PRODUCTION OF PDMS/ PVDF THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 SEPARATION

NORHIDAYA BINTI SUMMAH

UNIVERSITI MALAYSIA PAHANG

PRODUCTION OF PDMS/PVDF THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 SEPARATION

NORHIDAYA BINTI SUMMAH

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
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

To my parents,
Summah Lamasapa
Hasnah Djemingan
To my lovely brothers and sisters,
To my friends,
Nursyilla Mohd. Fauzi
Ma Umaira Suhaddha Zainal Abidin
Nadia Aida Che Mustapa
Nor Adila Said
Wafa Mohd Salleh
Intan Diana Musa
"Thanx for always supporting me all the way since the beginning of my studies. I love all of you.
May Allah bless all of you."

ACKNOWLEDGEMENT

All praise belongs to Allah S.W.T the most gracious and most merciful, Lord of the universe, with His permission I manage to completed this study. Praise to Prophet Muhammad S.A.W. His companions and to those on the path as what He preached upon, might Allah Almighty keep us His blessing and tenders.

First and foremost, I offer my sincere gratitude to Dr Sunarti Binti Abd Rahman for her supervision, advice and guidance from the very early stage of this research as well as spending her precious time to giving me experience and helping me in various ways.

I would like to record my tremendous appreciation to my parents, for their support and motivation during the tough time throughout the duration of this study. Many thanks go in particular to my lab partner Siti Khadijah Md Esa and my friend; Cristablle Melanie Bangga for their kindness to always helping me in accomplished this study. I also benefited by outstanding helps from all of the staff of the Chemical Engineering Department, UMP.

Thank you so much for all. May Allah S.W.T. the Almighty bless you all for your kindness and be with us all the time.

ABSTRACT

In this thesis, a thin film composite (TFC) membrane was prepared for separation of carbon dioxide (CO_2) and nitrogen (N_2). The main purpose of this research is to study the performance of polydimethyl siloxane (PDMS)/polyvinylidene fluoride (PVDF) thin film composite membrane in term of permeability and selectivity. The support layer was fabricated from PVDF and the coating layer was prepared from PDMS at various concentrations which are 3, 5, 8 and 10 wt. % PDMS. The coating of the membrane was done by the dip coating method. The permeations and selectivity of the prepared membranes for CO_2 and N_2 was tested using gas permeation test under the pressure up to 2 bars. Parameters such as the concentration of PDMS on the coating layer and various feed pressures that influence the performances of the membranes were evaluated. The results indicated that the permeability of the membranes is decrease with increment of the concentration of PDMS on the coating layer but increase in term of selectivity. The test also shows the correlation between the feed pressure applied and the performance of the membrane. Increment in the feed pressure is increasing the selectivity and permeability of the membranes. The morphology of the membrane is characterized using Scanning Electron Microscopy (SEM) and the chemical component of the membrane is analysed by Fourier Transforms Infrared (FTIR). The analysis from the membrane characterization is supporting the performance of the membrane. Membrane with 10 wt. % PDMS concentration shows the best performance with high feed pressure.

ABSTRAK

Membran filem nipis komposit telah dihasilkan dalam kajian ini untuk prosess pengasingan di antara gas karbon dioksida (CO_2) dan gas nitrogen (N_2). Tujuan utama kajian ini adalah untuk mengkaji prestasi membran polydimethylsiloxane (PDMS)/ fluoride polyvinylidene (PVDF) filem nipis komposit dalam jangka kebolehtelapan dan kemampuan pemilihan gas. Lapisan sokongan dibuat daripada PVDF dan lapisan salutan disedia dari PDMS pada kepekatan yang berbeza iaitu 3, 5, 8 dan 10 wt. % PDMS. Lapisan salutan membran dilakukan mengikut kaedah salutan berendam. Kebolehtelapan dan kebolehpilihan membrane yang telah siap untuk CO_2 dan N_2 telah diuji dengan menggunakan ujian penyerapan gas di bawah tekanan 1 dan 2 bar. Parameter seperti kepekatan PDMS pada lapisan salutan dan pelbagai tekanan suapan yang mempengaruhi prestasi membrane dinilai. Keputusan menunjukkan bahawa kebolehtelapan membran menurun dengan kenaikan kepekatan PDMS pada lapisan salutan tetapi peningkatan dalam tempoh pemilihan. Ujian ini juga menunjukkan kaitan antara tekanan suapan yang dikenakan dan prestasi membran. Kenaikan dalam tekanan suapan meningkatkan pemilihan dan kebolehtelapan membran. Morfologi membran dicirikan menggunakan Microscopy Imbasan Elektron (SEM) dan komponen kimia selaput dianalisis oleh Fourier mengubah Infrared (FTIR). Analisis daripada pencirian membran menyokong prestasi membran. Membran dengan berat 10. % Kepekatan PDMS menunjukkan prestasi terbaik dengan tekanan suapan yang tinggi.

