

PRODUCTION OF PDMS/PEG-PVDF THIN FILM
COMPOSITE MEMBRANE FOR CO₂/N₂ SEPARATION

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Thesis is submitted in fulfillment of the requirements for the award
of Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical Engineering and Natural Resources
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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project report and in my opinion this project is satisfactory in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering with Gas Technology (Honor)

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STUDENT'S DECLARATION

I hereby declare that the work in this report is my own except for quotations and summaries which have been duly acknowledged. The report has not been accepted for any degree and is not concurrently submitted for award of other degree.

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*To all family members,
I will always love you till the end of the time. Thank you for your support and
blessing.*

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ABSTRACT

A thin film composite (TFC) membrane was prepared for separation of carbon dioxide (CO₂) and nitrogen (N₂). The support layer was fabricated from different concentrations of polyethylene glycol (PEG) and the coating layer was prepared from different concentration of polydimethylsiloxane (PDMS). The concentration ratio of PDMS to PEG is 2:1, 1:1 and 1:2. Permeances and selectivity of the prepared membranes CO₂ and N₂ gases and their mixtures were measured under trans membrane pressure of 1 bar. The different concentration ratio of PDMS to PEG plays an important role for permeability and selectivity of CO₂/N₂ gas separation. It was shown that the highest permeability and selectivity was belong to membrane coating ratio of 1:2 (PDMS: PEG) followed by 2:1 (PDMS: PEG) and lastly 1:1 (PDMS:PEG). The result of permeation test was supported by the results from SEM and FTIR. SEM showed the membrane morphology for surface and cross section membrane. While, FTIR showed the functional group that exists within molecules in membranes.

ABSTRAK

Membran komposit filem nipis yang telah disediakan untuk pemisahan karbon dioksida (CO_2) dan nitrogen (N_2). Lapisan sokongan direka dari kepekatan yang berbeza polietilena glikol (PEG) dan lapisan salutan telah disediakan dari kepekatan yang berbeza polydimethylsiloxane (PDMS). Nisbah kepekatan PDMS untuk PEG 02:01, 01:01 dan 01:02. Kebolehtelapan dan pemilihan CO_2 membran yang disediakan dan gas N_2 dan campuran ini diukur di bawah tekanan membran trans 1 bar. Nisbah kepekatan yang berlainan PDMS untuk PEG memainkan peranan yang penting untuk kebolehtelapan dan pemilihan bagi pemisahan CO_2/N_2 gas pemisahan. Ia menunjukkan bahawa kebolehtelapan tertinggi dan pemilihan adalah milik membran salutan nisbah 1:2 (PDMS: PEG) diikuti oleh 02:01 (PDMS: PEG) dan akhir sekali 1:1 (PDMS: PEG). Hasil ujian penyerapan disokong oleh keputusan dari SEM dan FTIR. SEM menunjukkan morfologi membran untuk permukaan dan keratan rentas membran. Sementara itu, FTIR menunjukkan kumpulan berfungsi yang wujud dalam molekul dalam membran.

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LIST OF SYMBOLS

SYMBOLS	SPECIFICATION
$^{\circ}\text{C}$	Degree celcius
D_s	Diffusion coefficient of gas through membrane
Δp	Partial pressure different
$Q_{i/j}$	Volumetric flow rate of gas in standard temperature and pressure
A	Membrane active surface area
$\alpha_{i/j}$	Pure gas selectivity
C	Concentration
t	Time
N	Total number of particles in the system
r_i	Position vector of partical i
J_v	Viscous region
J_k	Knudsen region
ε	Membrane porosity
Δz	Membrane thickness
r	Pore radius

T	Thermodynamic temperature
M	Molar mass
R	Gas constant
μ	Gas dynamic viscosity
P_m	Average pressure

LIST OF ABBREVIATIONS

SYMBOLS	SPECIFICATION
CO ₂	Carbon Dioxide
N ₂	Nitrogen
DMAC	Dimethylacetamide
H ₂	Hydrogen
H ₂ O	Water
H(OCH ₂ CH ₂)NOH,	Polyethylene Glycol
N ₂	Nitrogen
NM	Nano Micro
PAN	Poly Acrylo Nitrile
PE	Polyethylene
PP	Polypropylene

PTFE	Poly Tetra Fluoro Ethylene
PVDF	Poly Vinylidene Fluoride
PVC	Poly Vinyl Chloride
PSF	Polysulfone
PVP	Polyvinylpyrrolidone
O ₂	Oxygen
TPU	Thermoplastic Polyurethane
TFC	Thin Film Composite

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, global warming has been identified as one of the major environmental issues. One of the gas contribute to global warming is CO₂. In order to limit the CO₂ emissions from oxidation of carbon-based fuel is to capture CO₂ and store it. Chemical solvents and physical absorbent are widely used in small scale CO₂ capture applications, but facing a problem in processing the large volume of CO₂ from fossil fuel combustion. Other than that, chemical solvents also facing problems in scale, efficiency and stability become barrier when chemical solvent use for high volume gas flow with smaller fraction of valuable products. In fact of that, they are required large amount of material undergoing significant changes in conditions and leading to high investment cost and also energy consumption. The alternative techniques under consideration involve material such as membrane. Membranes that include thin barriers allow selective permeation of certain gases which allowing one component in a gas stream to pass through faster than the others. Furthermore, membrane gas separations are widely used for H₂ recovery in ammonia synthesis, removal of CO₂ from natural gas, separation of CO₂ from N₂ and N₂ separation from the air.

The storage for CO₂ has been identified as one potential solution to greenhouse gases driven climate change. Membrane have been investigated for over 150 years and since 1980 gas separation membrane have been used commercially (Powell, 2005). Gas membrane separation is one of the method uses in industry. The advantages of using gas membrane separation are energy efficiencies and simplicity of membrane gas separation makes it extremely attractive for CO₂ capture.

1.2 Problem Statement

Gas membrane separation is one of the method uses to capture and storage CO₂. Instead of using solvent absorption, gas membrane separation is more compact, energy efficient and possibly more economical. The highest permeability and selectivity of membrane depends on material use for coating. Furthermore, the chosen of materials for coating plays an important role to get highest selectivity and permeability of CO₂/N₂ gas separation. The different concentration of coating material also plays an important role because the higher concentration of coating material, the higher will be their selectivity and permeability for CO₂/N₂ gas separation.

Uses membrane have been rapidly growing in the application of gas separation process. This research is concentrated on the ability performance of the membrane to separate the CO₂ and N₂. As mention before, CO₂ is a gas that can contribute to global warming and need to reduce CO₂ emission.

1.3 Research Objectives

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

- To produce TFC membrane.
- To characterise selectivity of TFC membrane.
- To investigate the permeability and selectivity of TFC membrane.

1.4 Scope of Research

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

- Develop a best formulation solution and produce the TFC membrane by using PDMS, PEG as coating layer and PVDF membrane as support layer.
- Study on performance of TFC membrane.
- Characterize on TFC membrane physically and chemically by using FTIR and SEM.

1.5 Rational and Significance of Research

- a) To increase the permeability and selectivity of CO₂ gas separation by membrane system.
- b) To developed the economical process for CO₂ capture to sustain supply the increasing gas demand.
- c) Build up extremely versatile capable medium to produce porous membrane for all separation stage.

CHARTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Membrane

Nowadays, membrane technology for gas separation are widely use because gas separation offer overall advantages such as reducing environmental impact and cost of industrial process. Based on Freeman (2005), gas separation membranes offer a number of benefits over other gas separation technologies. One of the benefit is membrane gas separation does not required a phase change. In addition, gas separation membrane unit are smaller than other types of plants, like stripping plants and therefore have relatively small footprints.

The term membrane most commonly refers as thin, film-like structure that separate or restrict certain molecules to flow through membrane. A membrane can be defined essentially as a semi-permeable barrier, which separates a fluid 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. The concept of membrane is simple and similar to a filter. Generally, CO₂ capture membranes are designed to be selective for small gases for example allowing N₂ to pass through while leaving a pure stream of CO₂ behind. **Figure 2.1** shows the separation of carbon dioxide and nitrogen used in industrial today.

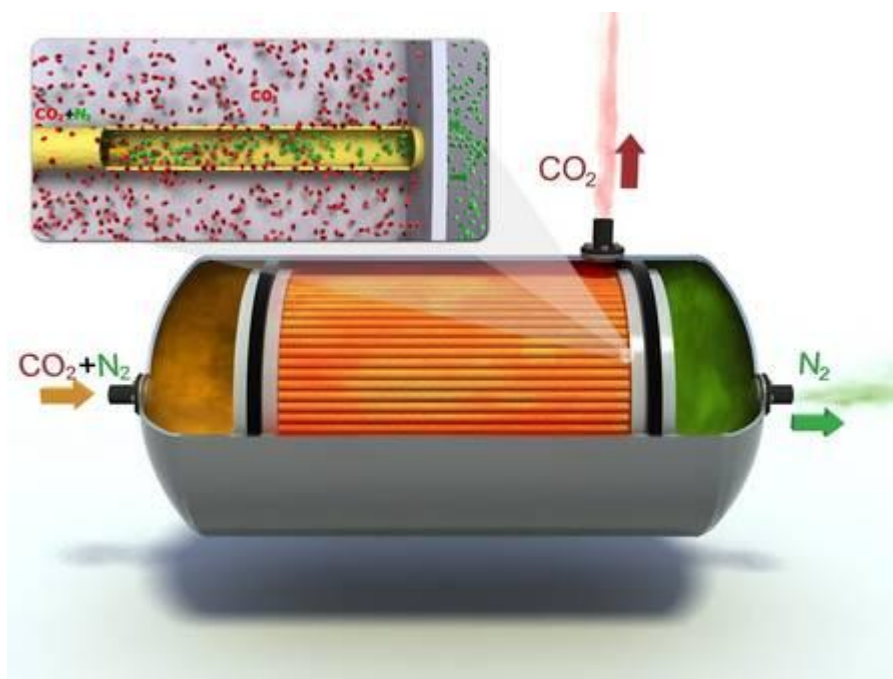


Figure 2.1 Separation of Carbon Dioxide and Nitrogen

2.1.2 Types of Membrane

The efficiency of the gas separation is based on permeability and selectivity of membrane material. Various types of membrane are widely use and produce today such as micro porous membranes, homogeneous membrane, asymmetric membrane, nonporous and dense membrane. **Table 2.1** show the types of membrane and their characteristic.

Table 2.1: Types of Membrane and Their Characteristic

Types of membrane	Characteristics	References
Micro porous membranes	The membrane behaves almost like a fibre filter and separates by a sieving mechanism determined by the pore diameter and particle size. Material that are used in making such membrane are ceramics, graphite, metal oxides, polymers and etc. The pores in the membrane may vary between 1 nm-20 microns.	Srikanth, (2004)
Homogeneous membranes	This is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. By using these membranes, chemical species of similar size and diffusivity can be separated efficiently when their concentrations differ significantly.	Srikanth, (2004)
Asymmetric membranes	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	Srikanth, (2004)

	<p>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.</p>	
Electrically charge membranes	<p>These are necessarily ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges. These are mainly used in the electro dialysis. Electrically charged membranes can be dense or micro porous, but are most commonly very finely micro porous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is referred to as an anion-exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane containing fixed negatively charged ions is called a cation-exchange membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much lesser extent by the pore size. The separation is affected by the charge and concentration of the ions in solution.</p>	Srikanth, (2004)
Flat film membranes	<p>Materials for flat film membranes are usually designs employ textiles, non-woven fabrics or porous polymeric sheets. Composite membranes of this construction enable the separating layer thickness to be reduced to a few microns. When high flux polymers are employed, the transport resistance of the non-selective support layer can</p>	Nunes, (2001)

	become a significant resistance. The effect of resistances in series with the separating layer resistance has the effect of reducing the overall membrane selectivity. Hence, much attention is given to minimizing the supporting layer's resistance.	
Nonporous, Dense Membranes	Nonporous, dense membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus, nonporous, dense membranes can separate permeants of similar size if their concentration in the membrane material (that is, their solubility) differs significantly. Most gas separation, pervaporation, and reverse osmosis membranes use dense membranes to perform the separation.	

