

**PERMEABILITY AND SELECTIVITY OF HYBRID MEMBRANE
(PES/PSU) FOR GAS SEPARATION**

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BORANG PENGESAHAN STATUS TESIS♦

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(PES/PSU) FOR GAS SEPARATION.**

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**PERMEABILITY AND SELECTIVITY OF HYBRID MEMBRANE (PES/PSU)
FOR GAS SEPARATION**

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A report submitted in partial fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

**Faculty of Chemical Engineering & Natural Resources
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APRIL 2009

I declare that this thesis entitled “Permeability and Selectivity of Hybrid Membrane (PES/PSU) 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 : 30 APRIL 2009

Dedicated to my beloved father, mother, and family....

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ABSTRACT

A hybrid membrane (PES/PSU) was prepared through a simple dry/wet phase inversion process. The casting solution developed in this research consists of PES, PSU, 1-methyl-2-pyrrolidone (NMP) and methanol. Hybrid membrane (PES/PSU) is divided into three categories; uncoated, coated with polydimethylsiloxane (PDMS) and coated with bromine solution. Permeation test was carried out by testing CO₂, CH₄, N₂ and O₂ onto the hybrid membrane to see the permeability and selectivity of the respective gas to CH₄. Different coating agent gives different rate of permeate to the hybrid membrane. The hybrid membrane (PES/PSU) that coated with PDMS shows higher selectivity compared to conventional hybrid membrane and hybrid membrane that coated with bromine solution. The selectivity of CO₂/CH₄ is approximately 0.563, it is believed that different coating agent strongly affects the hybrid membrane performance.

ABSTRAK

Membran hibrid (PES/PSU) telah disediakan menggunakan teknik yang ringkas iaitu penyongsangan fasa basah/kering. Larutan bahan teracuan yang disediakan untuk kajian ini mengandungi PES, PSU, 1 metil 2 pyrolidone (NMP) dan metanol. Membran hibrid (PES/PSU) adalah dibahagi kepada tiga kategori; tidak ditutup, disalutkan dengan polidimetilsiloksana (PDMS) dan disalutkan dengan larutan bromin. Ujian penelapan telah dijalankan dengan menguji gas CO₂, CH₄, N₂ dan O₂ ke atas membran hibrid untuk melihat ketelapan dan pemilihan bagi setiap gas terhadap gas CH₄. Ejen salutan berbeza memberi nilai ketelapan yang berbeza kepada membrane hibrid. Membran hibrid yang bersalut dengan PDMS menunjukkan pemilihan lebih tinggi berbanding dengan membran hibrid konvensional dan membran hibrid yang bersalut dengan larutan bromin. Pemilihan bagi CO₂ / CH₄ adalah 0.563 dimana dipercayai bahawa ejen salutan mempengaruhi prestasi membran hibrid.

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LIST OF ABBREVIATIONS

CO ₂	-	Carbon dioxide
PES	-	Polyethersulfone
PSU	-	Polysulfone
PDMS	-	Polydimethylsiloxane
NMP	-	N-Methyl-2-pyrrolidone
O ₂	-	Oxygen
N ₂	-	Nitrogen
H ₂	-	Hydrogen
Cl	-	Chlorine
H ₂ S	-	Hydrogen sulfide
C ₂	-	Carbon
J	-	Flowrate of gas through membrane
ℓ	-	The effective thickness of separation layer
D	-	Diffusion coefficient in membrane
ΔC	-	Concentration difference of gas in membrane
S	-	Solubility coefficient
P	-	External gas partial pressure
P/ℓ	-	Gas permeance
P	-	Permeability coefficient of separation layer
A	-	Membrane surface area
Δp	-	Pressure difference of penetrant across membrane
α	-	Selectivity of gas
SEM	-	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural gas is a gaseous fossil fuel consisting primarily of methane but including significant quantities of ethane, propane, butane, and as well as carbon dioxide, nitrogen, helium and hydrogen sulfide. It is found in oil fields either dissolved or isolated in natural gas fields, and in coal beds. When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas. Sources of biogas include swamps, marshes and landfills as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle (Rojey A. *et al.*, 1997).

In separation of gases, membranes offer the greatest potential. In interaction with a membrane, a high degree of permeability coupled with a large selectivity of a specific gaseous species ensures superior performances in the gas processing industry. Economically, the advantage of membrane separation technology is immense. The separation of natural gas by thin barriers termed as membranes is a dynamic and rapidly growing field, and it has been proven to be technically and economically superior to other emerging technologies. This superiority is due to certain advantages which membrane technology benefits from, including low capital investment, low weight, and space requirement and high process flexibility (Kohl *et al.*, 1997). In the past ten years the membrane gas separation technology has advanced greatly and can now be regarded as a competitive industrial gas separation method.

A high permeability and selectivity can be achieved by conducting a permeation test towards the gases. However, in the reality, a high permeability contributes to low selectivity and vice versa. Therefore, we can't expect the excellent result but we can improve the selectivity if it gives the high permeability. One method of improving it is by using the method of coating the membrane. Coating may lessen the defect skin layers which happen in the structure of membrane.

1.2 Problem Statement

Carbon dioxide (CO₂) which falls into the category of acid gas is commonly found in natural gas streams at levels as high as 80%. In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO₂ must be removed to prevent freezing in the low-temperature chillers (Tobin J., 2006).

A wide variety of acid gas removal technologies are available. They include absorption processes; cryogenic processes; adsorption processes; and membranes. Each process has its own advantages and disadvantages, but membranes increasingly are being selected for newer projects, especially for applications that have large flows, have high CO₂ contents, or are in remote locations.

Membranes have been widely used in two main CO₂ removal applications:

- Natural gas sweetening
- Enhanced oil recovery (EOR), where CO₂ is removed from an associated natural gas stream and reinjected into the oil well to enhance oil recovery

However the major problems confronting the use of the membrane based gas separation processes in a wide range of applications is the lack of membranes with high permeability and high selectivity. Therefore, a membrane which has high permeability and also not depleting in the level of selectivity is sought off in order to overcome this problem.

1.3 Objective of Study

The objective of this research is to study the permeability and selectivity Hybrid membrane (PES/PSU) using gases (N₂, CO₂, CH₄ and O₂) and to study the performance of Hybrid membrane treatment using coating and uncoating method.

1.4 Scope of Study

The scopes which need to be focused in order to meet the objective are:

- i. Develop and study the permeability and selectivity of the Hybrid membrane (PES/PSU) for gas separation
- ii. Study the effect of Hybrid membrane permeability and selectivity by coating and uncoating in order to reduce the defect skin layers.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Gas

Natural gas is a mixture of hydrocarbons, predominantly methane (CH₄). Most natural gas is extracted from gas and oil wells. Much smaller amounts are derived from supplemental sources such as synthetic gas, landfill gas and other biogas resources, and coal-derived gas. Natural gas that comes from oil wells is typically termed 'associated gas'. This gas can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). Natural gas from gas and condensate wells, in which there is little or no crude oil, is termed 'non-associated gas'. Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate (Rojey A. *et al.*, 1997).

Natural Gas that has been processed is a gaseous fossil fuel consisting primarily of methane and including significant quantities of ethane, propane, butane, and pentane. It did not contain heavier hydrocarbons because they were removed prior to use as a consumer fuel as well as carbon dioxide, nitrogen, helium and hydrogen sulfide. It is found in oil fields (associated) either dissolved or isolated in natural gas fields (non-associated), and in coal beds (as coalbed methane). When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas.

Sources of biogas include swamps, marshes, and landfills (see landfill gas), as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle.

2.2 Membrane Separation Process

Membrane separation processes have emerged during the last two decades as a promising alternative to some conventional separation processes and offer a number of important advantages for upgrading of crude natural gas. Essentially, a membrane can be defined as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane while the other is the gas concentrated flow out the reject stream.

Membrane separation process enjoys numerous industrial applications with the following advantages (Kohl *et al.*, 1997):

- Appreciable energy savings
- Environmentally benign
- Clean technology with operational ease
- Replaces the conventional processes like filtration, distillation, ion-exchange and chemical treatment systems
- Produces high, quality products
- Greater flexibility in designing systems.

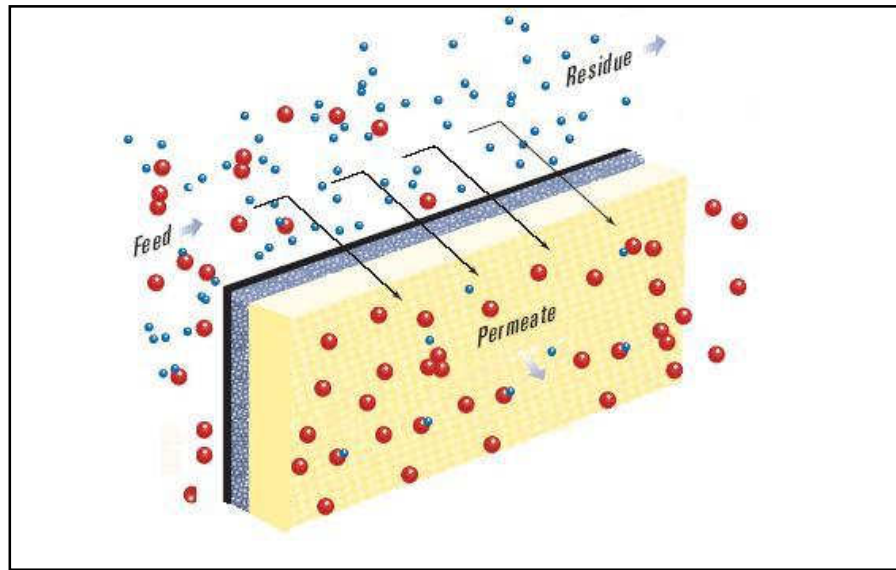


Figure 2.1: Schematic diagram of membrane separation process

Figure 2.1 show the mechanism of the transport of gases through nonporous membranes involves the following action (Kohl *et al.*, 1997):

- adsorption of the gas at one surface of the membrane,
- solution of the gas into the membrane,
- diffusion of the gas through the membrane,
- release of the gas from solution at the opposite surface, and
- desorption of the gas from the surface (permeate).

2.3 Type of Membrane Separation Process

Currently, there are seven type of membrane separation process which are reverse osmosis, nanofiltration, ultrafiltration, microfiltration, electrodialysis, gas permeation in a membrane and pervaporation. This membrane separation process is classified based on pore size (Srikanth G., 1999).