TABLE OF CONTENT

2 LITERATURE REVIEW

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

^oC	Degrees celcius
^oF	Degrees Fahrenheit
$\alpha_{i/j}$	Selectivity of pure gas
µm	Micro meter
Δp	Pressure drop
€	Euro currency symbol
A	Area
kg	Kilogram
kJ	Kilo Joule
kPa	Kilo Pascal
K	Kelvin
l	Thickness of membrane
m^2	Unit area, meter square
m^3	Unit volume, meter cubic
MPa	Mega Pascal
P_{us}	Upstream pressure
P_{ds}	Downstream pressure
Q_i	Gas flow
wt. %	Weight percentage
W	Watt

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
CA	Cellulose Acetate
CCS	Carbon dioxide Capture and Storage
CE	Cellulose Esters
CH_4	Methane
CN	Cellulose Nitrates
CO	Carbon monoxide
CO_2	Carbon dioxide
EPA	Environmental Protection Agency
FTIR	Fourier Transfer Infrared
GPU	Gas Permeation Unit
H_2	Hydrogen
H_2O	Water
IPCC	Intergovernmental Panel on Climate Change
N_2	Nitrogen
O_2	Oxygen
PA	Polyamide
PAN	Polyacrilinitrile
PDMS	Polydimethyl siloxane
PE	Polyethylene
PES	Polyethersulfone
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polysulfone
PTFE	Polytetrafluoro ethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
SEM	Scanning Electron Microscopy
STP	Standard Temperature Pressure
TFC	Thin Film Composite

CHAPTER 1

INTRODUCTION

1.1 Background of Research

In 2007, Intergovernmental Panel on Climate Change (IPCC) indicate that during 21^{st} century the global surface temperature is likely to rise a further1.1 to 2.9 ^{o}C (2 to 5.2 ^{o}F) for their lowest emissions scenario and 2.4 to 6.4 ^{o}C (4.3 to 11.5 ^{o}F) for their highest. It shows that the average temperature of Earth's atmosphere and oceans is rising and this situation referred as a global warming. The main root to this unequivocal warming of the climate system is certainly because of increasing in concentration of the greenhouse gasses produced by human activities such as deforestation and burning fossil fuels. The challenging issue is to controlling the greenhouse gasses like carbon dioxide (CO_2) emission to atmosphere.

Carbon dioxide Capture and Storage (CCS) is found as a promising way of reducing the emission of carbon dioxide and at the same time it is mitigating the contribution of fossil fuel emissions to global warming. The conventional process of CCS is by reversible solvent absorption which is based on capturing CO_2 from large point sources and storing it in such a way that it does not enter the atmosphere. However, capturing and compressing CO_2 consume high energy and it would increase the fuels need of a coal-fired plant and this cost will increase the cost of energy from a new power plant. It shows that the conventional process of CCS is less economical.

Therefore, gas membrane separation seems to be more economical process. Membrane separation operates without heating and is energetically lower than conventional thermal separation process. This type of separation decently physical and both permeate and retentate can possibly use. Its energy efficiency and simplicity is most attractive to CO_2 capture. In order to obtain a pure stream of CO_2 and attain the compact membrane facility, the membrane used must be high in term of selectivity and permeability.

Variety types of membrane can be used and this study will focused on the polymeric membrane for some purpose. The properties of the polymeric membrane makes it is well-suited to the low temperature application. The morphology of the membrane also can easily determine the permeability and selectivity of the membrane. The utmost important is it is easy to manufacture.