Membrane can be classified into few types. The classification of membrane can help to improve the membrane application by knowing to the membrane morphology. Membranes can be classified, according to their morphology. Before this, types of membrane have been shown. Now, **Figure 2.2** shows the membrane classification according to the morphology.

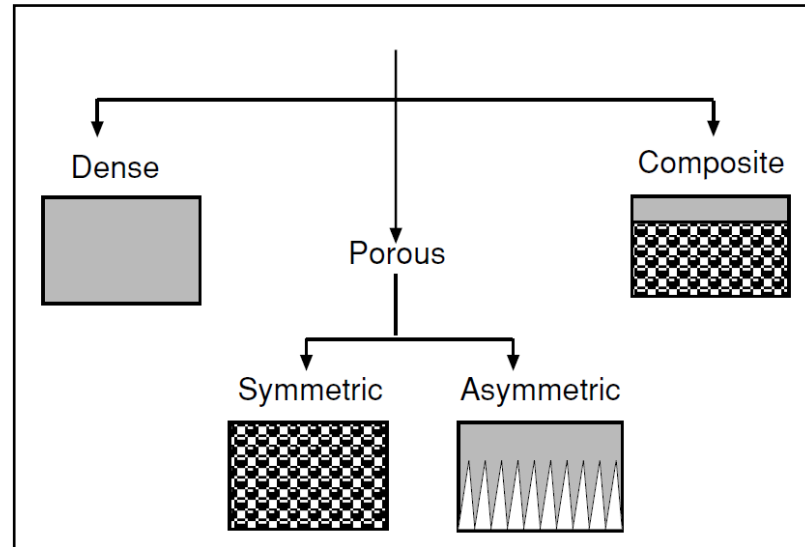


Figure 2.2 Membrane Classifications According to the Morphology (Nunes, 2006)

2.1.3 Mechanism for Gas Separation

There are two main membrane permeation mechanisms for gas separation mechanism such as dense membranes and porous membranes. Usually, dense membranes have high selectivity and gives low fluxes. However, larger pore gives higher fluxes but decrease selectivity.

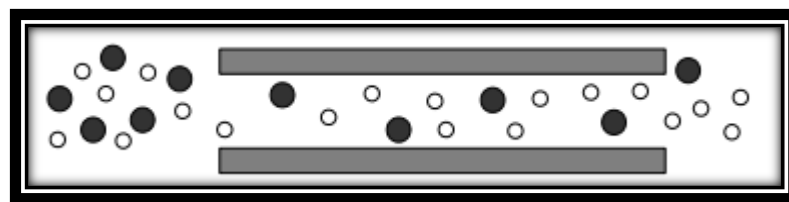
2.1.3.1 Dense Membrane Separation Mechanism

The solution or diffusion mechanism is the most commonly used physical model to describe gas transport through dense membrane. A gas molecule is

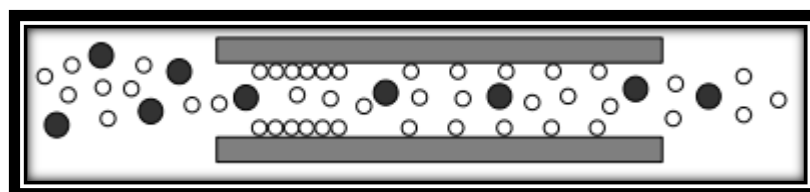
adsorbed on one side of the membrane, dissolves in the membrane materials, diffuses through the membrane and desorbs on the other side of the membrane.

2.1.3.2 Porous Membrane Separation Mechanism

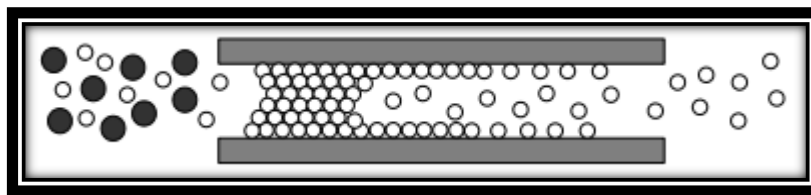
There are four types of diffusion mechanisms can be utilized to effect separation in porous membranes. In some cases, molecules can move through the membrane by more than one mechanism. These mechanisms can be described by Knudsen diffusion. The Knudsen diffusion gives low separation selectivity compare with surface diffusion and capillary condensation. In order to get high selectivity, shape selective separation and molecular sieving plays important role. The parameter need to be considered for separation mechanism depends strongly on pore size distribution, temperature, pressure and interactions between gases being separated and the membrane surfaces. **Figure 2.3** shows the transport mechanisms in porous membranes by Knudsen diffusion, surface diffusion, capillary condensation, molecular sieving.



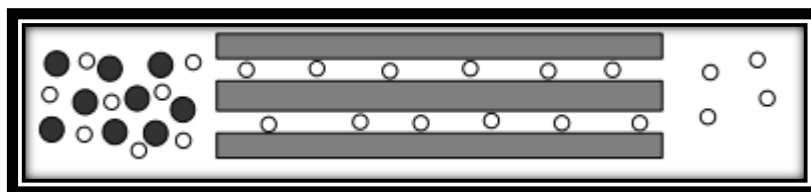
(i) Knudsen Diffusion



(ii) Surface Diffusion



(iii) Capillary Condensation



(iv) Molecular Sieving

Figure 2.3 Transport mechanisms in porous membranes: (i), (ii), (iii), (iv); (S.C.A. Kluiters, 2004)

Various mechanisms for gas transport across membranes have been proposed depending on the properties of both the permeant and the membrane. These include Knudsen diffusion, the molecular sieve effect and solution diffusion mechanism. **Figure 2.4** show the schematic presentation of mechanisms for permeation of gases through membrane.

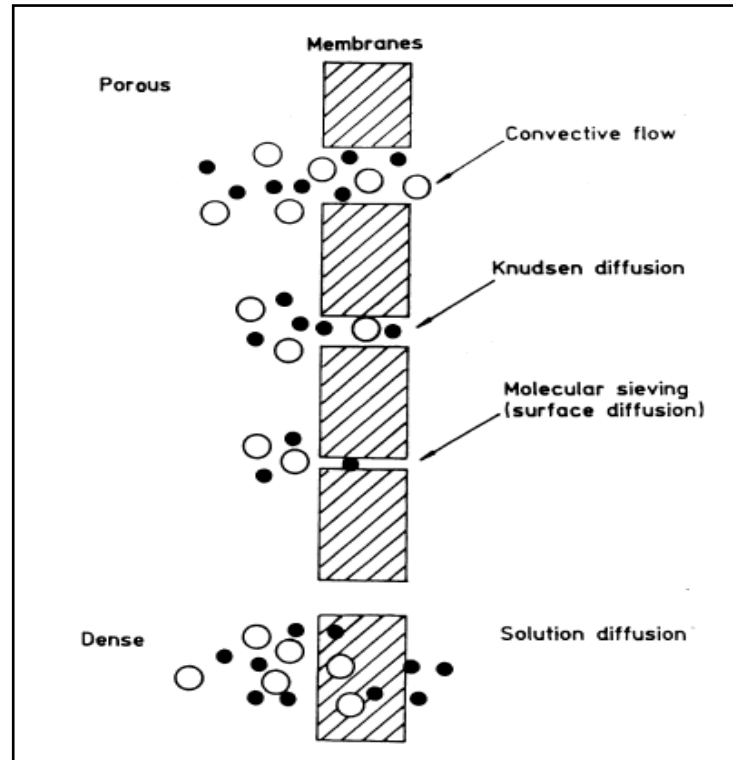


Figure 2.4 Schematic presentation of mechanisms for permeation of gases through membrane (Pandey, 1999)

2.2 Membrane Process

Membrane processing is a technique that permits concentration and separation without the use of heat. Particles are separated on the basis of their molecular size and shape with the use of pressure and specially designed semi-permeable membranes.

Table 2.2 show the application of membrane separation and membrane type. During the past two decades membrane separation processes have been developed and optimized for even large scale industrial applications. The most important of the processes include:

- Microfiltration and ultra-filtration
- Reverse osmosis
- Electro dialysis
- Gas separation
- Evaporation

Table 2.2: Application of Membrane Separation and Membrane Type

Membrane process	Membrane type	Application
Reverse osmosis	Asymmetric membrane	<ul style="list-style-type: none"> • used on a zinc sulfate rinse • operating on various copper sulfate rinses • Cadmium and chromium rinsewaters are also treated with RO • desalination and demineralization of saline water • demineralized or potable water
Ultrafiltration	Asymmetric membrane	<ul style="list-style-type: none"> • Biological buffers • Protein chemistry • Blotting and hybridization
Microfiltration	Symmetric membrane	<ul style="list-style-type: none"> • Purification of fluids in semiconductors • sterilization (in pharmaceutical)

Pervaporization	Non-porous membrane, composite membrane	<ul style="list-style-type: none"> • separation of more polar organics from less polar ones, • especially when water is absent • -water removal from liquids organics • -organic separation • -separation of liquid mixtures, especially of aqueous-organic azeotropes
Gas permeation	Non-porous membrane, asymmetric composite	<ul style="list-style-type: none"> • Prepurification of natural gas • hydrogen separation • biogas processing • splitting gas streams • removal or recovery of specific gases
Electro dialysis		<ul style="list-style-type: none"> • separation of microsolute and salts from macromolecular solution. • Removal of dissolved ions

2.3 Membrane Application

The applications of gas membranes separation are listed as below. **Table 2.3** shows a gas separation and its application (Nunes, 2006).

Table 2.3: Gas Separation and Its Applications (Nunes, 2006)

Gas Separation	Application
H ₂ /N ₂	Syngas ratio adjustment
CO ₂ /Hydrocarbon	Acid gas treatment and landfill gas upgrade
O ₂ /N ₂	Nitrogen generation and oxygen enrichment
H ₂ /CO	Syngas ratio adjustment
H ₂ S/Hydrocarbon	Sour gas treating
H ₂ O/hydrocarbon	Natural gas dehydration
H ₂ /Hydrocarbon	Refinery hydrogen, recovery
H ₂ O/air	Air dehydration
Hydrocarbons/air	Pollution control, hydrocarbon recovery
Hydrocarbons from process streams	Organic solvent recovery, monomer recovery.

2.4 Membrane in Gas Separation

The process that is considered in this work is membrane based gas separation process using polymeric membrane and organic membrane. **Figure 2.5** shows general membrane process that show how separation flows in membrane. As mention before, a membrane act as a barrier that separate into retentate, permeate and restrict transport of various chemical species in a selective manner. The stream that permeates through the membrane is the permeate stream, while the one retained by the membrane is the retentate. There are two characteristic of dictate the membrane performance, permeability and selectivity. Permeability is the flux of a specific gas

through the membrane and selectivity is the membrane's preference to pass one gas species and not another (Collin, 2008).

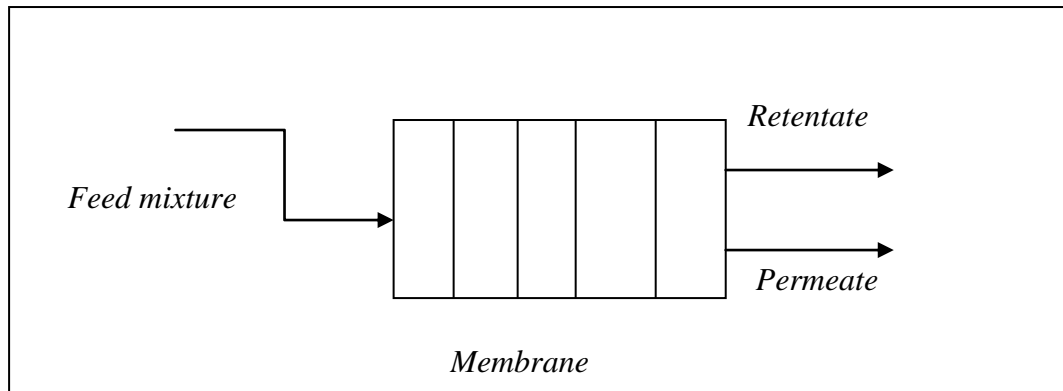


Figure 2.5 General Membrane Process

2.4.1 Polymeric Membrane

Polymeric membrane is one of the types of membrane used for gas separation. Polymeric membranes are the most popular membranes because of their high performance, easy synthesis, long life, good thermal stability, adequate mechanical strength and high resistance to gases and chemicals (Sadrzadeh, 2009). Moreover, polymeric membranes are characterized as a thin, dense selective surface skin on a less dense porous support that is non-selective (Colin, 2008). Membrane can be classified into two classes. There are porous and non-porous. A porous membrane is a rigid, highly voided structure with randomly distributed inner-connected pores. Non-porous that can be known as dense membranes provide high selectivity or separation of gases from their mixtures but the rates transports of the gases are usually low.