2.3.1 Reverse Osmosis (RO)

Reverse Osmosis (RO) is a pressure driven membrane diffusion process for separating dissolved solutes. The RO is generally used for desalination seawater for its conversion into potable water. The salient features of the process are that it involves no phase change and it is relatively a low energy process. Compared to water filtration, which can only remove some suspended materials larger than 1 micron, the process of RO will eliminate the dissolved solids, bacteria, viruses and other germs contained in the water. Almost all RO membranes are made polymers, cellulose acetate and matic polyamide types rated at 96% to 99% NaCl rejection. RO membranes are generally of two types, asymmetric or skinned membranes and thin film composite (TFC) membranes. The support material is commonly polysulfones while the thin film is made from various types of polyamines, polyureas etc.

RO membranes have the smallest pore structure, with pore diameter ranging from approximately $5-15 \text{ \AA}^0$ (0.5 nm - 1.5 nm). The extremely small size of RO pores allows only the smallest organic molecules and unchanged solutes to pass through the semi-permeable membrane along with the water. Greater than 95-99% of inorganic salts and charged organics will also be rejected by the membrane due to charge repulsion established at the membrane surface. Figure 2.2 shows the schematic diagram of reverse osmosis (Srikanth G., 1999).

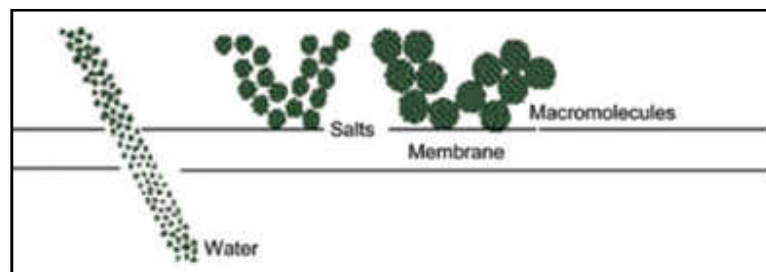


Figure 2.2: Reverse osmosis membrane process

2.3.2 Nanofiltration (NF)

Nanofiltration (NF) is a form of filtration that uses membranes to separate different fluids or ions. NF is typically referred to as "loose" RO due to its larger membrane pore structure as compared to the membranes used in RO, and allows more salt passage through the membrane. Because it can operate at much lower pressures, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removals are desired. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1000 daltons.

Membranes used for NF are of cellulosic acetate and aromatic polyamide type having characteristics as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate 300 molecular weight cut-off (MWCO) for organics. An advantage of NF over RO is that NF can typically operate at higher recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate. NF is not effective on small molecular weight organics, such as methanol (Srikanth G., 1999). Figure 2.3 shows the schematic diagram of nanofiltration process.

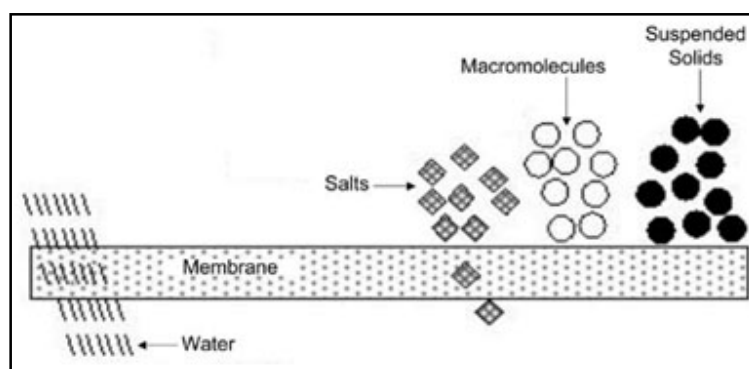


Figure 2.3: Nanofiltration membrane process.

2.3.3 Ultrafiltration (UF)

Ultrafiltration (UF) is used to separate a solution that has a mixture of some desirable components and some that are not desirable. UF is somewhat dependent on charge of the particle, and is much more concerned with the size of the particle. Typical rejected species include sugars, bio-molecules, polymers and colloidal particles. The driving force for transport across the membrane is a pressure differential. UF processes operate at 2-10 bars though in some cases up to 25-30 bars have been used. UF processes perform feed clarification, concentration of rejected solutes and fractionation of solutes. UF is typically not effective at separating organic streams.

UF membranes are capable of retaining species in the range of 300-500,000 daltons of molecular weight, with pore sizes ranging from 10-1000 Angstroms (10^3 -0.1 microns). These are mostly described by their nominal molecular weight cutoff (1000-100,000 MWCO), which means, the smallest molecular weight species for which the membranes have more than 90% rejection (Srikanth G., 1999). Figure 2.4 shows the schematic diagram of ultrafiltration process.

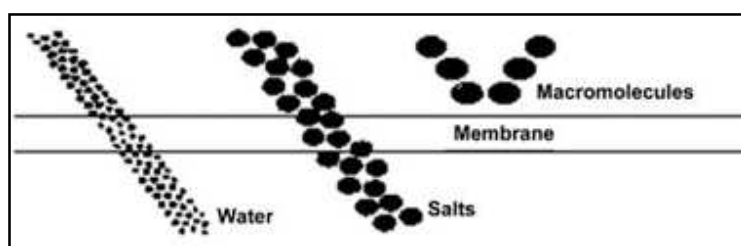


Figure 2.4: Ultrafiltration membrane process.

2.3.4 Microfiltration (MF)

Microfiltration (MF) is a process of separating material of colloidal size and larger than true solutions. A MF membrane is generally porous enough to pass molecules of true solutions, even if they are large. Microfilters can also be used to sterilize solutions, as they are prepared with pores smaller than 0.3 microns, the diameter of the smallest bacterium, *pseudomonas diminuta*. It is essentially a sterile filtration with pores (0.1-10.0 microns) so small that micro-organisms cannot pass through them.

MF membranes use *sieving mechanism* with distinct pore sizes for retaining larger size particles than the pore diameter. Hence, this technology offers membranes with absolute rating, which is highly desirable for critical operations such as sterile filtration of parental fluids, sterile filtration of air and preparation of particulate, free-water for the electronics industry.

The MF membranes are made from natural or synthetic polymers such as cellulose nitrate or acetate, polyvinylidene difluoride (PVDF), polyamides, polysulfone, polycarbonate, polypropylene, PTFE etc. The inorganic materials such as metal oxides (alumina), glass, zirconia coated carbon etc. are also used for manufacturing the microfiltration membranes (Srikanth G., 1999). Figure 2.5 shows the schematic diagram of microfiltration process.

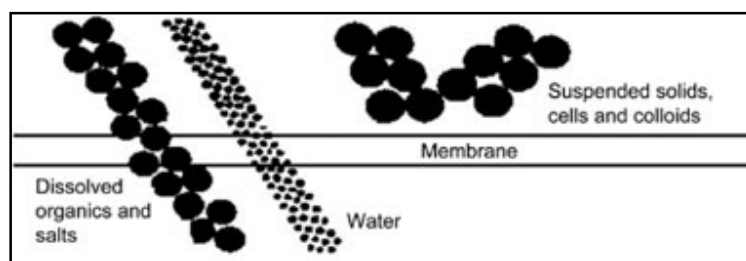


Figure 2.5: Microfiltration membrane process.

2.3.5 Electrodialysis (ED)

Electrodialysis (ED) is an electro-membrane process in which the ions are transported through a membrane from one solution to another under the influence of an electrical potential. ED can be utilized to perform several general types of separations such as separation and concentration of salts, acids and bases from aqueous solutions or the separation and concentration of monovalent ions from multiple charged components or the separation of ionic compounds from uncharged molecules. ED membranes are usually made of cross-linked polystyrene that has been sulfonated. Anion membranes can be of cross-linked polystyrene containing quaternary ammonium groups. Usually, ED membranes are fabricated as flat sheets containing about 30-50% water. Membranes are fabricated by applying the cation and anion-selective polymer to a fabric material.

The system consists of two kinds of membranes: cation and anion, which are placed in an electric field. The cation-selective membrane permits only the cations and anion-selective membrane only the anions. The transport of ions across the membranes results in ion depletion in some cells, and ion concentration in alternate ones. ED is used widely for production of potable water from sea or brackish water, electroplating rinse recovery, desalting of cheese whey, and production of ultrapure water (Srikanth G., 1999).

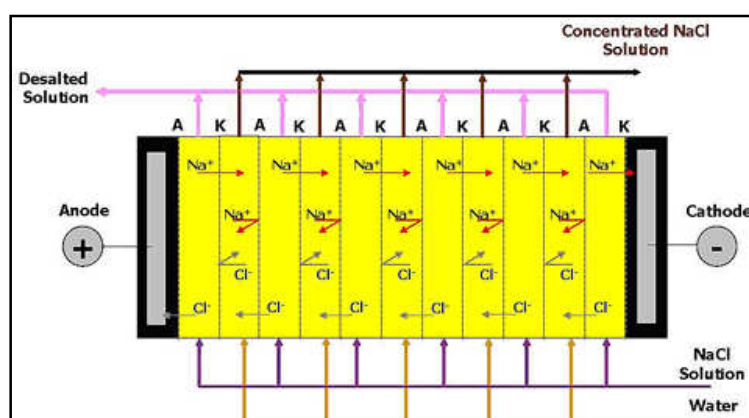


Figure 2.6: Electrodialysis membrane process

2.3.6 Gas Permeation in a Membrane

The membrane processes give certain advantages such as compactness and light in weight, low labour intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance (no moving parts), low energy requirements and low cost especially so for small sizes. Membranes made of polymers and copolymers in the forms of flat film or hollow fiber have been used for gas separation.

Different gases pass through certain membranes at significantly different rates, thus permitting a partial separation. The rate of permeation is proportional to the pressure differential across the membrane and inversely proportional to the membrane thickness. The rate of permeation is also proportional to the solubility of the gas in the membrane and also to the diffusivity of gas through the membrane. Figure 2.7 shows the gas permeation process.

Gas separation is thus affected by three key performance attributes of membranes that is selectivity towards the gases separated, membrane flux or permeability and the life of the membrane, maintenance and replacement costs.