Besides, previous researchers believe that significant advances in traditional polymeric membrane will be difficult to attain because we are currently approaching the limit of the technology. The trade-off between selectivity and permeability is based on traditional structure properties relations of polymeric materials. This upper bound still defines the properties of all truly solution process able polymeric materials today. This phenomenon had leads for the growing interest in the development of gas separation membranes based on materials that provide better selectivity, thermal stability and chemical stability than those already exist (Aizan *et al.*, 2006).

1.2 Problem Statement

In gas separation process, the main key of the good performance using membrane is depends on the permeability and selectivity of the membrane. The properties of the membrane material are the main factors in this separation process. Polymers such as polyamide, polidimethylsiloxane (PDMS) and polyvinylidene fluoride (PVDF) were known as good materials in producing membrane. However, previous study found that a pure polymer such as PDMS is a low selectivity material. The limitation in achieving the high selectivity and permeability membrane is the great challenge in producing membrane for a gas separation. The thin film composite (TFC) membrane based on PDMS and PVDF is considered to be one of the practical approaches to overcome the limitation. Therefore, the selection of the proper material needs a proper attention in order to produce the good membrane.

1.3 Research Objectives

The main purpose of this study is to perform the high performance in separate CO_2 from CH_4 in biogas purification by using PDMS/PVDF TFC membrane. The objectives of this study are:

1) To produce TFC membrane based PDMS/PVDF
2) To study on performance of TFC membrane to separate CO_2 and N_2.
3) To characterize the TFC membrane.

1.4 Scope of Research

This study has focused on several scopes in order to achieve its objective. The scopes are as follows:

1. Production of the TFC membrane based PDMS/PVDF.
2. Study the performance of the TFC membrane in term of permeability and selectivity.
3. TFC membrane characterization using Scanning Electron Microscopy (SEM) and Fourier Transforms Infrared (FTIR)

1.5 Significance of Research

Thin film composite membrane is one of the most effective membranes for gas separation because of its asymmetric and porous structure. The combination of the advantages of PDMS as the coating layer and PVDF as support layer in this membrane is the reason for its high performance. Besides, membrane separation process did not require any latent heat. Thus, it could save lost energy consumption. Membrane separation process is an environment friendly process since this process produces no waste that could harm the earth. Its simple process makes it is more economical to use membrane than other method for gas separation.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane

2.1.1 Definition

A membrane can be defined as a thin layer of material that used as a selective barrier between two bulk phase either homogenous or heterogeneous phase. It will allow some component passes through and it will retain some.

2.1.2 Principal

The principal of membrane separation is some components of the feed are transported through a thin film membrane and some will be retained. In gas separation, membrane acts as filter to separate one or more gases from feed mixture and generate specific gas rich permeate. The membrane performance is identified in term of permeability and selectivity.

Permeability is a measurement of the quantity of fluid that passes through the membrane per unit area of membrane per unit time. It is linearly depends on the permeability and the driving force and inversely depends on the membrane thickness. That mean, the flux will be greater when the membrane is thick and at higher permeability and driving force. Selectivity can be defined as a preference of the membrane to pass one species and not another (Stookey, 2001). The schematic principal of membrane in separation process is illustrated in the Figure 2.1 below.