2.4.2 Inorganic Membrane

Inorganic membrane was representing as an alternative gas separation technology. There are two types of inorganic membrane, porous and non-porous. Non-porous membranes are generally used in highly selective separation of hydrogen (H_2), where transportation is through alloy of palladium. While, porous inorganic membranes are generally cheaper but less selective (Colin, 2008). The large size CO_2 compare with H_2 , can result in achieving CO_2 rich permeate stream by simple molecular sieving. However, inorganic membrane overcomes this by functionalizing the pores of the membrane to increase the CO_2 loading. **Figure 2.6** shows schematic of inorganic membrane operation through Knudsen and surface diffusion (Colin, 2008).

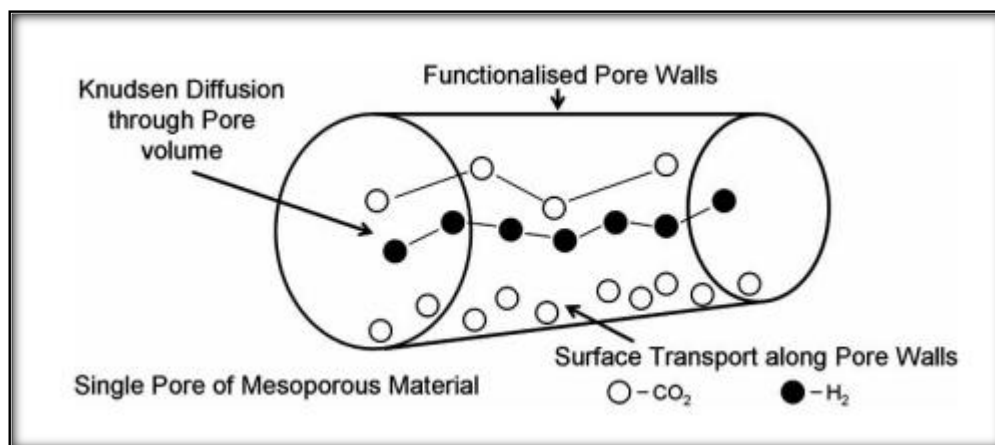


Figure 2.6 Schematic of Inorganic Membrane Operation through Knudsen and Surface Diffusion (Colin, 2008)

In order to get high selectivity and permeability, the correct membrane material and correct processing condition are needed. Selectivity is the ratio of the permeability of the CO_2 to other component in the stream (Mutun, 2010). The higher

the permeability, the less membrane is required for a given separation and result in lower cost. The higher the selectivity, the lower will be the losses of hydrocarbons when CO₂ is removed. **Table 2.4** shows the materials for gas separation membrane.

Table 2.4: Materials for Gas Separation Membrane (Nunes, 2001)

Organic polymer	Inorganic materials
Polysulfone, polyethersulfone	
Celluloseacetate	Carbon molecular sieves
Polyimide, polyetherimide	Nonporous carbon
Polycarbonate (brominated)	Zeolites
Polyphenyleneoxide	Ultramicroporous amorphous silica
Polymethylpentene	Palladium allys
Polydimethylsiloxane	Mixed conducting perovskites
Polyvinyltrimethylsilane	

2.5 Membrane Modification

Based on Jiang et al., (2008) research, rubbery thin film composite membrane have been used in petroleum and chemical industries to preferentially permeate volatile organic compound for many decades with the benefit of saving energy and

valuable hydrocarbons. Poly(dimethylsiloxane) (PDMS) is a favourable coating material in polymeric membrane-based gas separation due to its hydrophobicity and thermal stability. Its low glass transition temperature ($-129\text{ }^{\circ}\text{C}$) results in extremely high permeation through the membrane for a wide range of gases due to the flexible polymer backbone. However, it is limited in mechanical strength and selectivity particularly for highly condensable hydrocarbons in admixture with permanent gases. For example, Jiang, (2008) showed that PDMS coated membrane can be plasticized by propane and propylene, resulting in significant permeance increases for both hydrocarbons and nitrogen in a quaternary mixture of propane, propylene, ethylene and nitrogen, therefore, the selectivity of hydrocarbons to nitrogen were not as high as expected.

The materials used to fabricate membranes can be categorized as organic and inorganic. Organic materials are either cellulose-based or consist of modified organic polymers. Inorganic materials such as metals and ceramics are used in niche industrial applications, but are often cost prohibitive in wastewater treatment. Based on Stephenson, (2000) a partial list of available materials is given below:

- Titanium Dioxide/Zirconium
- Dioxide Cellulose Acetate
- Polyether Sulfone(PES)
- Poly Acrylo Nitrile (PAN)
- Polyamide, Polyimide
- Polyethylene (PE)
- Polypropylene (PP)
- Poly Tetra Fluoro Ethylene (PTFE)
- Poly Vinylidene Fluoride (PVDF)
- Poly Vinyl Chloride (PVC)

2.5.1 Polyvinylidene Fluoride (PVDF) Membrane

The use of polyvinylidene fluoride (PVDF) membrane as a support substrate layer for making a polyamide thin-film composite (TFC) has been hindered by the hydrophobic nature of PVDF. By the research of Kim et al., (2009) the objective of their study was to investigate whether the PVDF based microfiltration membrane could be modified to make it suitable for polyamide TFC membrane preparation. From their research, plasma modification of PVDF membranes enhances oxygen/methane (1:1) gas mixture is effective.

Nowadays, the types of support polysulfone (PSF) or polyethersulfone (PES) are mostly used as an interfacial polymerization. Due to the A.L. Ahmad (2008) and group, they found that Polypropylene (PP) and polyvinylidene fluoride (PVDF) are very attractive materials as a hydrophobic support for forming a TFC membrane due to its high durability and resistance to chemicals, pH variations, and a substantially wide range of solvents. They found that, the TFC with 6% w/v of glutaraldehyde based on PVDF achieved the highest permeance of 881.70 GPU and 18.08 for selectivity through the increase in effective layer and skin layer thickness. This TFC promises to provide porous and hydrophobic membranes for use in membrane gas absorption (MGA) processes. The absorption of CO₂ in deionized water was studied in MGA system in which the mass transfer coefficient (K) and CO₂ flux decreased with increasing CO₂ concentration in feed stream.

Polymeric membranes can be prepared by phase inversion process. The remixing of a polymer solution can be induced by compositional changes of constituents due to mass transfer in a system. Based on the research of Yuan et al., (2008) they are produced asymmetric blend hollow fibre membrane using new casting dope containing poly(vinylidene fluoride) (PVDF)/Thermoplastic polyurethane (TPU)/Polyvinylpyrrolidone (PVP) N, N dimethylacetamide (DMAc).

The additives are widely used for structure control of membranes such as polyvinylpyrrolidone(PVP) and Polyethylene glycol (PEG). **Figure 2.7** show the PVDF membrane.

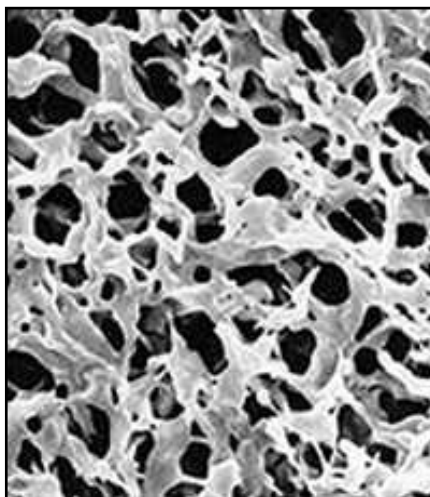


Figure 2.7 Polyvinylidene fluoride (PVDF) Membrane

2.5.2 Polyethylene Glycol (PEG)

Based on Wongchitphimon *et la.*, (2010), Polyethylene glycol (PEG) is one of the additives used to promote pore formation in the polymeric membranes. PEG is a linear polyether compound available in a variety of molecular weight, which is indicated by a numeric suffix followed the abbreviation (PEG). Its general formula is expressed as $H(OCH_2CH_2)_nOH$, where n is the average number of repeating oxyethylene groups. PEG is water-soluble. It is also soluble in many organic solvents including aromatic hydrocarbons. Thus PEG has been reported as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic membrane preparation, (Wongchitphimon *et la.*, 2010).

2.5.3 Poly (Dimethyl Siloxane) PDMS

Currently, poly(dimethyl siloxane) (PDMS) is the primary polymer used for olefin separations. In the mid-1950s, PDMS had been found to have a much higher permeability to gases than almost all other synthetic polymers known at that time, and even nowadays PDMS is still considered to be one of the most permeable polymers. This is shown by the research of Shi Y. *et al.* (2006), in their research, poly(dimethyl siloxane) (PDMS) thin film composite membranes originally developed for pervaporation applications for the separation of propylene from nitrogen, and the feasibility of adapting such membranes to olefin recovery from polyolefin purge gas. From their research, the PDMS composite membrane can be adapted to propylene separation from nitrogen that is relevant to propylene recovery from polypropylene degassing off gas.

2.5.4 Thin Film Composite Membrane (TFC)

Thin film composite membrane (TFC) is actually the combination of more than one polymer. TFC membrane has been widely applied in gas separation. It is normally fabricated by filling a high permeability and low selectivity polymer into the defects of a highly selective glass polymer asymmetric membrane. The structure of composite membrane can be divided into three layers based on the configuration of the membrane; they are coating layer, selective layer, and porous support layer. The coating layer serves to plug defects in the selective layer and reduce the risk of gas permeation through the defects. The performance and applicability of composite membrane largely depend on the defects filled by the coating material during the fabrication processes, (Zhang *et al.*, 2010).

Composite materials combine the desirable properties of multiple materials. In this sense, composite filters are created by sequential synthesis rather than simply mixing different chemicals. While a variety of approaches are used in their manufacture, most common is the controlled deposition of a material onto a preformed sheet or grid of support material. Composite materials are used when the physical features of one material (for example, the strength of the support material) need to be combined with the chemical features of another (for example, the high charge of the filter material).

Zhang et al., (2010) have been produce composite membrane by coating a thin layer of polyfluoropropylmethylsiloxane (PTFPMS) on the dense layer of asymmetric polyetherimide (PEI) membranes to plug the defects in order to separate O_2/N_2 and H_2/N_2 . Figure 2.5 show the thin film composite membrane with selective layer and porous support. Whereas in **Figure 2.8** shows the thin film composite membrane for RO membrane. **Figure 2.9** show the usual thickness of each layer. While **figure 2.10** shows the usual thickness of each layer (Nunes, 2006).