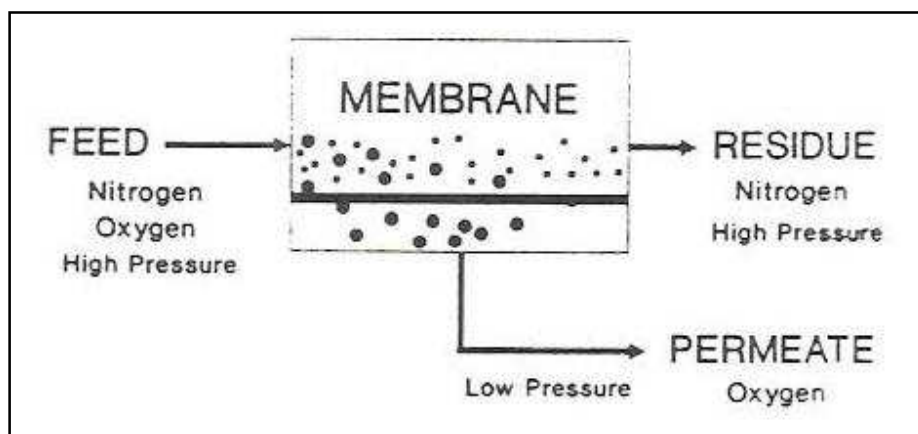


Figure 2.7: Gas permeation membrane process

2.3.7 Pervaporation

Pervaporation is a membrane based process for separating miscible liquids. The absorption of one of the components of the liquid by the membrane, diffusion of this component across the membrane and evaporation, as permeate vapour, into the partial vacuum applied to the underside of the membrane. Pervaporation differs from all other membrane processes because of the phase change of the permeate, non-porous. Transport through these membranes is affected by maintaining a vapour pressure gradient across the membrane. Pervaporation has been used for separation of ethanol-water mixture, solvent recovery, separation of heat sensitive products or enrichment of organic pollutants etc. (Mulder, 1996).

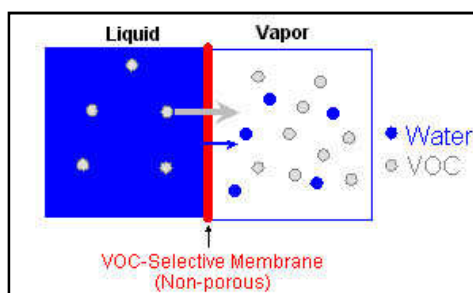


Figure 2.8: Pervaporation membrane process

2.4 Membrane Type and Application

Membranes can be generally classified into three groups which is artificial membrane, polymeric and semipermeable membrane. These three types of membranes differ significantly in their structure and functionality.

2.4.1 Artificial Membrane

An artificial membrane is also known as a synthetic membrane that usually use for separation tasks in laboratory and industry. The active part of the membrane which permits selective transport of material usually made of from polymers or ceramics, seldom glass or metals.

The driving force of the material transport is given by concentration, pressure, electrical or chemical gradient across the membrane. Membranes can be prepared in the form of flat sheets, tubes, capillaries and hollow fibers. Membranes are built in membrane systems like plate and frame, spiral-wound module, hollow fiber module, tube-in-shell module.

Some of the most common artificial membranes are polymeric membranes. Under some conditions ceramic membranes can be utilized with advantage. Such membranes are employed in a wide range of membrane operations, such as microfiltration, ultrafiltration, reverse osmosis, pervaporation, gas separation, dialysis or chromatography. The applications depend on the type of functionality incorporated in the membrane, which can be based on size-exclusion, chemical affinity or electrostatics.

2.4.2 Polymeric Membrane

Polymeric membranes are membranes that take the form of polymeric interphases, which can selectively transfer certain chemical species over others. There are several mechanisms that could be deployed in their functioning. Knudsen diffusion and solution diffusion are prominent mechanisms. Polymeric membranes are of particular importance in gas separation applications (Painter P. *et al.*, 1997). Figure 2.9

shows the polymeric membrane structure (Alsari A.M. *et al.*, 2001) that was scanned by scanning electron microscopy (SEM).

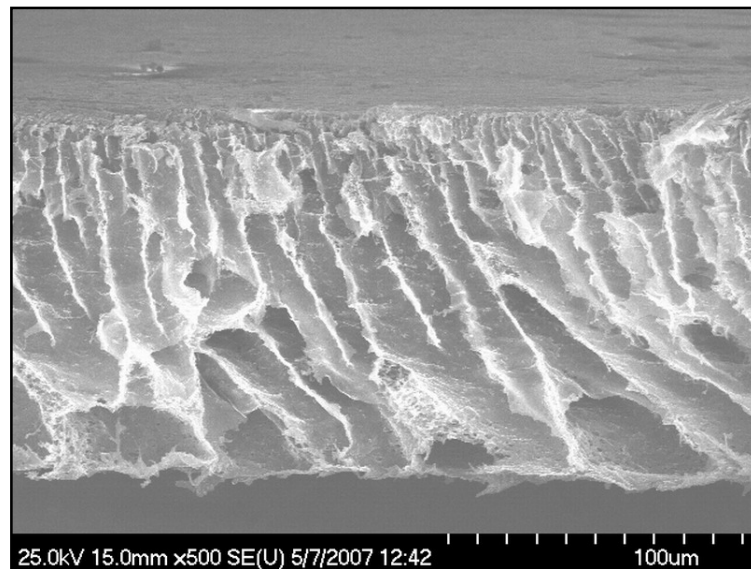


Figure 2.9: Polymeric membrane structure scanned by SEM

2.4.3 Semipermeable Membrane

A semipermeable membrane is a membrane that will allow certain molecules or ions to pass through it by diffusion and occasionally specialized "facilitated diffusion." It is also termed as selectively-permeable membrane, a partially-permeable membrane or a differentially-permeable membrane. The rate of passage depends on the pressure, concentration, and temperature of the molecules or solutes on either side, as well as the permeability of the membrane to each solute. Depending on the membrane and the solute, permeability may depend on solute size, solubility, properties, or chemistry. An example of a semi-permeable membrane is a lipid bilayer, on which is based the plasma membrane that surrounds all biological cells.

2.5 Structure of Membrane

Membranes (solid synthetic membranes) can be classified from its structure. The membrane structures are important to determine the separation mechanism and the application. Membrane structure can be divided into two groups that are symmetric membrane and asymmetric membrane.

2.5.1 Symmetric Membrane

The thickness of symmetric membranes (porous or nonporous) range roughly from 10 to 200 μm . The resistance to mass transfer was determined by the total membrane thickness. A decrease in membrane thickness results in an increase permeation rate.

2.5.1.1 Porous Membrane

A porous membrane is when the particle permeate through membrane and particle separation by membrane are considered, the size of the hole, which acts as a passage for the moving particles, becomes one of the indices and a membrane with many holes bored through of about 0.005 – 1 μm in diameter.

2.5.1.2 Non porous membrane

Non-porous membrane has hole smaller than 0.001 μm in diameter. However, it cannot be called a hole; it is a gap between particles based on thermal vibration of the polymer which constitutes the membrane. Mass transport through non-porous membrane is best described as “Solution-Diffusion Model” (Brüschke H., 1995).

2.5.2 Asymmetric Membrane

An asymmetric membrane comprises a very thin (0.1-1.0 micron) skin layer on a highly porous (100-200 microns) thick substructure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of membrane material or pore size, and the mass transport rate is determined mainly by the skin thickness. Porous sub-layer acts as a support for the thin, fragile skin and has little effect on the separation characteristics. These membranes combine the high selectivity of a dense membrane with the high permeation rate of a very thin membrane.

2.5.2.1 Porous Membrane

A porous membrane is when the particle permeate through membrane and particle separation by membrane are considered, the size of the hole, which acts as a passage for the moving particles, becomes one of the indices and a membrane with many holes bored through of about 0.005 – 1 μm in diameter.

2.5.2.2 Composites Membrane

A membrane composed of more than one kind of material is called a composite membrane. There are three group of composite membrane that is laminate membrane, coated membrane and plasma membrane. Laminate membranes are membrane that laminated with more than two kinds of membranes. A coated membrane is made by evaporating a solvent after coating the heterogeneous polymeric solution on a membrane surface. A plasma membrane is made by chemically combining heterogeneous organic substances using plasma.

2.6 Permeability and Selectivity of Gas Separation

Permeability is a volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time. Permeability gives the membrane productivity. Whereas selectivity is a measurement of a membrane material's ability to separate the components of a mixture or purity of the product separated by the membrane. It is the ratio of the permeabilities of any two components in the membrane.

The relationship between selectivity and permeability where a high value of selectivity tends to exhibits less permeability and vice versa. Gas transport through dense polymer membranes is governed by the expression:

$$j_i = \frac{D_i K_i (P_{i_o} - P_{i_i})}{\ell} \quad (2.1)$$

where j_i is the volume (molar) flux expressed as $[\text{cm}^3 \text{ (STP) of component } i]/\text{cms}$; ℓ is the membrane thickness, p_{i_o} is the partial pressure of component i on the feed side, and p_{i_i} is the partial pressure of component i on the permeate side. The diffusion coefficient, D_i , reflects the mobility of the individual molecules in the membrane material; the gas

sorption coefficient, K_i , with units [cm^3 (STP) of component i/cm^3 of polymer] pressure, reflects the number of molecules dissolved in the membrane material. The product D_iK_i can be written as P_i , which is called the membrane permeability, and is a measure of the membrane's ability to permeate gas. Permeability is a volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time (Kohl *et al.*, 1997).

$$\frac{P_i}{l} = \frac{Q}{AxP} \quad (2.2)$$

- p_i = Permeability for gas component ($\frac{\text{cm}}{\text{s.bar}}$)
- Q = Flowrate of gas (cm^3/s)
- l = the effective thickness of the separating layer (unknown)
- A = Area (cm^2)
- P = Pressure in system (bar)

The best measure of the ability of a membrane to separate two gases, i and j , is the ratio of their permeabilities, $a_{i/j}$, called the membrane selectivity, which can be written as

$$a_{i/j} = \frac{p_i}{p_j} = \left[\frac{D_i}{D_j} \right] \left[\frac{K_i}{K_j} \right] \quad (2.3)$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients and can be viewed as the sorption or solubility selectivity, reflecting the relative solubility of the two gases. In polymer materials, the diffusion coefficient decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity, D_i/D_j , always favors the permeation of small molecules over large ones. The sorption coefficient of gases and vapors is a measure of the energy required for the gas to be sorbed by the polymer, and increases with increasing condensability of the permeant.

This dependence on condensability means that the sorption coefficient usually increases with molecular size, because large molecules are normally more condensable than smaller ones. Hence the sorption selectivity, K_i/K_j , favors the permeation of larger, more condensable molecules, such as hydrocarbon vapors, over permanent gases, such as oxygen and nitrogen. It follows that the effects of permeant molecular size on the mobility and sorption selectivities are opposed.

2.7 Material for Membrane Fabricating

In fabricating the membrane, choosing the appropriate material is a crucial decision to produce a high quality membrane. Several materials has been chosen such as polysulfone, polyethersulfone, n-methyl-2-pyrrolidone, polydimethylsiloxane, hexane and methanol. These materials has been choosed based on its properties.

2.7.1 Polysulfone

Polysulfone is thermoplastic polymers that are known for their toughness and stability at high temperatures. The sulfone group is from the subunit aryl-SO₂-aryl. Polysulfones are used in specialty applications and often are a superior replacement for polycarbonates.