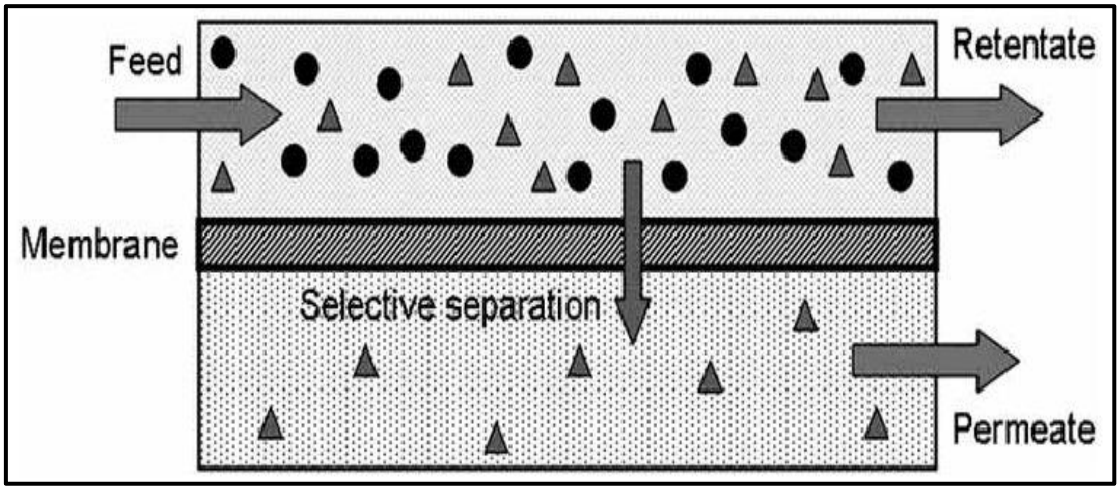


Figure 2.1: Schematic diagram of membrane separation (Sandra *et. al*, 2008)

There are two main types of flow; dead-end flow and cross-flow. The direction of dead-end feed flow is normal to the membrane surface. It is easy to implement but not preferred because of extensive membrane fouling and concentration polarization. The concentration polarization (particle backflow) was build up from the fouling membrane where the driving force was higher. It intends to the increasing of non-permeating species on the feed side with time. This means that, decrement in the concentration of the permeating species in the feed side is reducing the driving force and transportation of particle through the membrane.

In contrast, the cross-flow membrane process is the preferred one due to its tangential flow to the membrane surface. Further downstream, the retentate is removed and on the other side, the operation which is permeating flow is tracked. There is four cases of cross-flow operation which is co-current, counter-current, cross-flow with perfect permeate mixing and perfect mixing operation. The types of the feed flow are shown in the Figure 2.2 below.

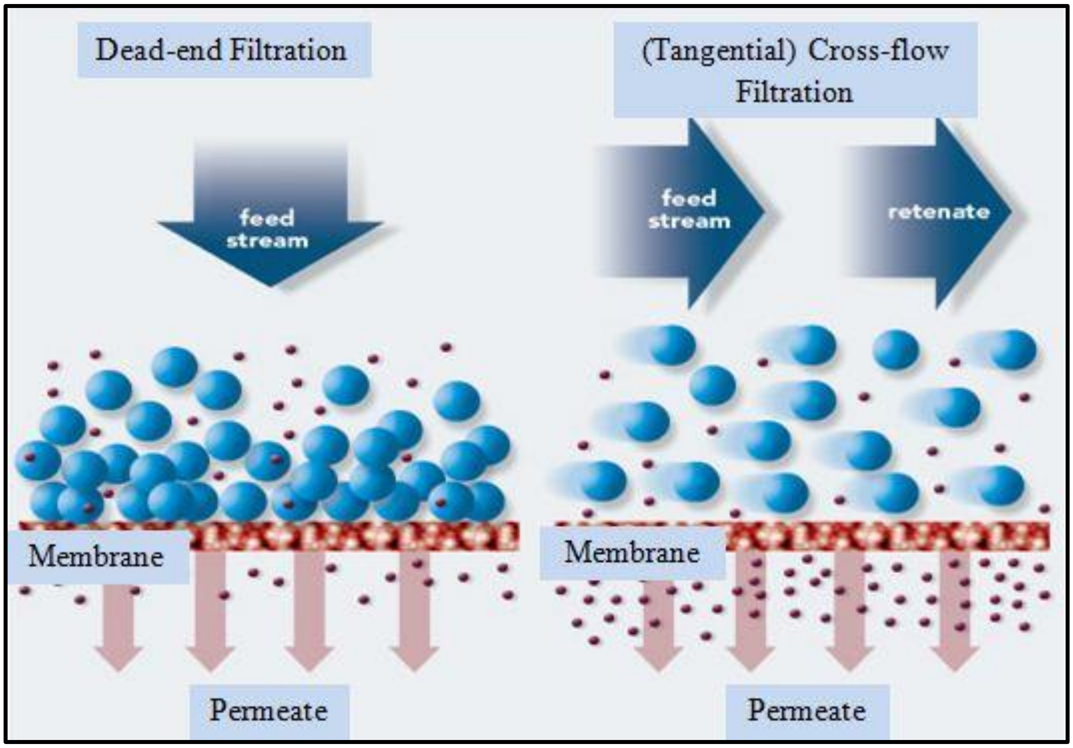


Figure 2.2: Feed flow illustration

2.1.3 Types of membrane

Generally, there are two types of membrane which is biological membrane and synthetic membrane. A biological membrane is a selective barrier layer that is around the cell which consists of lipid bilayer with embedded protein. The lipid and protein composition in this membrane is different due to its types.