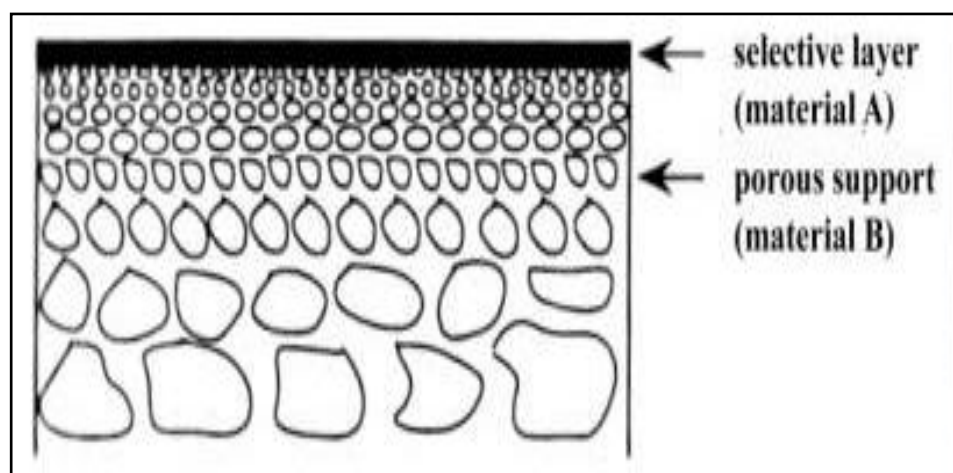


Figure 2.8 Thin Film Composite Membrane

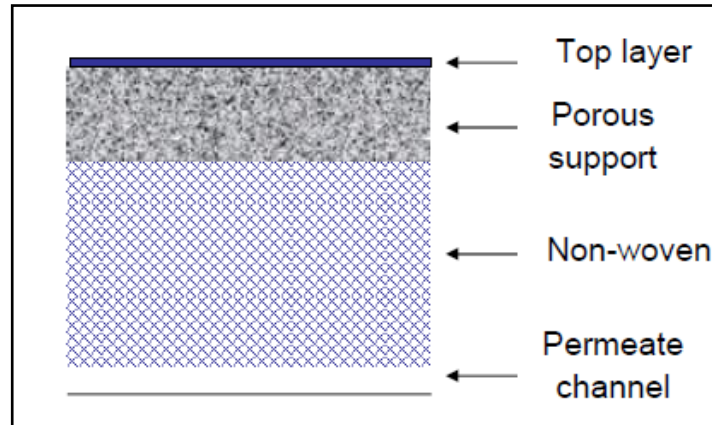


Figure 2.9 Thin Film Composite Membrane for RO Membrane

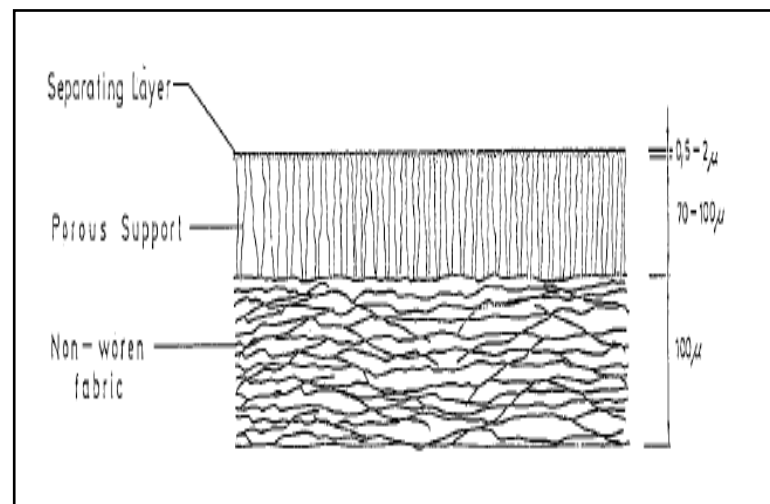


Figure 2.10 Usual Thickness of Each Layer (Nunes, 2006)

2.6 Membrane Module

Membranes that have been formulated in order to get the best separation results are based on the advanced technology in membrane separation. For some reason, a few types of membrane module are designed and already available in market. Following are the membrane module that largely used for industrial application:

- i) Plate and frame module
- ii) Spiral wound module
- iii) Tubular membrane module
- iv) Hollow fibre module

2.6.1 Plate and Frame Module

Figure 2.11 show a plate and frame modules that use flat sheet membranes. The flat sheet membranes are layered between spacers and support. From the source of United States Environmental Protection Agency, the supports also form a flow channel for the permeate water. The feed water flows across the flat sheets and from one layer to the next. Recent innovations have increased the packing densities for new design of plate-and-frame modules. Maintenance on plate and frame modules is possible due to the nature of their assembly. They offer high recoveries with their long feed channels and are used to treat feed streams that often cause fouling problems. Only recently advanced designs of plate-and-frame modules capable of operating up to 25% dissolved solids and operating pressures up to 4500 psia have been placed in operation in Germany (Stanford and Miller, 1994). This development

opens new opportunities for the use of reverse osmosis for concentration of metal finishing wastewaters.

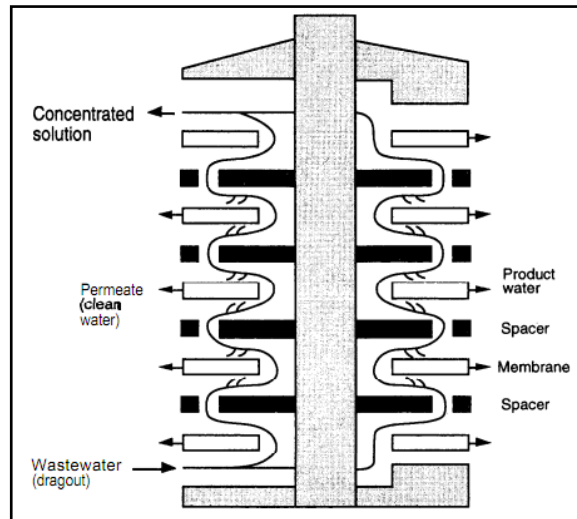


Figure 2.11 Plate and Frame Module

2.6.2 Spiral wound module

Briefly, as shown in **Figure 2.12** spiral wound modules use several layers of flat sheet membrane like wrapped spirally around a collection tube. The feed flows in against one end of the rolled spiral and along one side of the membrane sandwich. The support layers are designed to minimize pressure drop and allow a high packing density. Additionally, the spiral wound modules can be designed by equipment suppliers to promote turbulence and therefore increase the mass transfer across the membrane or to provide an uninterrupted flow path to decrease membrane fouling. Spiral wound modules offer greater packing densities, but maintenance is difficult.

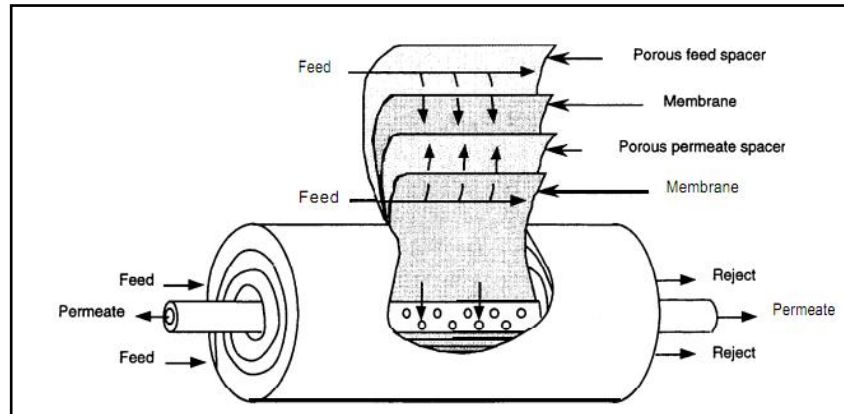


Figure 2.12 Spiral wound module

2.6.3 Hollow Fibre Module

As shown in **Figure 2.13**, hollow-fibre modules consist of small diameter membrane fibres bundled within cylindrical pressure vessels. The fibres are pressurized from the outside. The permeate flows to the interior bore or lumen of the fibre and down the length of the fibre to the product header. Fibres can also be pressurized from the inside, but greater mechanical strength of the fibres is necessary to prevent fibre rupture. By feeding on the shell side of the fibres, a lower pressure drop is encountered down the bore of the fibre since the permeate flow rate is less than the feed flow rate. Hollow-fibre modules offer the greatest packing densities of the configurations described.

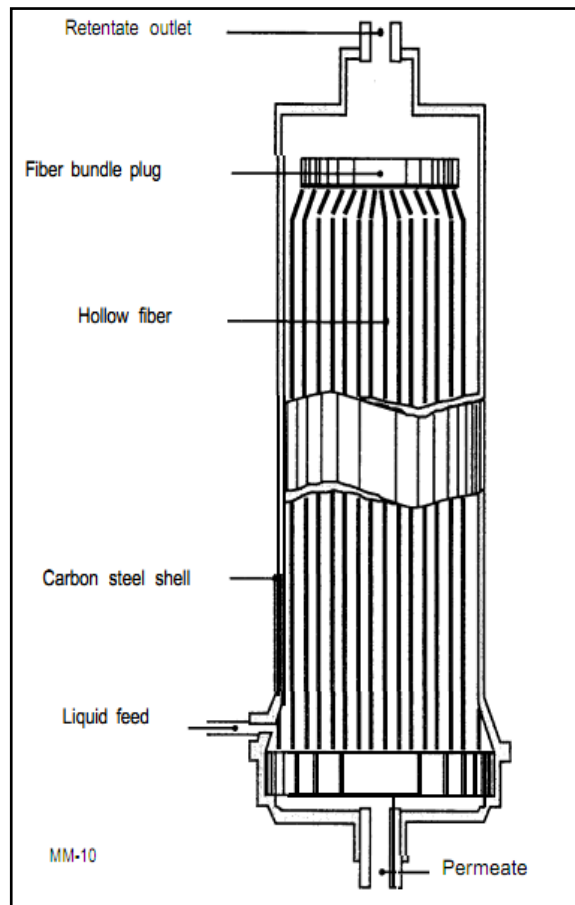


Figure 2.13 Hollow Fibre Modules

2.6.4 Tubular Module

Tubular modules have membranes supported within the inner part of tubes. The operator can easily service feed and permeate channels to remove fouling layers. Tubular modules are somewhat resistant to fouling when operated with a turbulent feed flow. This is accomplished with larger flow channels than those used with hollow fibre and spiral wound modules. The drawbacks of tubular modules are their high energy requirements for pumping large volumes of water, high capital costs,

and low membrane surface area per unit volume of module. **Figure 2.14** shows a tubular module.

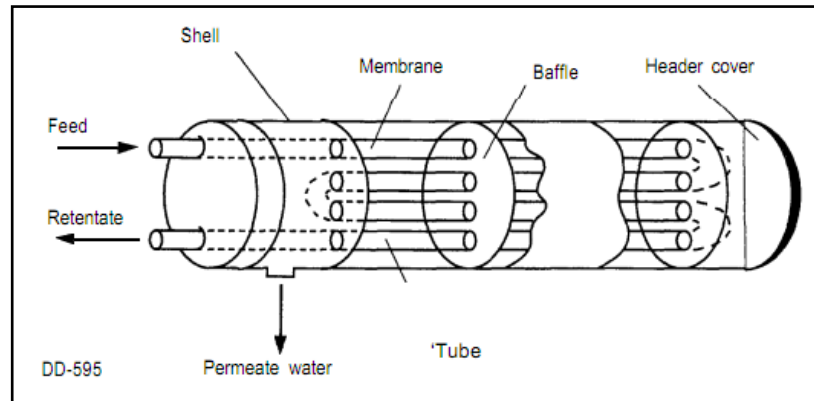


Figure 2.14 Tubular Module

The disadvantages and advantages of membrane module can be summarizing as shown in **Table 2.5**. **Table 2.5** shows the comparison for membrane module.

Table 2.5: Comparison for membrane module

System	Advantages	Disadvantages
Flat sheet/ Plate and frame	<ol style="list-style-type: none"> 1. Low hold up volume 2. Permeate from individual 3. Membrane replacement easy 	<ol style="list-style-type: none"> 1. Difficult to clean 2. Susceptible to plugging
Spiral	<ol style="list-style-type: none"> 1. Compact 2. Minimum energy consumption 3. Low capital 	<ol style="list-style-type: none"> 1. Not suitable for very viscous fluid Wound 2. Dead spaces 3. Difficult to clean

Hollow fibre	<ol style="list-style-type: none"> 1. Low hold up volume 2. Backflushing possible 3. Low energy consumption 	<ol style="list-style-type: none"> 1. Susceptible to end-face fouling 2. Not suitable for viscous fluid 3. Single fibre damage
Tubular	<ol style="list-style-type: none"> 1. Feed stream with particulate matter can be put through membrane 2. Easy to clean 	<ol style="list-style-type: none"> 1. High energy consumption 2. High hold-up volume

2.7 Theories

2.7.1 Knudsen Diffusion

Three types of processes can be considered depending on the membrane structure and permeation mechanism: Knudsen's diffusion through microporous barrier. Pandey. et al., (2001) described that Knudsen diffusion as the only transport mechanism contributing to the separation of various components in a gaseous mixture at elevated temperature in a porous membrane. Plus, gas permeation by Knudsen diffusion varies inversely with the square root of the molecular weight. The ideal separation for binary gas mixtures, therefore, equals the inverse of the square root of the ratio of the molecular masses. **Figure 2.15** show the Knudsen diffusion that is described by the Einstein relation as follows:

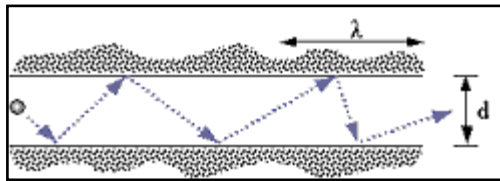


Figure 2.15 Transport in Small Pore of Knudsen Diffusion (Malek et al., 2003)

From the **Figure 2.15** Knudsen diffusion is described by the Einstein relation as equation (1):

$$D_s(c) = \lim_{n \rightarrow \infty} \frac{1}{6Nt} \sum_{i=1}^N [|ri(t) - ri(0)|]^2 \dots\dots\dots(1)$$

Where D_s is the self-diffusion coefficient, which depends on the concentration C , t is time, N is the total number of particles in the system, and ri is the position vector of particle i . Knudsen diffusion occurs when the mean free path is relatively long compared to the pore size, so the molecules collide frequently with the pore wall. Knudsen diffusion is dominant for pores that range in diameter between 2 and 50 nm.