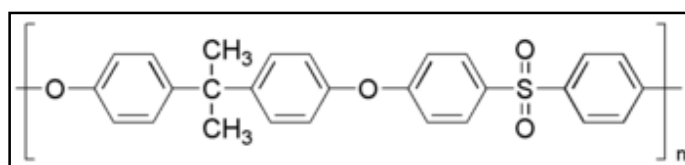


Figure 2.10: Polysulfone (PSU) molecular structure

Polysulfone (PSU) is rigid, high-strength, and transparent, retaining its properties between -100 °C and 150 °C. It has very high dimensional stability, the size change

when exposed to boiling water or 150 °C air or steam generally falls below 0.1%. Its glass transition temperature is 185 °C.

Polysulfone (PSU) is highly resistant to mineral acids, alkali, and electrolytes, in pH ranging from 2 to 13. It is resistant to oxidizing agents, therefore it can be cleaned by bleaches. It is also resistant to surfactants and hydrocarbon oils. It is not resistant to low-polar organic solvents (eg. ketones and chlorinated hydrocarbons), and aromatic hydrocarbons. Mechanically, Polysulfone (PSU) has high compaction resistance, recommending its use under high pressures. It is also stable in aqueous acids and bases and many non-polar solvents, however it is soluble in dichloromethane and methylpyrrolidone. Their physical properties are shown in Table 2.1.

Table 2.1: Physical properties of Polysulfone

Properties	PSU
Specific Gravity	1.24 to 1.25
Melt Mass Flow Rate (<i>g/10 min</i>)	3.8 to 17
Flexural Modulus (<i>psi</i>)	329000 to 407000
Tensile Strength (<i>psi</i>)	7090 to 11800
Tensile Elongation (%)	3.7 to 77
Rockwell Hardness	119 to 120
Notched Izod Impact (<i>ft·lb/in</i>)	0.800 to 1.72
DTUL @ 66 psi (0.45 MPa) (°F)	351 to 360
DTUL @ 264 psi (1.8 MPa) (°F)	334 to 346

2.7.2 N-Methyl-2-pyrrolidone (NMP)

N-Methyl-2-pyrrolidone (NMP) is a water-miscible organic solvent with formula C_5H_9NO . It is a hygroscopic colourless liquid to slightly yellow liquid with a mild amine odour. It miscible with water and conventional organic solvent. NMP belongs to dipolar aprotic solvent which also includes the dimethylformamide, dimethylacetamide and dimethyl sulfoxide. It can also refer as 1-methyl-2-pyrrolidone and m-pyrrole. The chemical structure of NMP can be view is illustrated in Figure 2.11.

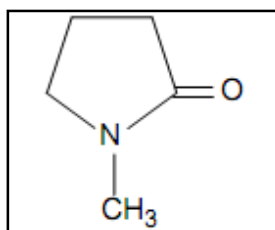


Figure 2.11: Chemical structure of N-Methyl-2-pyrrolidone (NMP)

NMP is used in the petrochemical industry, in the microelectronics fabrication industry, and in the manufacture of various compounds, including pigments, cosmetics, drugs, insecticides, herbicides, and fungicides. An increasing use of NMP is as a substitute for chlorinated hydrocarbons (CICAD). NMP is widely applied to aromatic hydrocarbons extracting, acetylene, and diolefine purification. NMP can be used as polymer solvents and polymerization process medium, such as polyamides, polyphenyl thioether. which are called engineering plastics; NMP can be used as aromatic fibre, insulate pesticide, pigment and detergent, etc. NMP can be used in battery, LCD, and semiconductor, etc.

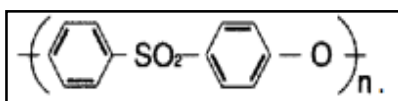
NMP is a volatile and widely use as solvent but it may enter the environment as emissions to the atmosphere or it may be released to water as a component of municipal and industrial wastewaters. The physical properties of NMP are tabulated in Table 2.2.

Table 2.2: Physical properties of N-Methyl-2-pyrrolidone (NMP)

Physical properties	Unit
Molecular weight	99.1 g/mol
Freezing point	-23.6 °C
Vapor pressure at: 40 °C	133 Pa
60 °C	465 Pa
80 °C	1270 Pa
Boiling point	204.3 °C
Viscosity at: 20 °C	1.7 mPa ^s
50 °C	1.0 mPa ^s
80 °C	0.9 mPa ^s
Density @ 25 °C	1.028 g/cm ³
Flash point	91 °C
Explosive limit :Lower	1.3 %
Upper	9.5 %
Water solubility at 20 °C	> 10% w/w

2.7.3 Polyethersulfone (PES)

Polyethersulfone is a heat resistant, transparent, amber, non crystalline engineering plastic having the molecular structure shown in Figure 2.12.

**Figure 2.12:** Polyethersulfone (PES) molecular structure

Polyethersulfone (PES) is tough and rigid resin similar to conventional engineering plastics, such as polycarbonate, at room temperature. The greatest

characteristics of Polyethersulfone (PES) are that it has by far better high-temperature properties than conventional engineering plastics. Specifically, Polyethersulfone (PES) remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200°C¹⁶. It has poor fatigue characteristics and is prone to environmental stress cracking but has good long term thermal ageing resistance and reasonable radiation resistance.

Polyethersulfone is also called as polyarylsulfone. Compare to polysulfone or polyetherimide, polyethersulfone offered a high temperature amorphous thermoplastic. Radel® A polyethersulfone offering a superior combination of good chemical resistance and higher dry heat capability making its good to make baby bottles and other food service application.

The major advantage of polyethersulfone is they have excellent flow rates, lot-to-lot and within-lot consistency, low extractable, no external wetting agents, compatible with a variety of sealing methods and can passed USP Class VI testing. Polyethersulfone have been applied widely in automotive electrical/electronic, automotive fuel systems, automotive lighting, as a coatings, composites, additives for gas separation, cookware, electrical contactors, switches and as a membranes for water purification, waste water recovery and hemodialysis. Their physical properties and thermal properties are shown in Table 2.3 and Table 2.4.

Table 2.3: Physical properties of polyethersulfone (PES)

Physical Properties	Unit
Density	1.37 g cm ⁻³
Flammability	V-0 @ 0.4mm
Limiting oxygen index	34-41%
Radiation resistance	Good-Fair
Water absorption - equilibrium	2.2 %
Water absorption - over 24 hours	0.4-1 %
Resistance to Ultra-violet	Fair

Table 2.4: Thermal properties of polyethersulfone (PES)

Thermal properties	Unit
Coefficient of thermal expansion	55 x10 ⁻⁶ K ⁻¹
Heat-deflection temperature - 0.45MPa	> 260 °C
Heat-deflection temperature - 1.8MPa	203 °C
Lower working temperature	- 110 °C
Thermal conductivity @23°C	0.13 – 0.18 W m ⁻¹ K ⁻¹
Upper working temperature	180 – 220 °C

2.7.4 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. The molecular formula of PDMS is (C₂H₆OSi)_n. Other name for PDMS is dimethicone and E900. It colorless and has some odor.

PDMS is optically clear, and is generally considered to be inert, non-toxic and non-flammable. It has been assigned CAS number 63148-62-9, and is occasionally called dimethicone. It is one of several types of silicone oil (polymerized siloxane). The structure of polydimethylsiloxane is shown in Figure 2.5.

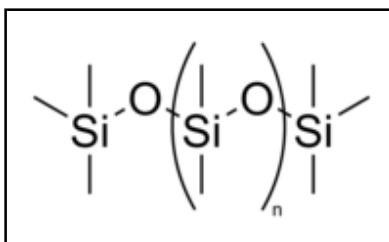


Figure 2.13: Structure of polydimethylsiloxane (PDMS)

PDMS is also used as a component in silicone grease and other silicone based lubricants, as well as in defoaming agents, mold release agents, damping fluids, heat transfer fluids, polishes, cosmetics, hair conditioners and other applications. PDMS has also been used as a filler fluid in breast implants, although this practice has decreased somewhat, due to safety concerns, despite some evidence that it may be protective against breast cancer. Table 2.5 shows the physical properties of PDMS.

Table 2.5: Physical properties of polydimethylsiloxane (PDMS)

Physical properties	Unit
Boiling Point	> 100 °C
Flash Point	250 °F / 121.1 °C
Density	965 kg m ⁻³
Specific Gravity @ 25°C	1.11
Viscosity	5000 cSt
Thermal Conductivity	0.18 Watts per meter K

2.7.5 Hexane

Hexane is an alkane hydrocarbon with the chemical formula $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$. 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. They are also common constituents of gasoline and glues used for shoes, leather products and roofing. Additionally, it is used in solvents to extract oils for cooking and as a cleansing agent for shoe, furniture and textile manufacturing.

In laboratories, hexane is used to extract oil and grease from water and soil before determination by gravimetric analysis or gas chromatography. Figure 2.14 shows the structure of n-Hexane.

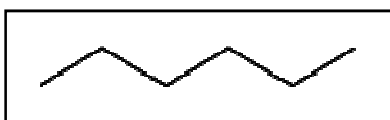


Figure 2.14: Structure of n-Hexane

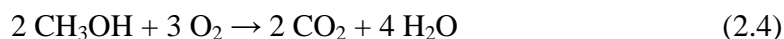
The physical properties of n-Hexane are tabulated in Table 2.6.

Table 2.6: Physical properties of n-Hexane

Physical properties	Unit
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

2.7.6 Methanol

Methanol is 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). Methanol 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). At room temperature it is a polar liquid and is used as an antifreeze, solvent, fuel, and as a denaturant for ethyl alcohol. It is also used for producing biodiesel via transesterification reaction. Methanol burns in air forming carbon dioxide and water:



A methanol flame is almost colorless, causing an additional safety hazard around open methanol flames. The structure of methanol is shown in Figure 2.15.

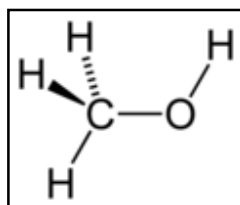


Figure 2.15: Structure of methanol

Methanol used as feedstock, automotive fuel, solvent, antifreeze in pipelines and windshield washer fluid. Methanol is also widely used in fuel in camping and boating stoves. The physical properties of methanol are shown in Table 3.7.