In the other hand, the synthetic membrane was produced from organic or inorganic materials. A membrane from inorganic materials such as silicon carbides, aluminium oxides or zirconium oxides is resistant to the strong solvent action and chemically and thermally stable. One of the popular membranes that used in the separation industry is a polymeric membrane.

A polymeric membrane is an organic synthetic membrane that can selectively transfer certain chemical species over others. Common polymers that commonly used in membrane synthesis are cellulose acetates (CA), cellulose nitrates (CN), cellulose esters (CE), polysulfone (PS), polyether sulfone(PES), polyacrilonitrile (PAN), polyamide (PA), polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polyvinylchloride (PVC).

Another type of membrane is micro porous membrane. This type of membrane is generally made by applying 1 to 3 thin layers to a porous support. The porous support can be in flat sheets, disks or tubes and can be either ceramic or metallic. Meanwhile the microporous layers are generally metal oxides and are often silica. Microporous membrane usually applied for coal gasification, reformed natural gas and in high-temperature electrolysis.

Homogenous dense and asymmetric membranes are also the main type of membrane that usually used. Homogenous dense membrane usually prepared by solvent evaporation from the solution or by extrusion of the melted polymer. This type of membrane is practical when it is made from highly permeable polymers like silicon.

2.1.4 Membrane structure

Membranes can be classified according to their morphology. The morphology of the membranes is illustrated on the Figure 2.3.

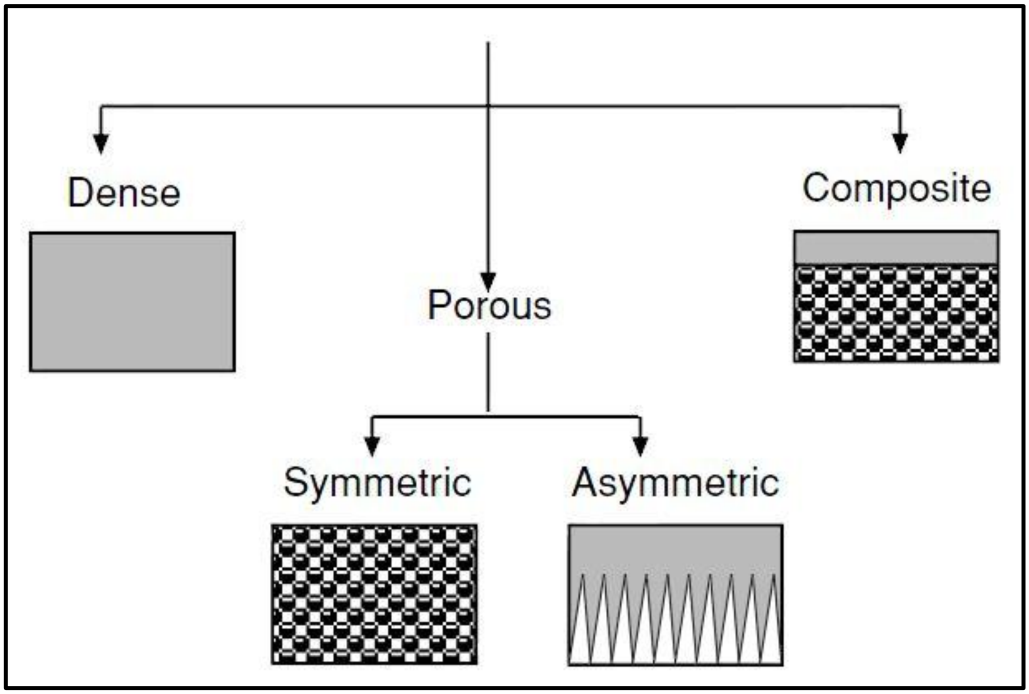


Figure 2.3: Membrane classification according to morphology (Nunes *et al.*, 2001)

A dense membrane usually prepared from highly permeable polymer in a minimal thickness in order to give the mechanical stability to the membrane. Therefore, most of application used porous membrane or composite membrane which combines the dense layer at the top and porous membrane at the bottom.