Knudsen number can be used to characterize the flux mechanism of gas permeating through a membrane, which is defined as the ratio of the gas molecule mean free path length to the pore diameter (d) of the membrane. When $K_n=1$, the flux is the viscous flow dominant. When $K_n=1$, the flux is the Knudsen diffusion dominant. The gas permeance through the membrane in the viscous region J_v and Knudsen region J_K can be defined as equation (2) and (3) (Zhang et al., 2010):

$$J_V = 2986.7 \times \frac{\varepsilon r^2}{8\mu RT \tau \Delta z} P_m \dots\dots\dots(2)$$

$$J_K = 2986.7 \times \frac{4\sqrt{2}}{3} \times \frac{\varepsilon r}{\Delta z \sqrt{(RT \pi M)}} \dots\dots\dots(3)$$

where ε is the membrane porosity, Δz is the membrane thickness (m), r is the pore radius (m), T is the thermodynamic temperature (K), M is the molar mass (kg mol⁻¹), R is the gas constant (J mol⁻¹ K⁻¹), μ is the gas dynamic viscosity (Pa s), and P_m is the average of pressures at both sides of the membrane (Pa).

CHAPTER 3

METHODOLOGY

3.1 Research Design

The experimental work involved in this study is depicted in a flowchart as shown in **Figure 3.1:**

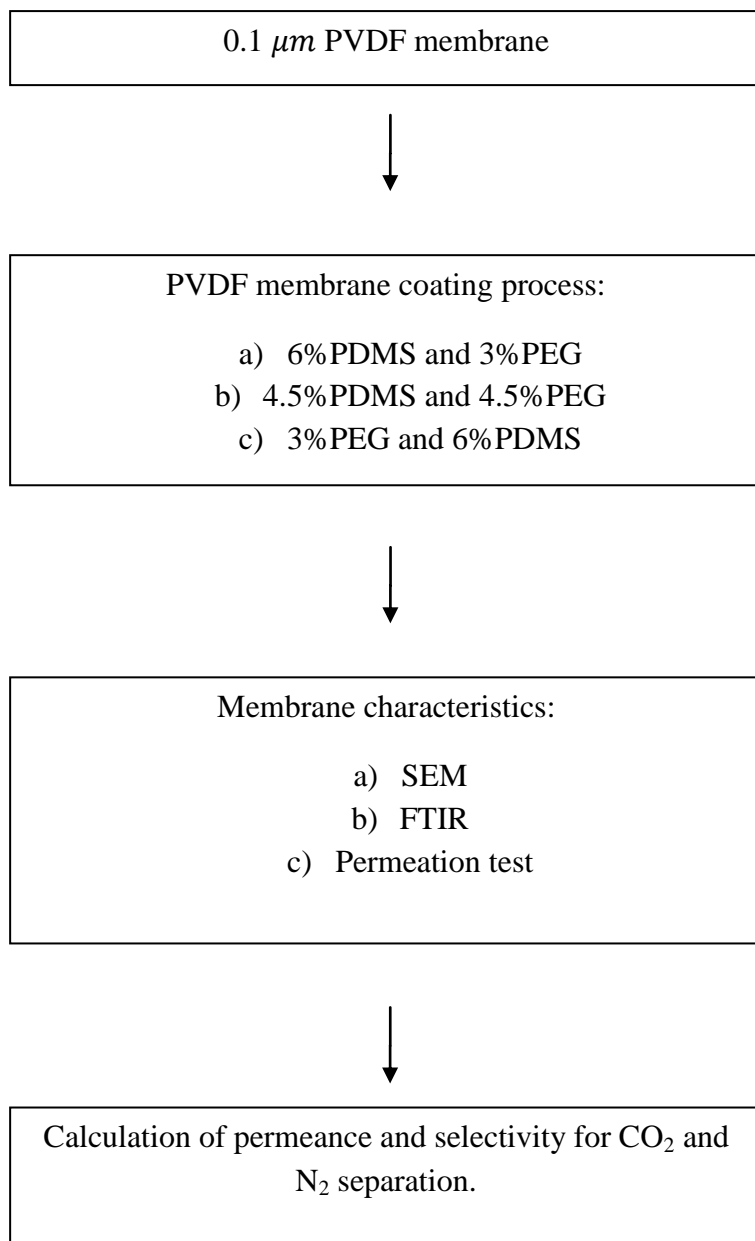


Figure 3.1 The Experiment Workflow of Research Study

3.2 Material Selection

In this study, already made PVDF is used instead of preparing them. It is easier way to just directly coat the already made PVDF membrane with PDMS and PEG. Coating concentration is in the range of PDMS and PEG with different concentration with 2:1, 1:2 and 1:1 respectively.

3.2.1 Polyvinylidene Fluoride (PVDF)

As state earlier, already made membrane was used. **Figure 3.2** shows the main chemical structure of PVDF. As a semi-crystalline polymer, PVDF is fit for membrane material due to its excellent chemical resistance, physical and thermal stability, high strength and flexibility. However, the hydrophobicity of PVDF remains a problem and limits its application, thus, hydrophilic modification of PVDF membranes is one of the hotspots in membrane science. **Table 3.1** shows the characteristics of PVDF.

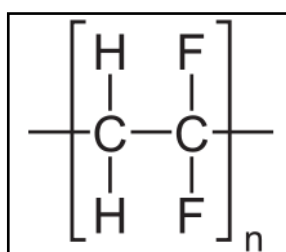


Figure 3.2 Chemical Structure of Poly Vinylidene Fluoride (PVDF)

Table 3.1: Characteristics of Polyvinylidene Fluoride (PVDF)

Properties	Characteristic
Molecular fomular	$-(C_2H_2F_2)_n-$
Appearance	Whitish or translucent solid
Solubility in water	Not soluble in water
IUPAC name	Poly-1,1-difluoroethane

3.2.2 Poly Dimethyl Siloxane (PDMS)

PDMS commonly referred as silicones. Plus, it is widely used for silicon-based organic polymer. Generally, PDMS is clear, inert, non-toxic and non-flammable. Its applications range from contact lenses and medical devices to elastomers; it is present, also, in shampoos (as dimethicone makes hair shiny and slippery), food (anti-foaming agent), caulking, lubricating oils, and heat-resistant tiles. **Figure 3.3** show the molecular structure for PDMS. While, **Table 3.2** shows the characteristics of PDMS.

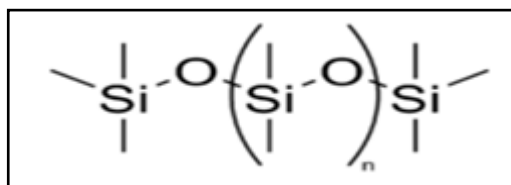
**Figure 3.3** Molecular Structure of Poly Dimethyl Siloxane (PDMS)

Table 3.2: Characteristics for Poly Dimethyl Siloxane (PDMS)

Items	Specification
Molecular formula	$(C_2H_8OSi)_n$
Density	965 kg m^{-3}
Melting point	N/A (vitrifies)
Boiling point	N/A (vitrifies)

3.2.3 Poly Ethylene Glycol (PEG)

Polyethylene glycol is a polyether compound also known as polyethylene oxide (PEO) or polyoxyethylene (POE) depending on their molecular weight. Figure 3.4 show a structural of polyethylene glycol. PEG is a linear polyether compound available in a variety of molecular weight, which is indicated by a numeric suffix, followed the abbreviation (PEG).

Its general formula is expressed as $H(OCH_2CH_2)_nOH$, where n is the average number of repeating oxyethylene groups. PEG is water-soluble. It is also soluble in many organic solvents including aromatic hydrocarbons. Thus PEG has been reported as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic membrane preparation, (Wongchitphimon, 2010).

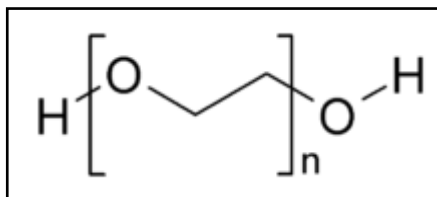


Figure 3.4 Chemical Structure of Poly Ethylene Glycol (PEG)

3.2.4 Nitrogen (N₂) and Carbon Dioxide (CO₂) Gases

The membranes were tested using pure CO₂ and CH₄ as test gases. **Table 3.3** shows the properties of pure CO₂ and CH₄.

Table 3.3: Properties of Pure Methane (CH₄) and Carbon Dioxide (CO₂)

Properties	Nitrogen (N ₂)	Carbon dioxide (CO ₂)
Molecular weight, (gmol ⁻¹)	14.01	44.01
Melting point, (°C)	-210	-78
Critical temperature, (°C)	-195.8	31
Critical pressure, (bar)	33.56	73.83

3.3 Membrane analysis

In membrane characterization method, the prepared thin film composite membrane is characterized on the FTIR and SEM.

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through. However, FTIR provides some information or advantages such as it can identify unknown materials, determine the quality or consistency of a sample and can determine the amount of components in a mixture. **Figure 3.5** shows FTIR that can be used to analyse membrane.



Figure 3.5 Fourier Transform Infrared Spectroscopy (FTIR)

3.3.2 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. The advantages of SEM are to know the structure of membrane for example cross section and surface of membrane. **Figure 3.6** shows SEM uses to analyse membrane structure.



Figure 3.6 Scanning Electron Microscope (SEM)

3.3.3 Gas Permeation Tests

Gas permeation test is used to measure the gas permeability, pore size and surface porosity is important in studying mass transfer in the porous membranes for gas absorption. Pure CO_2 and CH_4 gases were utilized in the permeation test. Moreover, volumetric gas permeation rates were measured with soap bubble flow meter at 25°C . **Figure 3.7** show the set up for gas permeation test.