Table 2.7: Physical properties of methanol

Physical properties	Unit
Molar mass	32.04 g/mol
Appearance	colorless liquid
Density	0.7918 g/cm ³ , liquid
Melting point	-97 °C (176 K)
Boiling point	64.7 °C (337.8 K)
Solubility in water	Fully miscible
Acidity (p <i>K</i> _a)	~ 15.5
Viscosity	0.59 mPa·s at 20 °C
Dipole moment	1.69 D (gas)
Flash point	11 °C

2.8 Permeation Testing

In running the permeation test, the gases that has been choosed to use were based on the common gases that was found in crude natural gas. It contains methane, ethane, propane, butane, carbon dioxide, oxygen, nitrogen and hydrogen sulphide. But in my research, only several gases that has been considered which is carbon dioxide, nitrogen, oxygen and methane based on its availability in chemical laboratory.

2.8.1 Carbon Dioxide (CO₂)

Carbon dioxide (CO₂) is the most important greenhouse gas produced by human activities, primarily through the combustion of fossil fuels. Its concentration in the Earth's atmosphere has risen by more than 30% since the industrial revolution.

Carbon dioxide (CO₂) is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. The carbon dioxide structure and molecule bonding are shown in Figure 2.16.

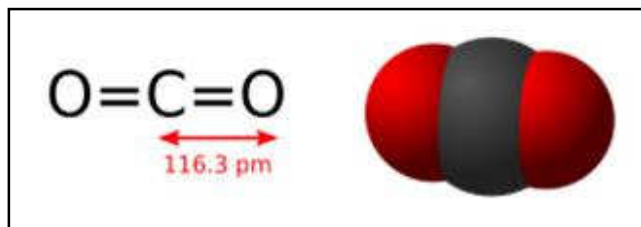


Figure 2.16: Carbon dioxide (CO₂) structure & molecule bonding

It is a gas at standard temperature and pressure and exists in Earth's atmosphere in this state. It is currently at a globally averaged concentration of approximately 387 ppm by volume in the Earth's atmosphere. Atmospheric concentrations of carbon dioxide fluctuate slightly with the change of the seasons, driven primarily by seasonal plant growth in the Northern Hemisphere. Concentrations of carbon dioxide fall during the northern spring and summer as plants consume the gas, and rise during the northern autumn and winter as plants go dormant, die and decay. Carbon dioxide is a greenhouse gas as it transmits visible light but absorbs strongly in the infrared and near-infrared.

Carbon dioxide is produced by all animals, plants, fungi and microorganisms during respiration and is used by plants during photosynthesis. This is to make sugars which may either be consumed again in respiration or used as the raw material to produce cellulose for plant growth. It is, therefore, a major component of the carbon cycle. Carbon dioxide is generated as a by-product of the combustion of fossil fuels or the burning of vegetable matter, among other chemical processes. Large amounts of carbon dioxide are emitted from volcanoes and other geothermal processes such as hot springs and geysers.

2.8.2 Nitrogen

Nitrogen is a chemical element that has the symbol N and atomic number 7 and atomic weight 14.0067. Elemental nitrogen is a colorless, odorless, tasteless and mostly inert diatomic gas at standard conditions, constituting 78.08% by volume of Earth's atmosphere. Nitrogen is a nonmetal, with an electronegativity of 3.0. It has five electrons in its outer shell and is therefore trivalent in most compounds. The triple bond in molecular nitrogen (N₂) is one of the strongest in nature. Nitrogen is generally unreactive at standard temperature and pressure. N₂ reacts spontaneously with few reagents, being resilient to acids and bases as well as oxidants and most reductants. When nitrogen reacts spontaneously with a reagent, the net transformation is often called nitrogen fixation.

Nitrogen gas is acquired for industrial purposes by the fractional distillation of liquid air, or by mechanical means using gaseous air (i.e. pressurised reverse osmosis membrane or pressure swing adsorption). Commercial nitrogen is often a byproduct of air-processing for industrial concentration of oxygen for steelmaking and other purposes. When supplied compressed in cylinders it is often referred to as OFN (oxygen-free nitrogen).

Nitrogen gas has a wide variety of applications, including serving as an inert replacement for air where oxidation is undesirable;

- To preserve the freshness of packaged or bulk foods (by delaying rancidity and other forms of oxidative damage)
- In ordinary incandescent light bulbs as an inexpensive alternative to argon
- On top of liquid explosives for safety measures
- The production of electronic parts such as transistors, diodes, and integrated circuits
- Dried and pressurized, as a dielectric gas for high voltage equipment
- The manufacturing of stainless steel

- Use in military aircraft fuel systems to reduce fire hazard.
- Filling automotive and aircraft tires due to its inertness and lack of moisture or oxidative qualities, as opposed to air, though this is not necessary for consumer automobiles.

The carbon dioxide structure and molecule bonding are shown in Figure 2.17



Figure 2.17: Nitrogen (N_2) structure & molecule bonding

2.8.3 Oxygen

Oxygen is a colorless, odorless, tasteless gas that is slightly soluble (3.08 cm^3 per 100 cm^3 of water) at room temperature. It is considerably more soluble in some organic solvents, such as ethyl alcohol, carbon tetrachloride, and benzene. Oxygen is less soluble in sea water than in pure water, although still soluble enough to support the survival of marine organisms.

Oxygen exists in three allotropic forms, monatomic oxygen (O), diatomic oxygen (O_2), and triatomic oxygen (O_3). The first of these is sometimes called nascent oxygen, and the last is more commonly known as ozone. Oxygen is one of the most active of all chemical elements. The oxygen-oxygen bond in diatomic oxygen is relatively strong, but once broken, the atomic oxygen formed (O) reacts readily with the vast majority of elements. The noble gases and noble metals are the most important exceptions, although oxy compounds of most of these elements are also known and can be prepared by indirect methods.

The reaction between oxygen and another element generally results in the formation of a binary compound known as an oxide. The reaction itself is known as oxidation. For example, the oxidation reaction between oxygen and sodium produces sodium oxide. In many cases, an element may form more than one oxide. Copper, as an example, forms both copper (I) (cuprous) oxide and copper (II) (cupric) oxide.

Nitrogen forms five oxides: nitrous oxide (N_2O), nitric oxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), and dinitrogen pentoxide (N_2O_5). In many cases, the reaction between oxygen and another element is highly exothermic. One of the best known of such reactions is the one that takes place between carbon and oxygen, to form (usually) carbon dioxide and carbon monoxide. It is this reaction, which takes place when coal burns, that was responsible to a significant extent for the development of huge new energy sources during the Industrial Revolution that transformed human society. Table 2.8 in next page shows the physical properties of oxygen.

Table 2.8: Physical properties of oxygen

Physical Properties	Unit
Atomic Number	8
Molecular Weight	15.9994(3) amu
Oxidation State	-2
Boiling Point	$-182.97\text{ }^{\circ}\text{C} / 90.18\text{ K}$
Melting Point	$-218.40\text{ }^{\circ}\text{C} / 54.75\text{ K}$
Density (gas) @ OC	1.429 g/L
Density (liquid) -183 C	1.14 g/L
Molar Volume	$17.36 \times 10^{-6}\text{ m}^3/\text{mol}$
Heat of Vaporisation	3.4099 kJ/mol
Heat of Fusion	0.22259 kJ/mol
Specific Heat Capacity	920 J/(kg•K)
Electronegativity	3.44 (Pauling)
Crystal Structure	cubic

2.8.4 Methane

Methane is a chemical compound with the molecular formula CH_4 . It is the simplest alkane, and the principal component of natural gas. Methane's bond angles are 109.5 degrees. Figure 2.18 shows the structure of methane.

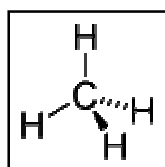


Figure 2.18: Structure of methane

Burning methane in the presence of oxygen produces carbon dioxide and water. Methane is the major component of natural gas, about 87% by volume. At room temperature and standard pressure, methane is a colorless, odorless gas; the smell characteristic of natural gas is an artificial safety measure caused by the addition of an odorant, often methanethiol or ethanethiol. Methane has a boiling point of $-161\text{ }^{\circ}\text{C}$ at a pressure of one atmosphere. As a gas it is flammable only over a narrow range of concentrations (5–15%) in air. Liquid methane does not burn unless subjected to high pressure (normally 4–5 atmospheres). The physical properties of methane are shown in Table 2.9.

Table 2.9: Physical properties of methane

Physical Properties	Unit
Molar mass	16.0425 g/mol
Appearance	Colorless gas
Density	0.717 kg/m^3 , gas
Melting point	$-182.5\text{ }^{\circ}\text{C}$, 91 K, $-297\text{ }^{\circ}\text{F}$
Boiling point	$-161.6\text{ }^{\circ}\text{C}$, 112 K, $-259\text{ }^{\circ}\text{F}$

2.9 Membrane Formation

A number of different techniques are available to prepare polymeric membranes. The techniques are sintering, stretching, track-etching, phase inversion, sol-gel process, vapour deposition and solution coating (Mulder, 1996). In this research, the membrane was prepared by phase inversion techniques (Nordin M. R., 2004) and can be categorized into four different techniques as shown in Figure 2.19

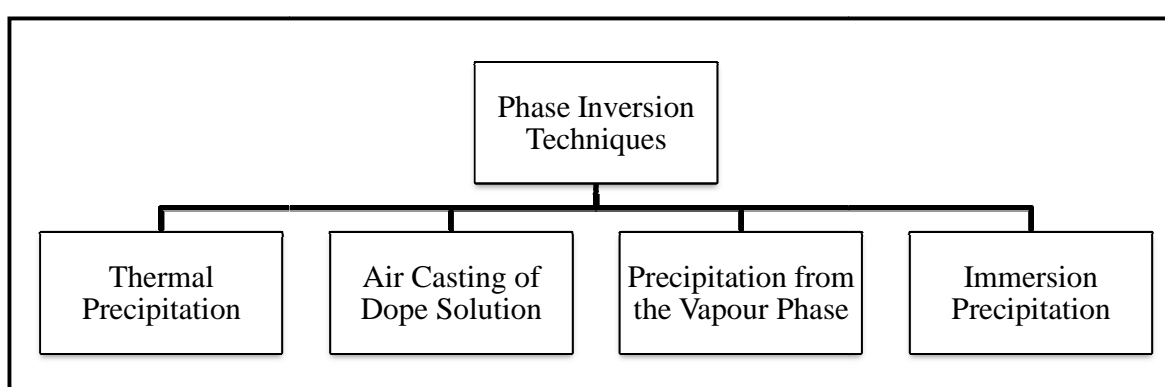


Figure 2.19: Phase inversion techniques

2.9.1 Thermal Precipitation

This technique based on the phenomenon that the solvent quality frequently decreases when the temperature decreased. In this process, a low molecular weight component usually acts as a solvent at high temperature and as non-solvent at low temperature. It is then removed after formation of the porous structure. Although the thermal process can be applied to a wide range of polymers, it is especially interesting for those with poor solubility, such as polypropylene, which can be hardly manufactured into a porous membrane by other phase inversion processes (Nunes S.P. et al, 2001).