A symmetric membrane have a constant diameter pores and it is resistance to mass transfer due to its thickness. In contrast, asymmetric membrane has a different pore sizes between the top surface and the bottom one. The size difference unable the particle to pass through the membrane and the plugging must be avoided. One best solution to this problem is by using composite membrane. The top layer of the composite will be the membrane selectivity to the porous one at the bottom. The bottom layer has high porosity and high thickness.

2.1.5 Mechanism of membrane

Mechanism of membrane in separation process can be divided into:

i. By size

   Macropores, mesopores and micropores are three terms that defined the pore sizes in membrane for microfiltration, ultrafiltration and nanofiltration membrane. This type of membrane is used to removed contaminants based on sized.

ii. Different in solubility and diffuse of materials

   This type of mechanism is based on the diffusion of solute and solvent. The membrane has a small pores and only solvent passes through it by sorption-diffusion method. A composite of homogenous film is the good example.

iii. By charge

   This mechanism used in an ion exchange membrane where the same charge ion is excluded in the same phase. It is practically used in electrolytic cell separator.

There are three types of mechanism used in the gas separation membrane; Knudsen diffusion, molecular sieving and solution-diffusion. In Knudsen diffusion mechanism, the component of the gas is separated according to the difference in mean path of the gas molecules. In contrast, the gas is separated based on the diameter size of molecule in molecular sieving mechanism. A solution-diffusion happen when permeates dissolved in the membrane material and separation is achieved because of differences in amount of material dissolves in the membrane and rate of material that diffuse. Figure 2.4 below shows the mechanism in gas separation.

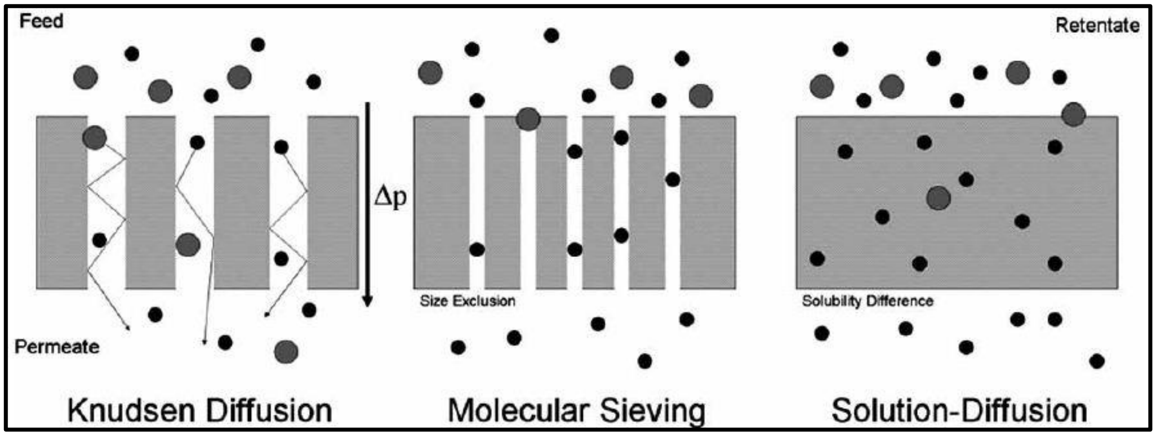


Figure 2.4: Illustrations of membrane mechanism (Sandra *et al.*, 2008)

2.2 Membrane Process

Based on previous study, Aizan *et al.*, 2006 claimed that the membrane separation process is characterized by several aspects. There are:

- Separation goal
- Nature of species retained (size of the species)
- Nature of species transported through membrane, electrodylasis or volatile
- Minor or major species of the feed solution transported through membrane
- Driving forces
- Phase of feed and permeate stream
- Mechanism for transport/selectivity

The membrane separation processes are summarized in the Table 2.1 and characterized based on the mechanism used; feed stream, trans membrane driving force and its application in the industry.