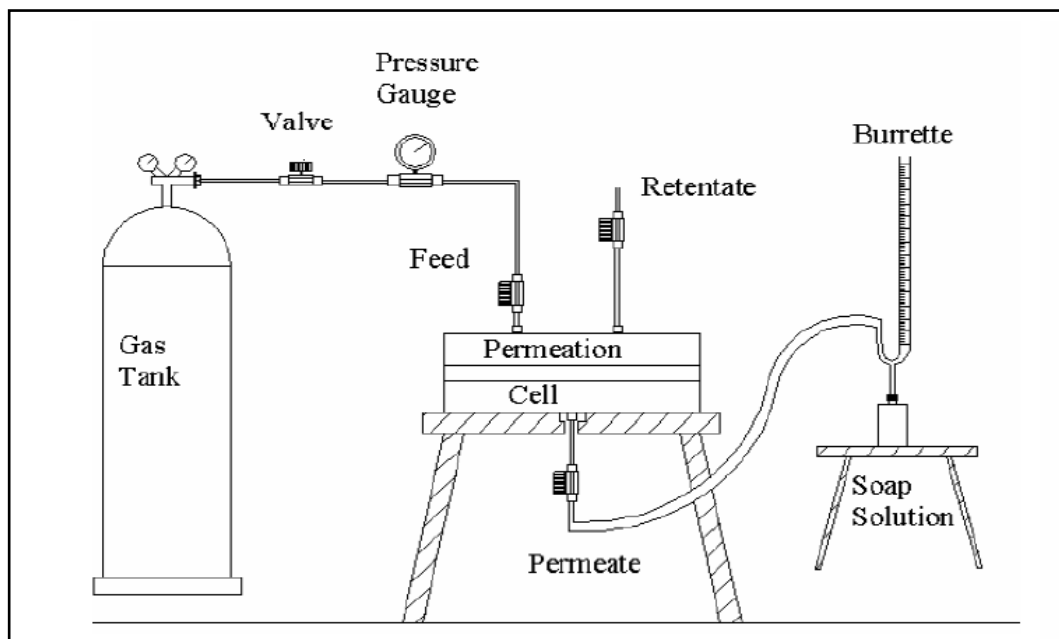


Figure 3.7 Gas Permeation Test (Mutun, 2010)

3.4 Gas Permeation Measurement

The pressure normalized fluxes of the membrane were determined by a variable volume method using pure CO₂ and N₂ at room temperature of 28°C by using pressure of 1 bar. Once membranes were in the permeation cell, the pure gas such as CO₂ and N₂ would permeate by letting CO₂ through the membrane first with pressure 1 bar. Volumetric gas permeation rates were determined with a simple soap bubble flow meter. The time the first bubble was taken until required volume reached. The time taken for each sample of membrane was taken by at least three averages. The pressure normalized flux $(P/1)_{i/j}$ is calculated as **equation 3.1**.

$$\frac{P}{1} = \frac{Q_{i/j}}{(\Delta p)(A)} \quad \text{Eq 3.1}$$

$Q_{i/j}$ is the volumetric flow rate of gas 'i or j' at standard temperature and pressure, Δp is the trans-membrane pressure difference, and A is the membrane active surface area. Permeance are calculated in gas permeance unit, GPU, as shown in **equation 3.2**.

$$\text{GPU} = 1 \times 10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2 \text{sec} \cdot \text{cmHg}} \quad \text{Eq 3.2}$$

The pure gas selectivity is determined by taking the ratio of the pure gas permeances as shown in **equation 3.3**.

$$\alpha_{i/j} = \frac{\left(\frac{P}{1}\right)_i}{\left(\frac{P}{1}\right)_j} \quad \text{Eq 3.3}$$

CHAPTER 4

RESULT AND DISCUSSION

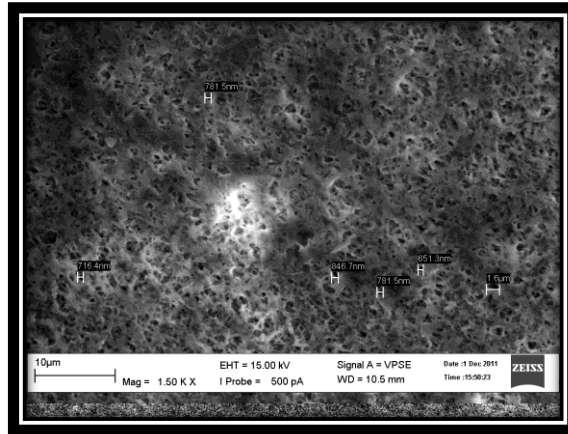
The aim of this research was to achieve the main objectives of this study which are to produce TFC membrane, to characterise selectivity of TFC membrane and also to investigate the permeability and selectivity of TFC membrane. The characterisation of membrane surface and cross section is characterised by using SEM and FTIR. Permeation test is done to investigate their selectivity and permeability of CO₂/N₂ gases separation.

4.1 Scanning Electron Microscope (SEM)

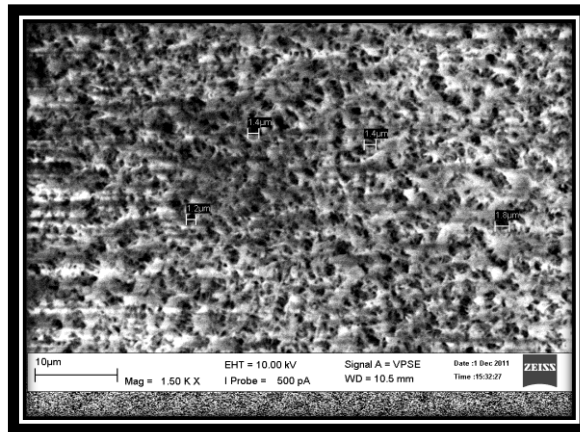
Scanning electron microscopy (SEM) was used to investigate the morphology and topography of the membranes. The membrane for cross-sectional sample was prepared by freezing the membrane first using the liquid nitrogen and then breaking the sample. Scanning electron photomicrograph of membrane coating with 4.5%PDMS and 4.5%PEG, 6%PDMS and 3%PEG and 6%PEG and 3%PDMS was shown in **Figure 4.1** respectively. The membrane surface for **Figure 4.1 (iii)** is smoother compare membrane in **Figure 4.1 (i)** and **(ii)**. The defect is identified by present of pores size. While membrane coated with 6%PEG and 3%PEG have less

membrane defects compare membrane in **figure 4.1 (i)** and **(ii)**. Figure 4.2 shows SEM image for unmodified PVDF membrane which consist of defects (Boributh, 2009). This PVDF membrane shows more defects than modified membrane. In order to decrease the defects, coating process is suitable way process to reduce the defects.

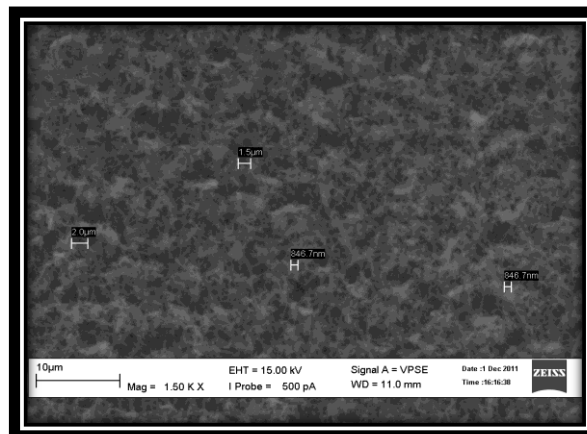
Morphology of membrane surface must be fewer defects in order get the highest selectivity of CO₂/N₂ gas separation. One of the characteristic in order to get the highest selectivity is smoother surface of membrane. The reasons of membrane defects are improperly done during coating of PDMS and PEG. Other than that, cutting process after immersed in nitrogen liquid must be properly done without affect the membrane surface. PEG and PDMS is one of the methods reducing the defects of membrane. Based on Wongchitphimon et. al., PEG is one of the additives used to promote pore formation in the polymeric membranes. The characteristic of PEG itself makes them suitable for coating. These characteristics are water-soluble which are soluble in many organic solvents including aromatic hydrocarbons, as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic membrane such as PVDF membrane. PVDF membrane is hydrophobic membrane and PEG helps PVDF membrane to achieve the highest permeability and selectivity.



(i) 4.5% PDMS and 4.5% PEG



(ii) 6% PDMS and 3% PEG



(iii) 6% PEG and 3% PDMS

Figure 4.1 SEM Images of Top Surface for 1500X Magnification

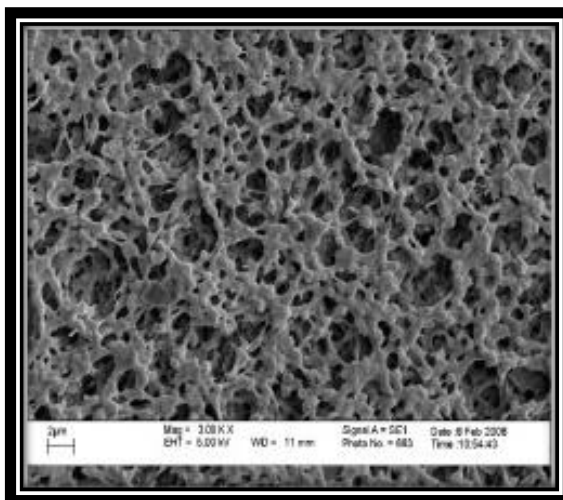
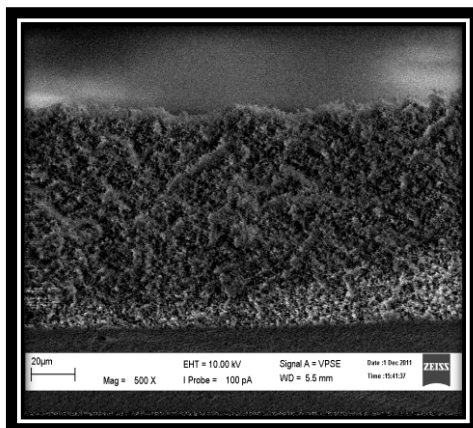


Figure 4.2: SEM Image of Unmodified PVDF Membrane (Boributh, 2009)

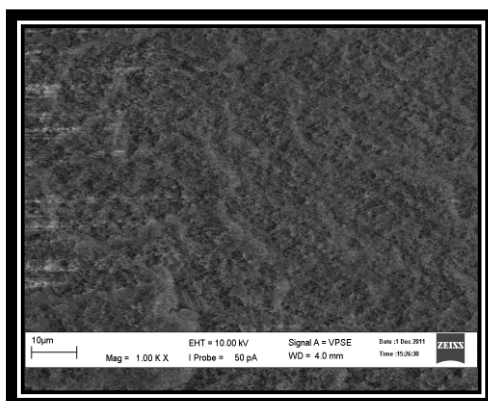
Figure 4.3 shows the cross section of membrane coating with 4.5% PEG and 4.5% PDMS, 6% PDMS and 3% PEG and 6% PEG and 3% PDMS. Each figure shows the dense layer. It means that, this membrane produced thin film composite membrane which showing the top is dense layer and bottom is porous support layer. Based on **figure 4.3** shows that dense layer is formed at top of the membrane. PDMS or known as silicon rubber produce dense layer and provide a resistance against the gas flow through the membrane. The higher the concentration of coating layer, the higher will be resistance. As mentioned before, PEG is one of the additives used to promote pore formation in the polymeric membranes. The characteristic of PEG itself makes them suitable for coating. PEG as a pore former to enhance the permeation properties for not only hydrophilic membranes but also hydrophobic membrane such as PVDF membrane. PVDF membrane is hydrophobic membrane and PEG helps PVDF membrane to achieve the highest permeability and selectivity. It can be concluded that the higher the concentration of PEG the higher permeability and selectivity of CO₂/N₂ separation.

Figure 4.4 shows the PVDF membrane without any coating layer. The difference between modified membrane and unmodified membrane is modified

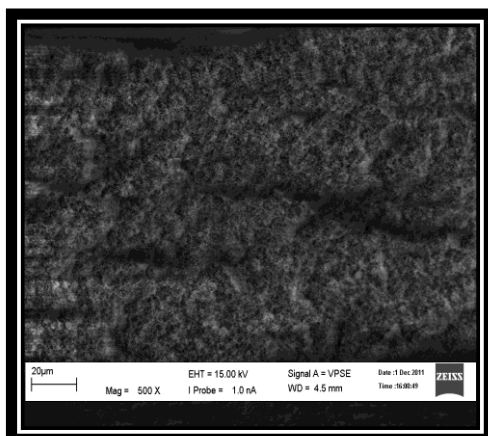
membrane more dense compare with unmodified membrane. In order to get high permeability and selectivity, coating is one way to solve this problem.