2.9.2 Air Casting of Dope Solution

In the air casting technique process, the polymer is dissolved in a mixture of a volatile solvent and less volatile nonsolvent. Since the solvent is more volatile than the nonsolvent, the composition shift during evaporation to a higher nonsolvent and polymer content. This leads eventually to the polymer precipitation leading to the formation a skinned membrane (Mulder, 1996).

2.9.3 Precipitation from the Vapour Phase

A cast film, consisting of a polymer and a solvent, is placed in a vapour atmosphere where the vapour phase consists of a nonsolvent saturated with the same solvent. The high solvent concentration in the vapour phase prevents the evaporation of solvent from the cast film. Membrane formation occurs because of the penetration (diffusion) of nonsolvent into the cast film. This leads to a porous membrane without toplayer. With immersion precipitation an evaporation step in air is sometimes introduced and if solvent is miscible with water precipitation from the vapour will start at this stage. An evaporation stage is often introduced in the case of hollow fiber preparation by immersion precipitation ('wet-dry spinning') exchange between the solvent and nonsolvent from the vapour phase leading to the precipitation (Mulder, 1996).

2.9.4 Immersion Precipitation

Immersion precipitation is widely used to produce commercial gas separation membranes and other membrane based-separation. In the immersion precipitation case, a polymer is cast as a thin film on a support or extruded through a die, and is subsequently

immersed in a nonsolvent bath. Precipitation can occur because of the good solvent in the polymer solution is exchanged with nonsolvent in the coagulation bath.

Immersion precipitation technique is divided into three categories; wet phase inversion technique, dry phase inversion technique and dry/wet phase inversion technique (Baker W.R., 2002).

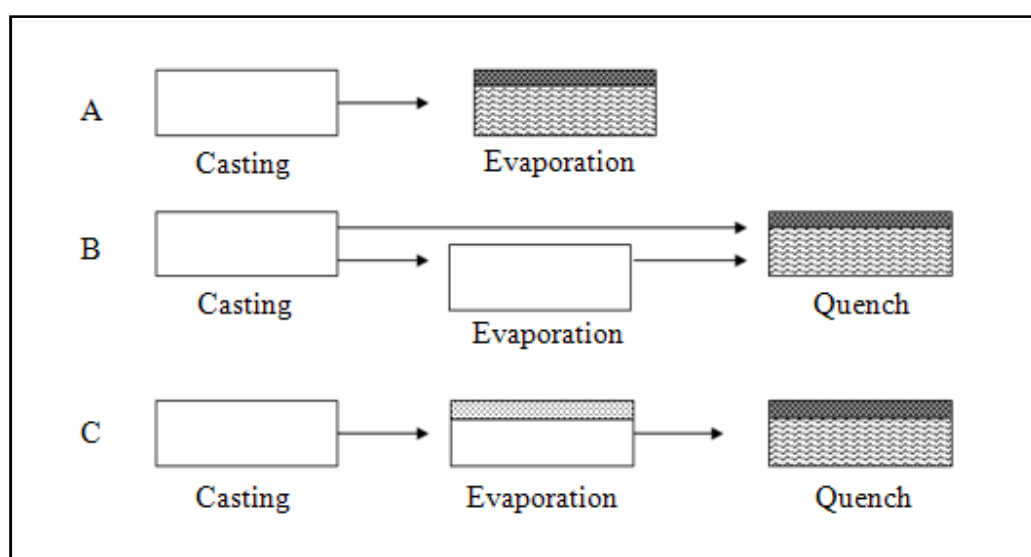


Figure 2.20: Schematic representation of phase inversion processes: (A) dry phase inversion, (B) wet phase inversion, (C) dry/wet phase inversion

2.9.4.1 Dry Phase Inversion Processes

Generally, flat sheet asymmetric membranes are made by casting a solution consisting of polymer, solvents and additives onto a suitable substrate. If the nonsolvent components are less volatile than the solvents components, evaporation will ultimately produce a critical nonsolvent concentration that causes the membrane to be transform from a single-phase to a two-phase structure. If the solvents and nonsolvents

components are removed solely by evaporation, membrane formation is defined as a dry phase inversion process (Baker W.R., 2002).

2.9.4.2 Wet Phase Inversion Processes

The wet phase separation process is characterized by the mixing of a stable, homogenous polymer solution in a nonsolvent precipitation bath. The casting solution generally consists either of binary mixture of polymer and solvent or combination of polymers, solvents and nonsolvents. A brief evaporation period is often used concentrate the outermost region of the nascent membrane prior to coagulation. Phase separation, however, takes place by the diffusion exchange of solvents and nonsolvents in the coagulation bath (Baker W.R., 2002).

2.9.4.3 Dry/wet Phase Inversion Processes

Evaporation step was done before immersion in a nonsolvent bath to prepare a defect-free asymmetric membrane. This process applied when all the stages is included in the membrane preparation process;

- (a) Preparation of solution
- (b) Spreading the polymer solution on a solid surface, porous support surface (in this case composite membranes are to be prepared), or forming hollow fiber in the form of stream through a spinneret.
- (c) Solvent evaporation
- (d) Immersion precipitation
- (e) Washing
- (f) Drying
- (g) Annealing

As a result of this evaporation step, the volatile solvent will evaporate from the surface and a driving force has been generated for diffusion of solvent from the bottom side to the top side.

CHAPTER 3

RESEARCH AND METHODOLOGY

3.1 Research Design

In conducting this research, several steps have been done to prepare the hybrid membrane. The steps involves are preparing the dope solution, casting the membrane and coating the membrane. After that, the hybrid membrane will run through the permeation test to study its permeability and slectivity. The flowchart of the membrane preparation and permeation test is as shown in Figure 3.1.

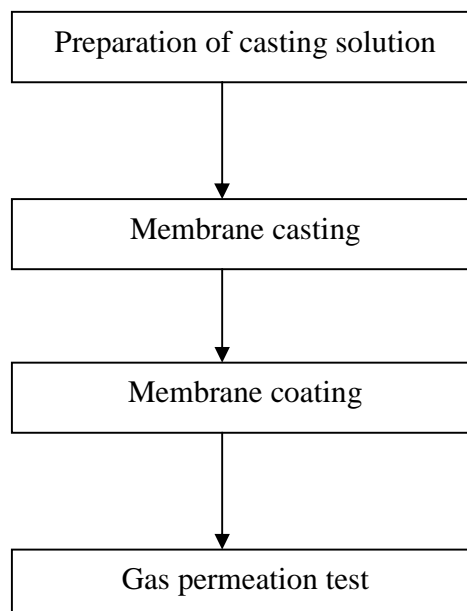


Figure 3.1: Flowchart of membrane preparation and permeation test

3.2 Membrane Preparation

Membrane preparation was divided to three part which are preparing the dope solution, casting the membrane and coating the membrane.

3.2.1 Preparation of Casting Solution (Dope)

For hybrid membrane, Polyethersulfone and Polysulfone were used to prepare the casting solution. Before the polymers were dissolved, the polymers were dried for 1 day in a vacuum oven at temperature of 150°C in order to remove all absorbed water vapor. Then, the polymer was dissolved in NMP and nonsolvent additive (methanol). Nonsolvent additive was used to prevent complete removal of the glycol during routine washing such that the membrane as produced is hydrophobic. The nonsolvent additive can be any low molecular weight aliphatic glycol which not sufficiently attracted to the polyethersulfone. The solution stirred about 4 to 6 hours with heating temperature of 40°C - 60°C to achieve complete homogeneity. The solution was kept in a storage bottle and degassed by using ultrasonic bath to remove any traces air bubbles present in the solution. The apparatus is assemble is shows in Figure 3.2.

For PES membrane, Polyethersulfone was used to prepare the casting solution. Before the polymers were dissolved, the polymer was dried for 1 day in a vacuum oven at temperature of 150°C in order to remove all absorbed water vapor. Then, the polymer was dissolved in NMP and nonsolvent additive (methanol). Nonsolvent additive was used to prevent complete removal of the glycol during routine washing such that the membrane as produced is hydrophobic. The solution stirred about 4 to 6 hours with heating temperature of 40°C - 60°C to achieve complete homogeneity. The solution was kept in a storage bottle and degassed by using ultrasonic bath to remove any traces air bubbles present in the solution.

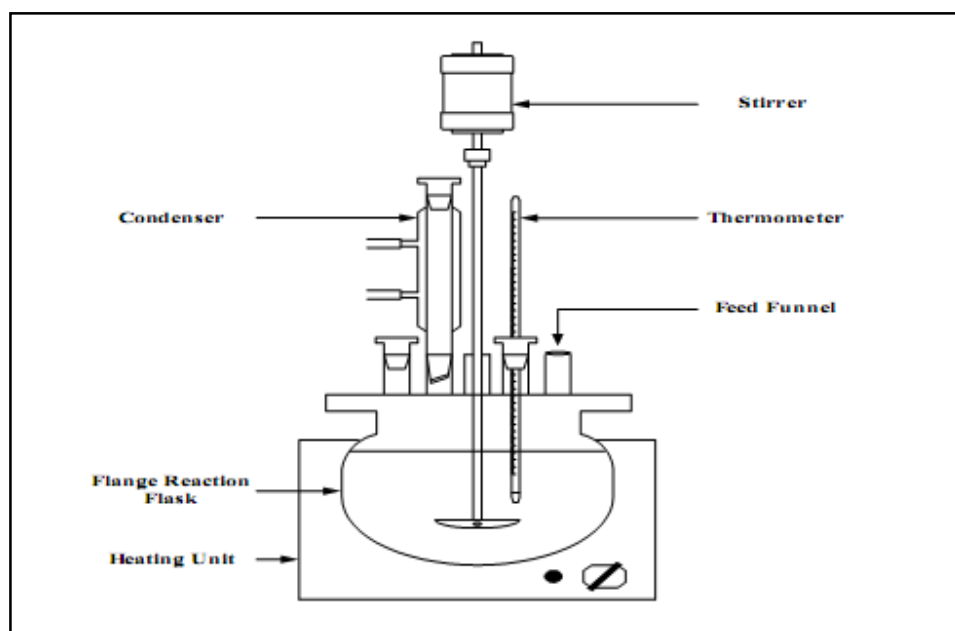


Figure 3.2: Preparation of casting solution system (Dope preparation system)

3.2.2 Membrane Casting

Using hand casting knife, asymmetric polyethersulfone membranes is prepared according to dry/wet phase separation process. Three steps procedure is involve;

- (a) Casting of homogeneous casting solution
- (b) Immersion in a nonsolvent bath
- (c) Washing and drying the membrane

Casting process will be conduct at room temperature ($30^{\circ}\text{C}\pm 2$) and approximately 84% relative humidity. A small amount of casting solution is pour onto a glass plate with a casting knife gap setting of $150\mu\text{m}$. Figure 3.3 shows the casting knife used in casting process.

