	0.64	
Coated with I_2	18.32	0.81	25.21	15.51	0.66	13.55	0.63	
Coated with PDMS	498.29	1.36	367.47	376.74	1.02	271.23	0.69	
Uncoated	25.17	0.74	38.26	22.52	0.71	22.77	0.66	**27**
Coated with Br_2	18.28	0.67	28.09	16.92	0.62	19.70	0.65	
Coated with I_2	17.29	0.71	25.2	15.1	0.62	15.73	0.63	
Coated with PDMS	947.1	0.96	1257.19	538.05	0.52	485.17	0.41	

(P/l)GPU =measured in unit of $cm^3/s.cm^2cmHg$*; GPU=1 x* 10^{-6} $cm^3/s.cm^2cmHg$*, S=Selectivity*

It was showed from Table 4.4 that at 4°C the permeability decreases about 50% and selectivity increase about 30% compared to PSU membrane immersed in 27°C coagulation bath. At 4°C, the permeability for CO_2, CH_4, N_2 and O_2 were 4.98×10^{-3}, 3.67×10^{-3}, 3.77×10^{-3}, and 2.71×10^{-3} $cm^3s^{-1}cm^{-2}cmHg$ respectively.

The results stated in Table 4.4 emphasized that with the structure of membrane that were effected by the coagulation bath temperature and also the coating agent, a superior membrane performance can be achieved. As mentioned earlier, lowering the coagulation bath temperature produced the membrane pores to be most likely smaller than normal. Thus, bigger gas molecules were trapped before going through the membrane and at the same time, lowering the value of permeability of that gas.

By utilizing a suitable coating agent to treat the membrane, a defect free membrane can be achieved and thus, result a higher value of selectivity towards the desired gas. Among three types of coating agent were used, PDMS showed the highest selectivity and lower permeability towards CO_2.

The combination of coagulating bath temperature and also a perfect coating agent has proved that the membrane performance can be optimized by these two parameters. Figure 4.1 showed the performance of PSU membrane selectivity.

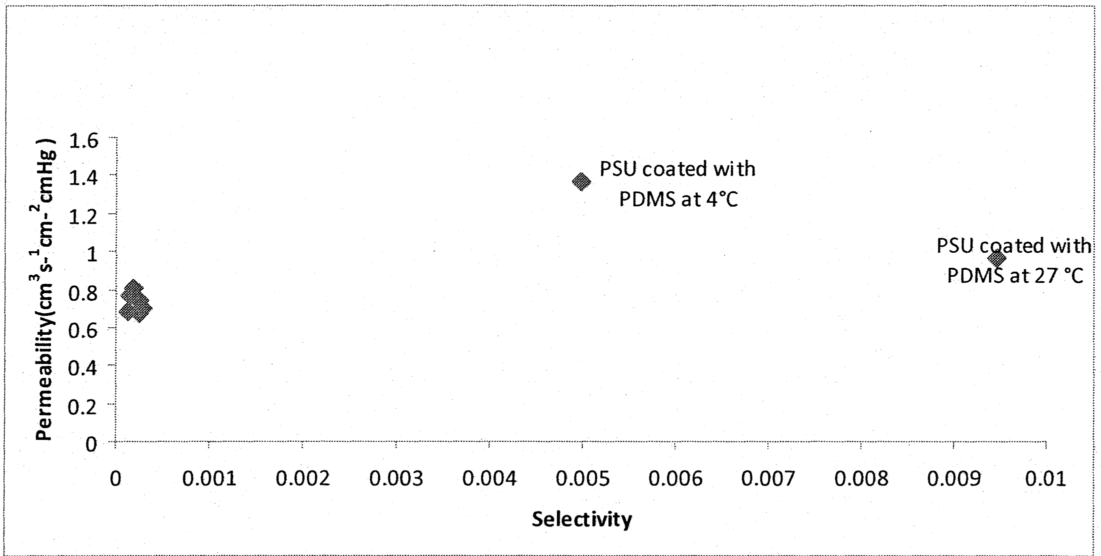

Figure 4.1: Selectivity CO_2/CH_4 vs Permeability CO_2

Figure 4.1 showed the selectivity of CO_2 in opposition to permeability CO_2 and from this figure it can be concluded that the best condition of PSU membrane to have a high permeability and a high selectivity was PSU membrane immersed in a 4°C coagulating bath and treated with PDMS. Other condition only gave end result, a range of permeability from 0.6 to 0.83 cm^3/s.cm.cmHg and a range of selectivity from 0.001 to 0 which was actually very poor performances.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the entire test that has been done, it was claimed that with various parameters set up for the experiments, it showed that PSU membrane is one of the membrane that perform well in separating CO_2. From the expertiment, PSU membranes that were immersed in different coagulation bath temperature and also PSU that were treated with three types of coating agent were produced. The performance determination of CO_2 separation study was successfully completed.

All the data collection and results were consistent with literature studies. In this observation, the temperature of coagulation bath and also the coating agent used in treating the membrane create an impact toward PSU membrane permeability and also its selectivity. It was found that the best performance condition of the PSU membrane immersion in a 4°C coagulation bath and was treated with PDMS. This condition has given the best permeability value of 498.29 GPU and a selectivity value of 1.36. Among all data collected, the lowest permeability value obtained was 17.29 GPU (PSU membrane immersed in 27°C and coated with I_2) and the lowest selectivity was 0.67 (PSU membrane immersed in 27°C and coated with Br_2).

From the result data and supported theories by various researchers, it can be concluded that permeability and selectivity of CO_2 gas was affected by two parameters which were the temperature of the coagulation bath and also the coating agent for PSU membrane treatment.

5.2 Recommendation

The conventional method of making the membrane is economical, simple yet time consuming. PSU membrane has the ability and credibility to become one of the membranes that can be use in the industry for CO_2 separation. Casting or fabricating the membrane manually using human hands can not bring the optimum efficiency of the membrane surface. Thus, with proper fabrication i.e using automatic casting machines can overcome the dilemma of having defected surfaces of membrane.

There were several polymers that can be tested for further research in solving the dilemma of CO_2 separation. A recommendation in future, that the study should be used polytrimethylsilylprpopyne (PTMSP) to replace polysulfone (PSU) as membrane material. PTMSP may have a broad opportunity to separate CO_2 in gas separation. All the parameter tested in this experiment should be tested to PTMSP to see the outcomes and it can be compared to PSU membranes.

Further studies were needed in order to expand the knowledge in chemical or related industries. Research on differentiations of permeability and other parameters of PSU membrane can also be applied to other related or similar type of membrane as to PSU. The study of this related topic also has to emphasize in improving the emerging technology such as CO_2 membrane separation can be produced for industrial purposes.

The contribution of PSU membrane as in their character, price, feasibility of easy handling and performances can enhance economic status of any industry that wanted to isolate CO_2 in their products. May this research will help lighter the burden of the industry and make membrane gas separation prosper and developed for future purposes.

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