(i) 4.5% PDMS and 4.5% PEG



(ii) 6% PDMS and 3% PEG



(iii) 6% PEG and 3% PDMS

Figure 4.3 SEM Image of Cross Section Membrane

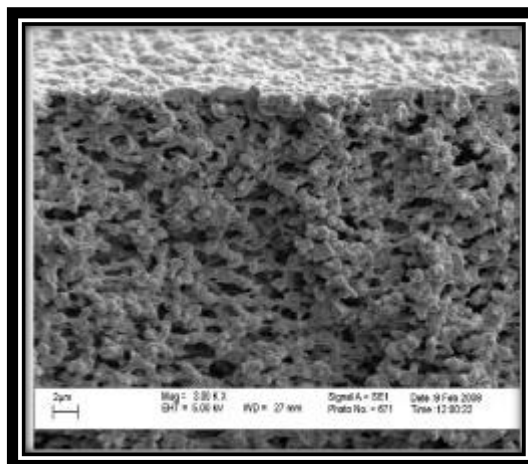


Figure 4.4 SEM image of Unmodified Cross Section Membrane (Boributh, 2009)

4.2 Fourier Transform Infrared Spectroscopy (FTIR)

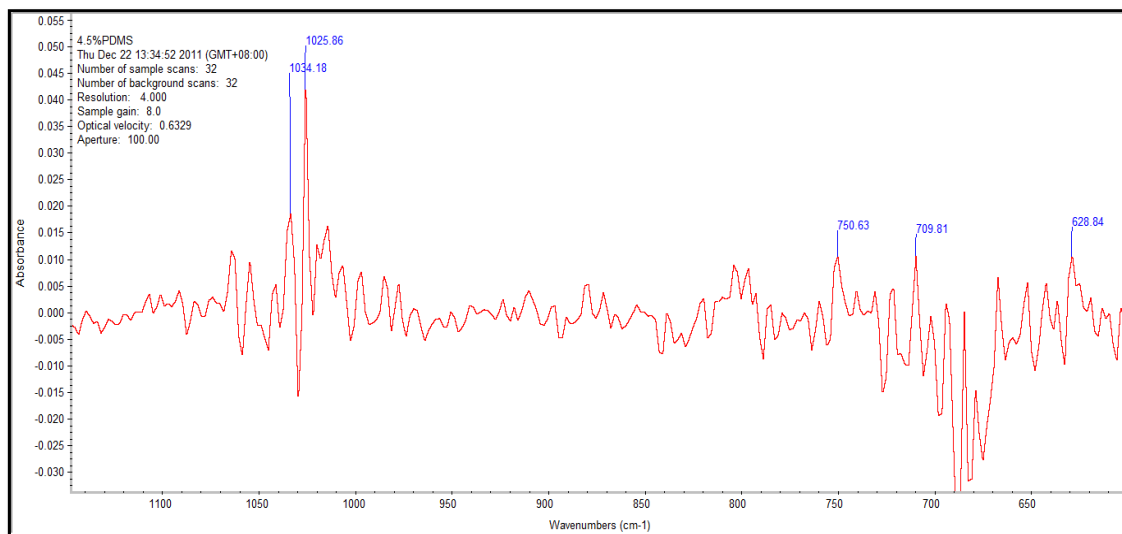
The chemical structures of the modified membrane coating with PDMS and PEG were characterized by FTIR. **Figure 4.5** illustrated the polarized infrared spectrum capture from membrane coated of 4.5% PDMS and 4.5% PEG, 6% PDMS and 3% PEG and 6% PEG and 3% PDMS. Each of these figures was characterize on **table 4.1, 4.2** and **4.3** respectively.

Table 4.1 shows functional group that contain in membrane coated with 4.5% PDMS and 4.5% PEG. For the FTIR spectra of membrane coated with 4.5% PDMS and 4.5% PEG, consist of backbone made up of aliphatic amines (C-N), alkyl halides (C-Cl) and alkynes (-C=C-H: C-H). The strong absorption due to asymmetric and

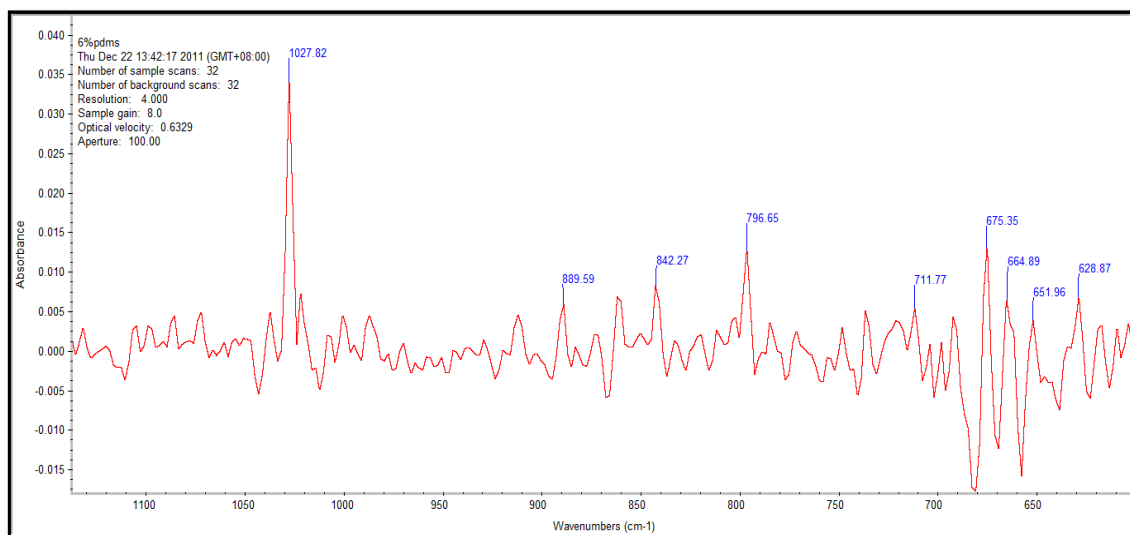
symmetric stretches of alkynes group in PVDF membrane were found at around 628.84 cm^{-1} . The band around 1025.86 cm^{-1} and 1034.18 cm^{-1} referred to C-N stretching. There are also medium absorption bands in the region of bands at around 750.63 cm^{-1} and 628.84 cm^{-1} . There are C-Cl and -C=C-H: C-H respectively.

Table 4.2 shows functional group contain in membrane coated with 6% PDMS and 3% PEG. The PVDF membrane consists of a backbone made up of aromatics (C-H), aliphatics amines (C-N) and alkyl halides (C-Cl). This PVDF membrane contains aromatics functional group at around 889.59 cm^{-1} , 842.27 cm^{-1} , 796.65 cm^{-1} and 711.77 cm^{-1} . The others functional group are medium bonds.

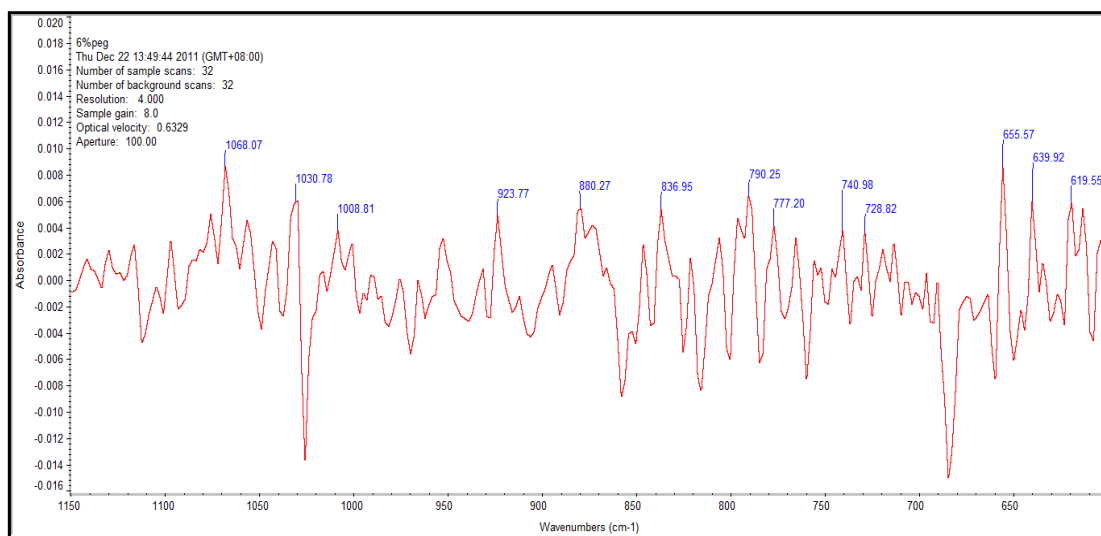
Table 4.3 shows functional group contain in membrane coated with 6% PEG and 3% PDMS. The PVDF membrane consists of backbone made up of aliphatic amines (C-N), alkyl halides (C-Cl), aromatics (C-H 'oop') and alkynes (-C=C-H: C-H). The strong absorption is belonging to the alkynes that consist of double bond (-C=C-H: C-H) at 619.56 cm^{-1} , 639.92 cm^{-1} and 655.57 cm^{-1} . Aromatics group is also the strong bond exists in this membrane structure. The others are in medium strength as shown in **figure 4.3**.



(i) 4.5% PDMS and 4.5% PEG



(ii) 6% PDMS and 3% PEG



(iii) 6% PEG and 3% PDMS

Figure 4.5: FTIR Spectra of Membrane with Difference Concentration of PEG and PDMS

Table 4.1: Characteristic IR Absorptions for membrane coated with 4.5% PDMS and 4.5% PEG

Frequency, cm^{-1}	Bond	Functional group
1250-1020(m)	C-N stretch	Aliphatic amines
850-550(m)	C-Cl stretch	Alkyl halides
700-610(b,s)	-C=C-H:C-H bend	Alkynes

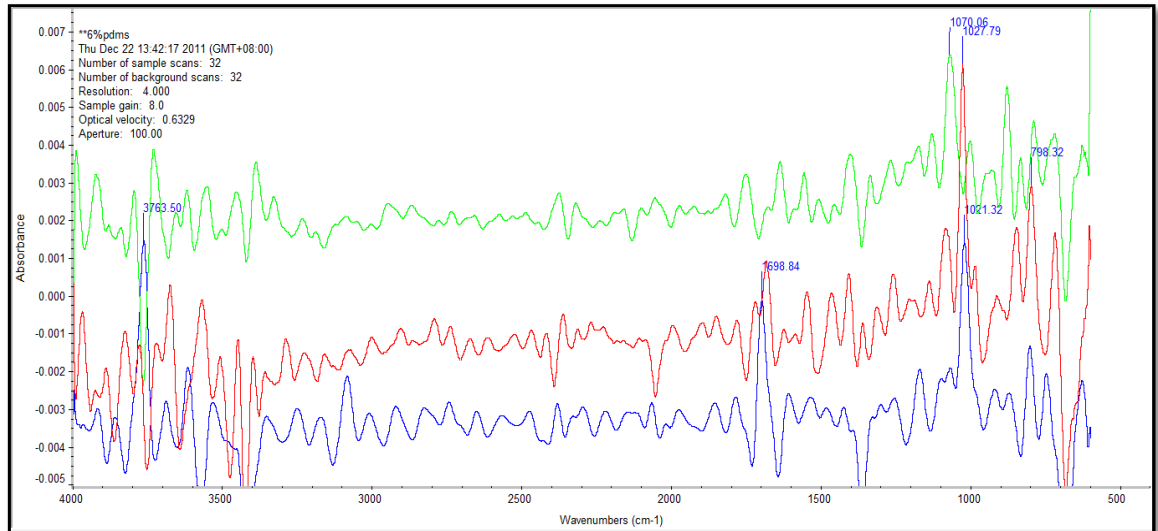
Table 4.2: Characteristic IR Absorptions for membrane coated 6% PDMS and 3%PEG

Frequency,cm ⁻¹	Bond	Functional group
1250-1020(m)	C-N stretch	Aliphatic amines
900-675(s)	C-H 'oop'	Aromatics
850-550(m)	C-Cl stretch	Alkyl halides

Table 4.3: Characteristic IR Absorptions for membrane coated with 6% PEG and 3% PDMS

Frequency,cm ⁻¹	Bond	Functional group
1250-1020(m)	C-N stretch	Aliphatic amines
900-675(s)	C-H 'oop'	Aromatics
850-550(m)	C-Cl stretch	Alkyl halides
700-610(b,s)	-C=C-H:C-H bend	alkynes

Figure 4.6 shows the combined result from FTIR. It shows that the graph looks similar. Membrane coated with 6%PEG and 3%PDMS consist strong bonds such as alkynes and aromatics bond. While membrane coated with 6%PDMS and 3% PEG consist aromatics bond. The strong bonds was determined how strength the membrane was.