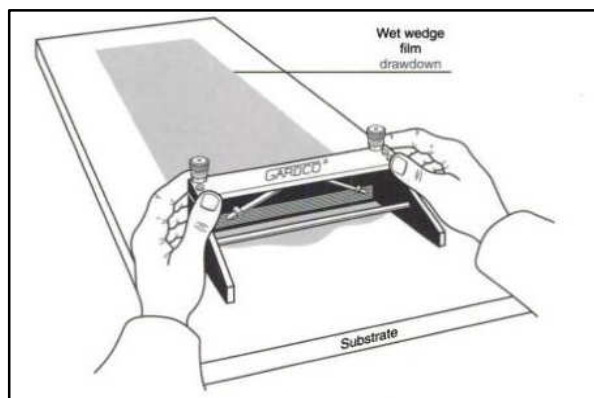


Figure 3.3: Casting knife for casting process

Then the solution was cast by the casting knife. After that, both glass plate and the membrane were immersed into the coagulation bath (compose of water as the coagulant medium). Finally, the membrane was washed with methanol for 1 day before was air dried for at least 48 hr at room temperature to remove any residual organic compounds (Nordin M. R., 2004).

3.2.3 Membrane Coating

The hybrid membrane was coated with two different coating agent which are polydimethylsiloxane (PDMS) and bromine water. The objective of coating is to improve the performance of the permeability and selectivity of the hybrid membrane.

3.2.3.1 Membrane Coating with PDMS

A 3 wt% of coating solution was prepared by dissolving polydimethylsiloxane (Sylgard-184) in n-hexane. The hybrid membrane was cut into a circular disc in a range of 12~14cm² in area. The solution was slowly pouring on to the top layer of the membrane for 5 min. Then, removed it and allowed cure at room temperature for 1 day

3.2.3.2 Membrane Coating with Bromine Water

A 40% of bromine water was prepared by mixing it with 300 mL of distilled water to achieve pH 2. The hybrid membrane was cut into a circular disc in a range of 12~14cm² in area. The hybrid membrane was deep in the solution for 24 hours. The treated hybrid membranes were washed with distilled water and dried at room temperature for at least 2 days.

3.3 Gas Permeation Test

By using industrial oxygen, nitrogen, carbon dioxide and methane with purity 95% the permeation rate was determined. Membrane was cut into a circular disc of 13.5 cm² in area. By set the pressure drop of 2 bar, these experiments was carried out at ambient temperature of (30±2°C). Rate of gas permeation was measured by using a soap bubble flow meter. This is to ensure any degree aging to reduce the productivity loss. The permeation unit is shown in Figure 3.4.



Figure 3.4: Photo of permeation unit use in this experimen

The permeation rate can be calculated by using equation (3.1)

$$\frac{p_i}{l} = \frac{Q}{AxP} \quad (3.1)$$

where;

Q = Flowrate of gas (cm³/s)

A = Area (cm²)

P = Pressure in system (bar)

l = the effective thickness of the separating layer (unknown)

p_i = Permeability for gas component ($\frac{cm}{s.bar}$)

The selectivity can be calculated by using the equation (3.2)

$$\text{Selectivity, } S = P_i / P_j \quad (3.2)$$

where;

P_i = Permeability of one gas component

P_j = Permeability of another gas component

CHAPTER 4

RESULT AND DISCUSSION

Gas separation is based on a difference in the rates of permeation rather than on an absolute barrier to one component, the recovered component that flows through the membrane (the permeate) is never 100% pure (Kohl et al., 1997). For an effective gas separation using membrane, the membrane must be very permeable with respect to methane (the permeate) to be separated, which passes through the membrane driven by pressure difference, and it must be relatively impermeable to carbon dioxide. Permeation happened by diffusion across a porous polymer film. There are several factors that affect effectiveness of membrane formation. A polymer type and coating agent are mainly determining the ultimate membrane performance (flux and selectivity).

4.1 Effect of Mixing Polymers on Casting Solution

Hybrid membrane of polyethersulfone (PES) & polysulfone (PSU) was prepared in aiming to acquire the improved structural and operational stability of the resulting membranes. Mixture of 20wt% of PES & PSU was used to prepare the membrane. The result of mixing the polymers was shown in Table 4.1.

Table 4.1: Separation properties for Hybrid (PES/PSU) Uncoated Membrane and PES Membrane.

Membrane Type	O ₂ (GPU)	N ₂ (GPU)	CO ₂ (GPU)	CH ₄ (GPU)	$\alpha(\text{O}_2/\text{CH}_4)$	$\alpha(\text{N}_2/\text{CH}_4)$	$\alpha(\text{CO}_2/\text{CH}_4)$
Hybrid Membrane (PES/PSU)	716	912	936	1730	0.41	0.53	0.54
	794	920	921	1650	0.48	0.56	0.56
	823	854	907	1650	0.5	0.52	0.55
Mean	778	895	921	1680	0.46	0.53	0.55
PES Membrane	395	414	368	457	0.87	0.91	0.81
	195	204	181	313	0.62	0.65	0.58
	37	35.4	429	43	0.86	0.82	0.99
Mean	209	218	197	271	0.78	0.79	0.79

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

From Table 4.1, the hybrid membrane shows high permeation of CO₂ gas. The effect of mixing the polymers in rearranging the molecular structure of the membrane can be discerned from Figure 4.1 which plot CO₂/CH₄ selectivity versus CO₂ permeability.

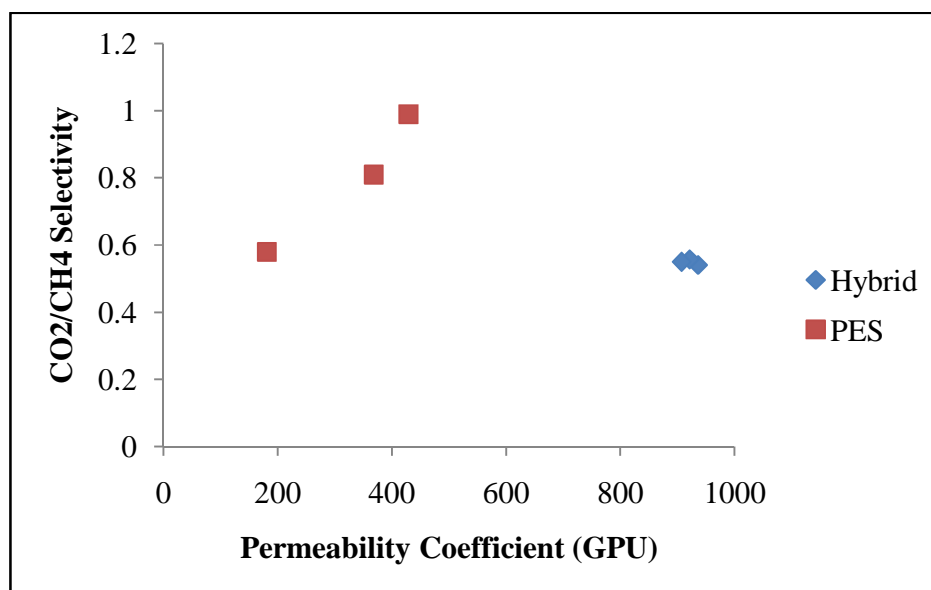


Figure 4.1: Permeability and selectivity of CO₂ gas for Hybrid membrane and PES membrane

Based on the Figure 1, Hybrid membrane shows a good sign of selectivity rather than PES membrane. According to the selectivity equation that was used before,

$$\alpha_{ij} = P_i/P_j \quad (4.1)$$

if the value of α_{ij} is lower than 1, the component i which is CO₂ will hardly permeate through the membrane. Very high (or very low) separation factors result in easy separations and no separation is possible if $\alpha_{ij} = 1$ (Kohl et al., 1997).

4.2 Effect of Coating Agent to the Membrane Performance

All of the uncoated membranes seem to exhibit higher permeability but less of the selectivity. This is probably due to the defects and enhancement of free volume in the ultrathin skin layers. The flux of a membrane is the reciprocal of its thickness. To reach a high flux the membranes should be made as thin as possible while being completely defect-free.

Tiny defects in the skin can cause a dramatic decrease in selectivity. In order to separate a mixture of gas with a porous membrane the pore size of the membrane must be much smaller than the mean free path of the gases. In this case, the transport is governed by the Knudsen flow mechanism. Since Knudsen flow is molecular weight dependent (smallest moves more rapidly), separation will occur when gases with different molecular weight pass through the membrane. Table 4.5 shows the summary average value of separation properties of uncoated membrane, membrane coated with bromine water and membrane coated with polydimethylsiloxane based on O₂,N₂,CO₂ and CH₄ for pressure-normalized flux and selectivity.

Table 4.2: Separation properties for Hybrid (PES/PSU) Uncoated Membrane

Sample	O ₂ (GPU)	N ₂ (GPU)	CO ₂ (GPU)	CH ₄ (GPU)	$\alpha(\text{O}_2/\text{CH}_4)$	$\alpha(\text{N}_2/\text{CH}_4)$	$\alpha(\text{CO}_2/\text{CH}_4)$
1	716	912	936	1730	0.41	0.53	0.54
2	794	920	921	1650	0.48	0.56	0.56
3	823	854	907	1650	0.5	0.52	0.55
Mean	778	895	921	1680	0.46	0.53	0.55

1 GPU = 1×10^{-6} cm³/s.cm².cmHg

All of the uncoated membranes exhibited a poor selectivity for each gas that pass through the membrane. This is probably due to the existent of defects at the surface layer. Figure 4.2 shows the permeability of test gases versus the polymer concentration for the uncoated membrane from the result of the experiment.

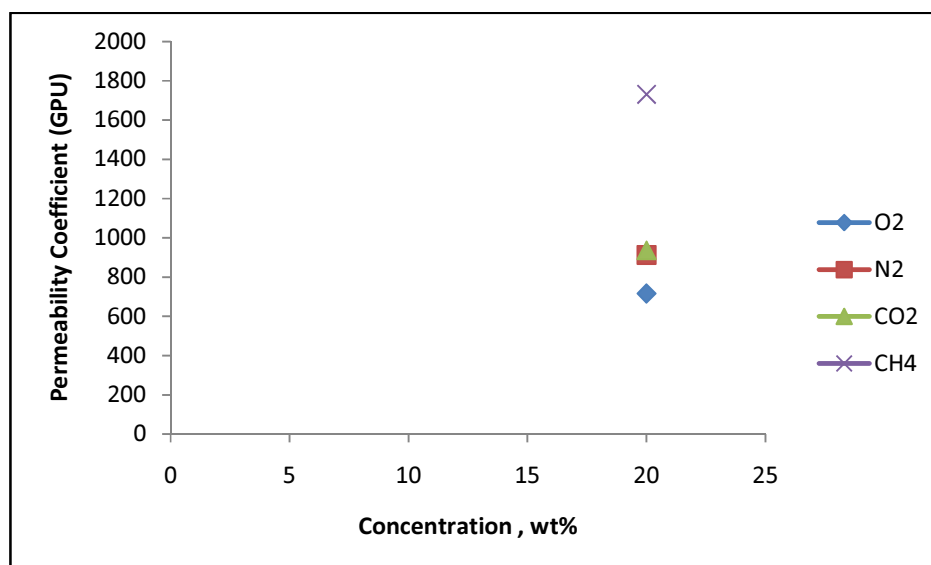


Figure 4.2: Permeability of each gas due to polymer concentration for uncoated membrane

For this uncoated membrane the CH₄ gas is permeate higher than other test gases. It might be due to the molecular weight of methane which is 16 g/mol, much lighter than carbon dioxide (44 g/mol), nitrogen (28 g/mol) and oxygen (32 g/mol). The small molecular weight the more rapid of the gas pass through the membrane. It shows the thicker the membrane, the slower the gas can surpass through the membrane with existent of defects. Therefore, to obtain high performances hybrid (PES/PSU) membrane, surface layer should be coated. The surface layer of the membrane has been coated with two coating agent which is Bromine water and PDMS.

Table 4.3: Separation properties for Hybrid (PES/PSU) coated with Bromine water

Sample	O ₂ (GPU)	N ₂ (GPU)	CO ₂ (GPU)	CH ₄ (GPU)	$\alpha(O_2/CH_4)$	$\alpha(N_2/CH_4)$	$\alpha(CO_2/CH_4)$
1	1240	849	909	1790	0.69	0.47	0.51
2	834	865	886	1750	0.48	0.5	0.51
3	731	812	1030	1750	0.42	0.47	0.59
Mean	934	842	941	1762	0.53	0.48	0.53

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

From Table 4.3, the membrane coated with bromine water shows improvement in selectivity than the uncoated membrane with higher pressure-normalized flux. Figure 2 shows the graph of permeability of each gas due to polymer concentration for membrane coated with bromine water.

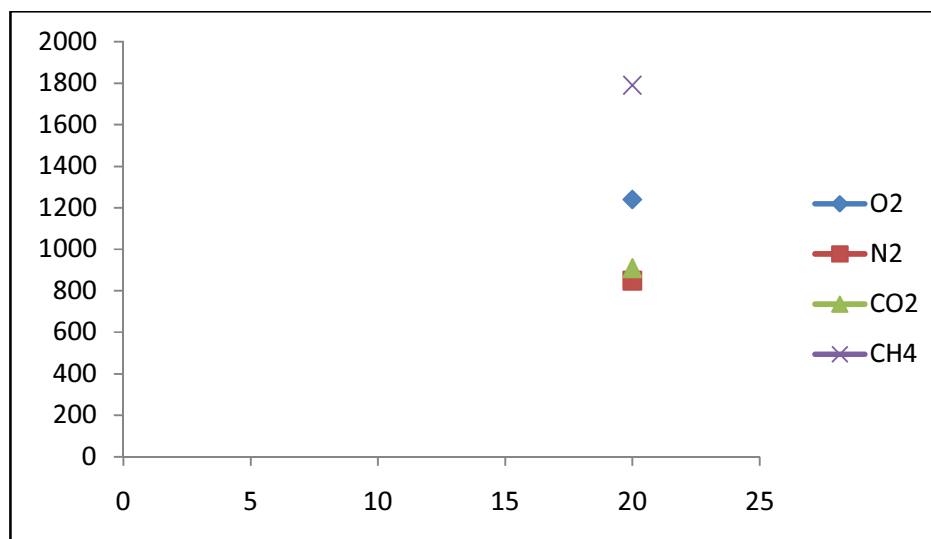


Figure 4.3: Permeability of each gas due to polymer concentration for membrane coated with bromine water.

The large increase in selectivity and relatively small decrease in CO₂ permeability indicate the presence of Br₂ molecules in the polymer matrix affects the free volume distribution in a manner that influences the transport of CH₄ to a greater extent than the transport of CO₂.

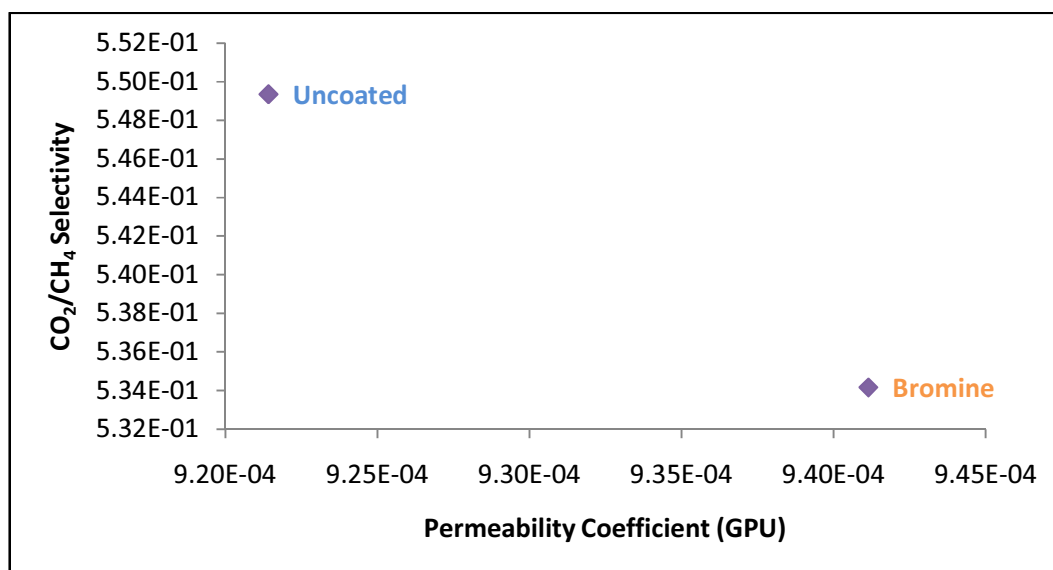


Figure 4.4: Permeability and Selectivity of CO₂ Gas for Uncoated Hybrid Membrane and Bromine Coated Hybrid Membrane.

Also shown in Figure 4.4 for comparison is data for two families of glassy polymers. The presence of large bromine water molecules in the polymer will change the free volume treatment and influence the magnitude of the permeability coefficient. The distribution of free volume also will change which will affect the selectivity (Ismail A.F. et al., 2002). It is evident that Br₂ treatment improved the transport properties of PSF membranes.

Table 4.4: Separation properties for Hybrid (PES/PSU) coated with PDMS

Sample	O ₂ (GPU)	N ₂ (GPU)	CO ₂ (GPU)	CH ₄ (GPU)	$\alpha(O_2/CH_4)$	$\alpha(N_2/CH_4)$	$\alpha(CO_2/CH_4)$
1	599	571	939	1680	0.36	0.34	0.56
2	816	794	1040	1870	0.43	0.42	0.56
3	590	561	920	1600	0.37	0.35	0.58
Mean	668	642	967	1720	0.387	0.371	0.563

1 GPU = 1×10^{-6} cm³/s.cm².cmHg

From Table 4.4, the hybrid membrane coated with PDMS shows a better selectivity towards O₂ and N₂ whereas for a good separation the value of α must either be over 1 or very low than 1. Compared to the membrane coated with bromine ($\alpha_{N_2/CH_4}=0.48$, $\alpha_{O_2/CH_4}=0.53$) which a bit higher in selectivity.

Table 4.5: Summary of average value of separation properties for uncoated and coated membranes.

Membrane Type	(P/l)O ₂ (GPU)	$\alpha(O_2/CH_4)$	(P/l)N ₂ (GPU)	$\alpha(N_2/CH_4)$	(P/l)CO ₂ (GPU)	$\alpha(CO_2/CH_4)$	(P/l)CH ₄ (GPU)
Uncoated	778	0.46	895	0.53	921	0.55	1680
Coated with bromine	934	0.53	842	0.48	941	0.53	1762
Coated with PDMS	668	0.387	642	0.371	967	0.563	1720

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

According to Table 4.5 above, Hybrid membrane coated with PDMS (967 GPU) shown and improvement in permeability for CO₂ where uncoated membrane (921 GPU) was the lowest. The value of permeability and selectivity of CO₂ for the three type membrane shown not much different that might give a huge change in separation of CO₂ gases but coating really do helps to reduce the defect and also covered the free volume in the ultrathin skin layers (Barbari, T.A. et al., 1995).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

From the research done, the permeability and selectivity of hybrid membrane (PES/PSU) has been determined successfully. The analysis is to determine the permeability and selectivity of different gases that can pass through the hybrid membrane (PES/PSU). Mixing two polymers together has been identified as one of the factor influence the effect on the flat sheet membrane as well as the coating agent. All of the uncoated membranes exhibited a poor selectivity but higher in permeability, probably due to the pores (defects) and the enhancement of free volume in the ultrathin skin layers.

Silicone rubber coating was successful increasing the membrane selectivity compared to uncoated membrane. It exhibited average CO₂ pressure-normalized flux of 967 GPU and CO₂/CH₄ average selectivity of 0.563. From selectivity aspect, this hybrid membrane show poor selectivity compared to PES membrane ($\alpha_{(CO_2/CH_4)} = 0.79$). Compared to permeation, this hybrid membrane shown high permeability (967 GPU) where the PES membrane only exhibit 197 GPU. From the result, hybrid membrane can be used for gas separation as it can act as a filter where “the permeate” will be methane and it filtered carbon dioxide. As according to the formula below, a very high or very low separation factors (α) will result in easy separation (Kohl et al., 1997).

$$\alpha_{ij} = P_i/P_j \quad (5.1)$$

It is strongly recommended that further research should be done in order to figure out the effectiveness of mixing two different polymers. On the other hand, other coating agent could be used for membrane treatment in order to enhance the productive of the membrane without a significant decrease in selective with defect-frees while being as thin as possible.

Therefore, the membrane application can be use as large scale in natural gas purification process where the improving in the membrane technology could reduce the capital investment with low environmental impact.

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