- 4.5% PDMS and 4.5% PEG
- 6% PDMS and 3% PEG
- 6% PEG and 3% PDMS

Figure 4.6 FTIR Spectra Combine Result

4.2 Gas Permeation Test

Colin (2008) explained that CO_2 has a smaller kinetic diameter than N_2 . Besides that, CO_2 permeate more quick through membrane compare to N_2 which permeate slower through membrane. **Table 4.4** shows the time taken for CO_2 permeate through the TFC membrane at 1 bar. While, **Table 4.5** shows the time taken for N_2 permeate through the TFC membrane at 1 bar. Based on the results, membrane coated with 6% PEG and 3% PDMS have the fastest permeation of CO_2 followed by

membrane coated with 6%PDMS and 3%PEG and the slower permeation of CO₂ is membrane coated with 4.5%PDMS and 4.5%PEG. Membrane that have thin membrane, dense top layer and porous was good for permeability of CO₂.

While, the fastest permeability for N₂ is membrane coated with 6%PEG and 3%PDMS followed membrane coated with 6%PDMS and 3%PEG and lastly membrane coated with 4.5%PEG and 4.5%PDMS. A good membrane is a membrane that has higher selectivity. Selectivity can be defined as the permeability ratio of CO₂ to N₂. Instead of that, the permeability of CO₂ must be higher than N₂.

Table 4.4: Result of Permeation Test of CO₂ at 1 Bar on Membranes

Concentration of membrane	Time (s)			Average (s)
	Membrane 1	Membrane 2	Membrane 3	
4.5%PEG and 4.5%PDMS	24.68	18.48	9.99	17.72
6%PDMS and 3%PEG	2.35	17.43	8.30	9.36
6%PEG and 3%PDMS	2.25	1.98	1.93	6.16

Table 4.5: Result of Permeation Test of N₂ at 1 Bar on Membrane

Concentration of membrane	Time (s)			Average (s)
	Membrane 1	Membrane 2	Membrane 3	
4.5%PEG and 4.5%PDMS	75	66	11	51.33
6%PDMS and 3%PEG	40.7	25.18	32.68	32.85
6%PEG and 3%PDMS	12.66	13.69	35.68	20.68

Table 4.6: Permeation Properties of TFC Membrane Coating with 4.5%PEG and 4.5%PDMS; t=27°C, Δp = 1 bar

Membrane	4.5%PEG and 4.5%PDMS		
	Permeability (GPU)		Selectivity CO ₂ /N ₂
	CO ₂	N ₂	
1	311	102	3.05
2	416	116	3.59
3	769	698	1.10
Mean	499	305	2.58

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

Table 4.7: Permeation Properties of TFC Membrane Coating with 6%PDMS and 3%PEG; $t=27^{\circ}\text{C}$, $\Delta p = 1 \text{ bar}$

Membrane	6%PDMS and 3%PEG		
	Permeability (GPU)		Selectivity CO_2/N_2
	CO_2	N_2	
1	3270	189	17.30
2	441	305	1.45
3	926	235	3.94
Mean	1546	243	6.36

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

Table 4.7: Permeation Properties of TFC Membrane Coating with 6%PEG and 3%PDMS; $t=27^{\circ}\text{C}$, $\Delta p = 1 \text{ bar}$

Membrane	6%PEG and 3%PDMS		
	Permeability (GPU)		Selectivity CO_2/N_2
	CO_2	N_2	
1	3416	607	5.63
2	3881	561	6.92
3	3982	215	18.52
Mean	3760	461	8.16

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

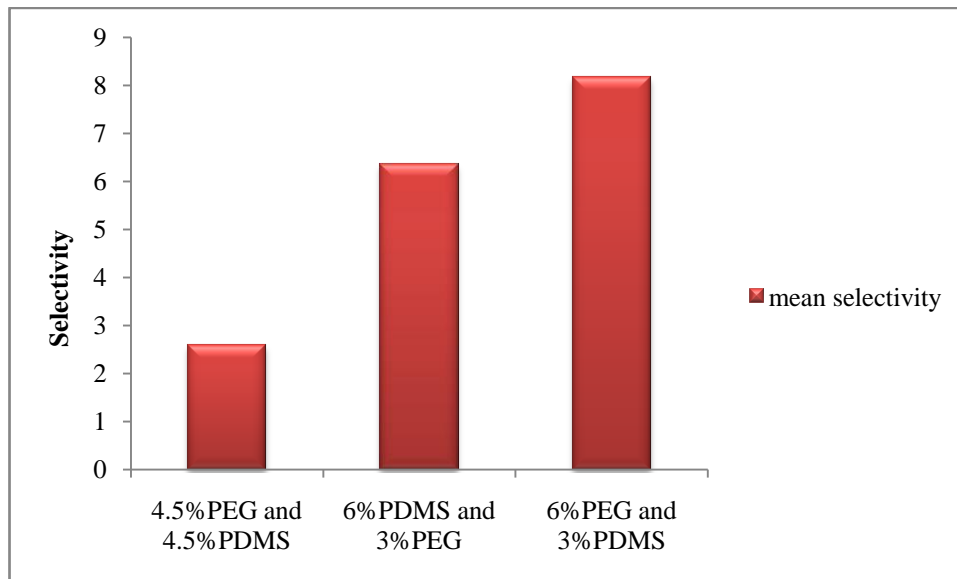


Figure 4.7 Comparison between the Means Selectivity on Each Coating Membrane

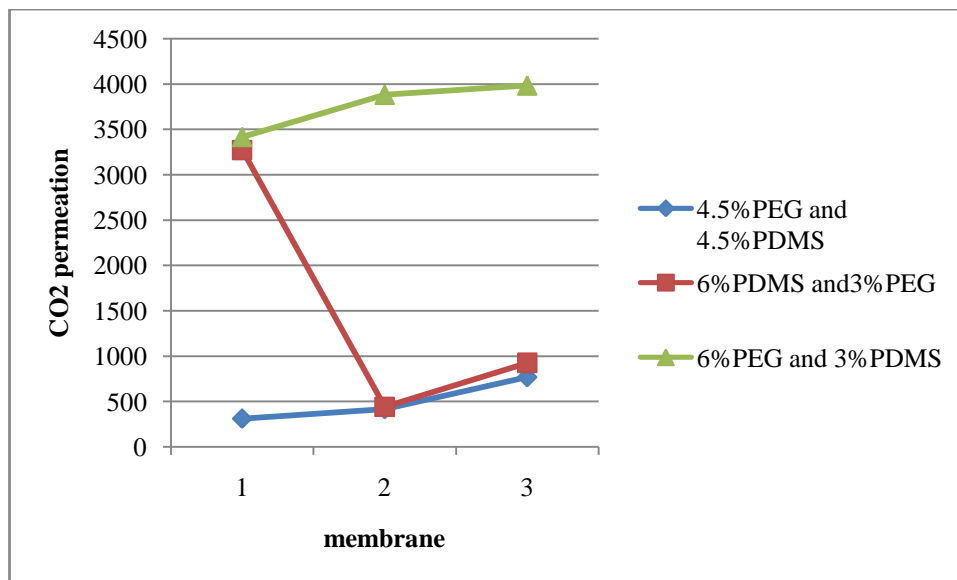


Figure 4.8 Permeability of CO₂ for Membrane Coating with 4.5% PEG and 4.5% PDMS, 6% PDMS and 3% PEG, 6% PEG and 3% PDMS

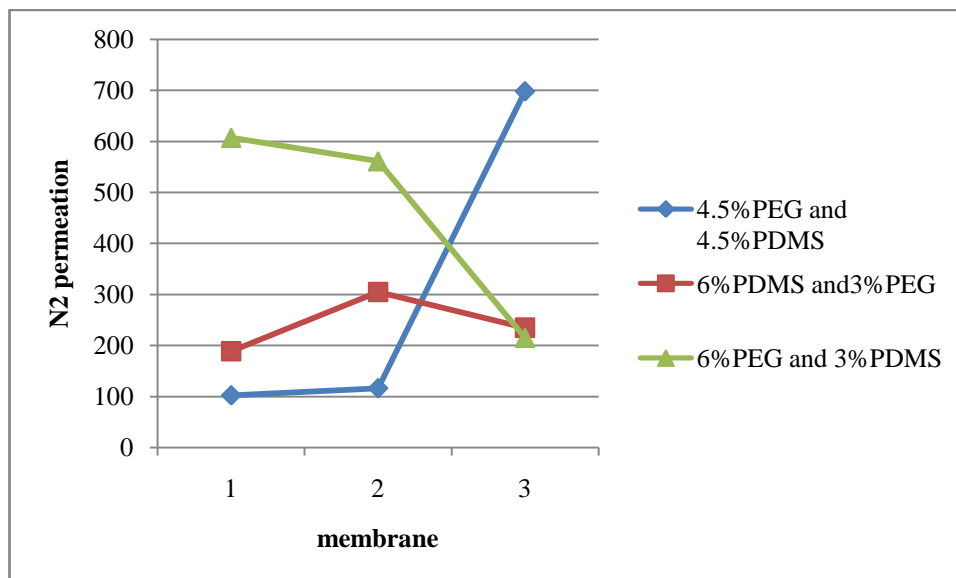


Figure 4.9 Permeability of N₂ for Membrane Coating with 4.5%PEG and 4.5%PDMS, 6%PDMS and 3%PEG, 6%PEG and 3%PDMS

Figure 4.7 shows the comparison of the mean number of selectivity of the membrane coating with different concentration ratio of PDMS and PEG. Based on the result, membrane coated with 6%PEG and 3%PDMS has the highest mean selectivity followed by 6%PDMS and 3%PEG and lastly membrane coated with 4.5%PEG and 4.5%PDMS for CO₂/N₂ separation. The selectivity of the CO₂/N₂ of the membrane coated with 6%PEG and 3% PEG show an average of 8.16, 6.36 for membrane coated with 6%PDMS and 3%PEG and 2.58 for membrane coated with 4.5%PEG and 4.5%PDMS.

Figure 4.8 shows the comparison of the permeability of the CO₂ between membrane of different PDMS and PEG concentration. The highest permeability of CO₂ is membrane coated with 6%PEG and 3%PDMS followed by 6%PDMS and 3%PEG and lastly is membrane coated with 4.5%PEG and 4.5%PDMS. A good CO₂ permeability is the good selectivity of the membranes. Furthermore, the characteristic of CO₂ itself makes them quick in permeation through membrane. CO₂

itself have smaller molecules size compare with N_2 . So that, CO_2 is supposed to have the highest permeability compare with N_2 . **Figure 4.9** shows the comparison of the permeability of the N_2 between membrane of different PDMS and PEG concentration. The highest permeability of N_2 is belong to membrane coated with 6%PEG and 3%PDMS followed by membrane coating with 6%PDMS and 3%PEG and the slower will be membrane coated with 4.5%PDMS and 4.5%PEG. When the permeation of N_2 is low, it means that the membrane is good in CO_2/N_2 selectivity. All of this reason shows that, the best membrane for CO_2/N_2 separation is when permeability of CO_2 is fast compare with permeability of N_2 .

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The permeance and selectivity of the PDMS/PEG-PVDF composite membrane, with different ratio of coating of PDMS/PEG and support layer concentration, were elucidated for CO₂/N₂ separation. The following conclusions are drawn:

- i) Coating layer plays important role in the separation of CO₂/N₂ gas mixture. The concentration of PDMS and PEG in the support affects the membrane performance. The highly concentrated supports leads to a dense structure. This results in less permeability for nitrogen.
- ii) The membrane selectivity is improved by the increasing percentage ratio of PDMS and PEG coating layer.

Membrane coating with 6%PEG and 3%PDMS have been identified as the best membrane for CO₂/N₂ separation due to the highest value of CO₂/N₂ mean selectivity. This calculated value is supported with the membrane morphology of cross section membrane and surface membrane. The membrane morphology for surface membrane shows less defects and more smoother compare with the other two membranes. FTIR results also shows the strong functional group contain in membrane coated with 6%PEG and 3%PDMS. As for conclusion, ratio of PDMS and PEG plays important roles in order to know the permeability and selectivity for CO₂/N₂ separation.

5.2 Recommendations

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

- i) The membrane sheet should be test in different pressure ratio in order to know the strength of the membrane.
- ii) The concentration of PEG should be variety to know the result for permeability and selectivity. So that, the comparison of different concentration of PEG can be identified.

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