Table 2.1: Membrane separation process (Aizan *et al.*, 2006)

Separation process	**Separation mechanism**	**Feed stream**	**Typical trans membrane driving force**	**Example of industrial use**
Microfiltration	Sieving	Liquid or gas	$\Delta p < 10\text{-}21$	Processing of corn stillage streams, concentration of emulsions, cell suspension concentration
Ultrafiltration	Sieving	Liquid	$\Delta p < 50$psi	Auto-paint recovery, microemulsion oil recovery, biomolecule and virus separation from aqueous stream
Dialysis	Sieving and sorption-difusion	Liquid	$\Delta p < 0$ to small Δp sometimes	Hemodialysis primarily
Reverse osmosis	Sorption-difusion	Liquid	$\Delta p <$often to overcome osmotic pressure, so $\Delta p - \Delta\pi > 0$, usually<1500 psi	Water desalination, wastewater treatment
Pervaporation	Sorption-difusion	Liquid	Δ(fugasity of i) set by fed liquid mole fraction and permeate vacuum	Dehydration of organic stream and removal of trace organics from aqueous streams
Gas and vapor permeation	Sorption-difusion	Gas and vapor	Δ (fugasity of i) usually equal to partial pressure difference, Δpi typically<120 psi	Separation of O_2/N_2, H_2/CH_4, CO_2/CH_4, H_2/N_2, H_2/CO, H_2O/CH_4, and organic vapors from air

2.3 Membrane Module

Membrane module can be defined as the building block of the membrane and generally its configuration can divided into two; flat and tubular.

2.3.1 Plate and frame module

This plat membrane is placing parallel to each other with a spacer plate that separates the feed flows. In order to use the membrane surface as efficiency as possible, the stop disc was used to improve the flow pattern. It helps in reducing the tendency of the flow to moves at fixed pathway. The packing density of this module is around 100-400 m^2/m^3 (EPA, 2005). Figure 2.5 below display the plate and frame membrane module.

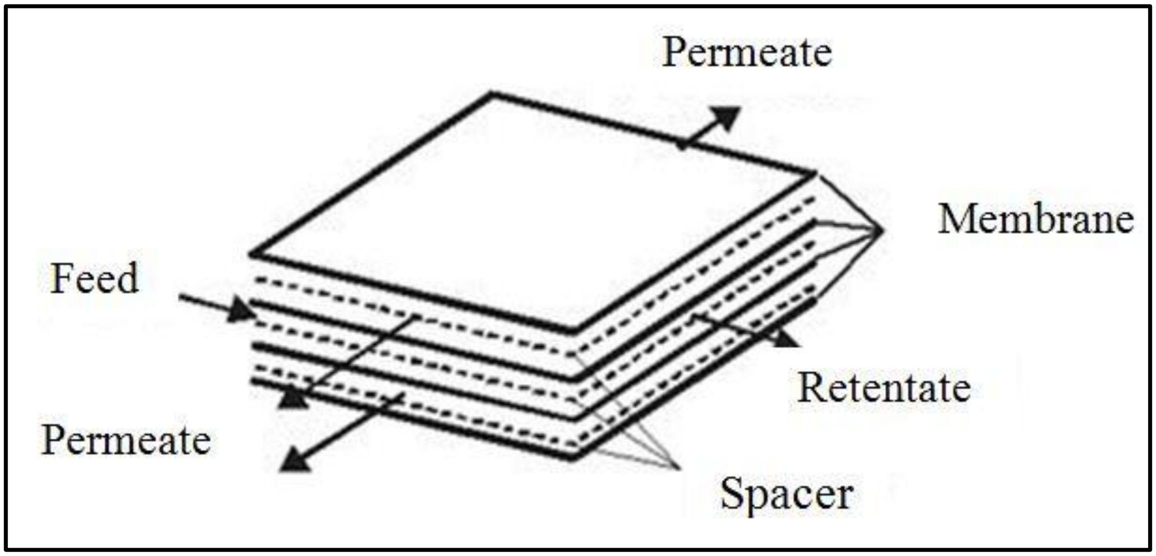


Figure 2.5: Schematic diagram for plate and frame module (EPA, 2005)

2.3.2 Spiral-wound module

Spiral wound module is a two layers membrane that placed onto a permeate collector fabric and wrapped around a central placed permeate. It makes the cylinder density is high, 300-1000 m^2/m^3. The feed flows in an axial direction while the permeate run in radial direction towards the centre of cylinder. It should be placed at the moderate high to prevent the plugging happen. The spiral wound membrane module shown in the Figure 2.6.

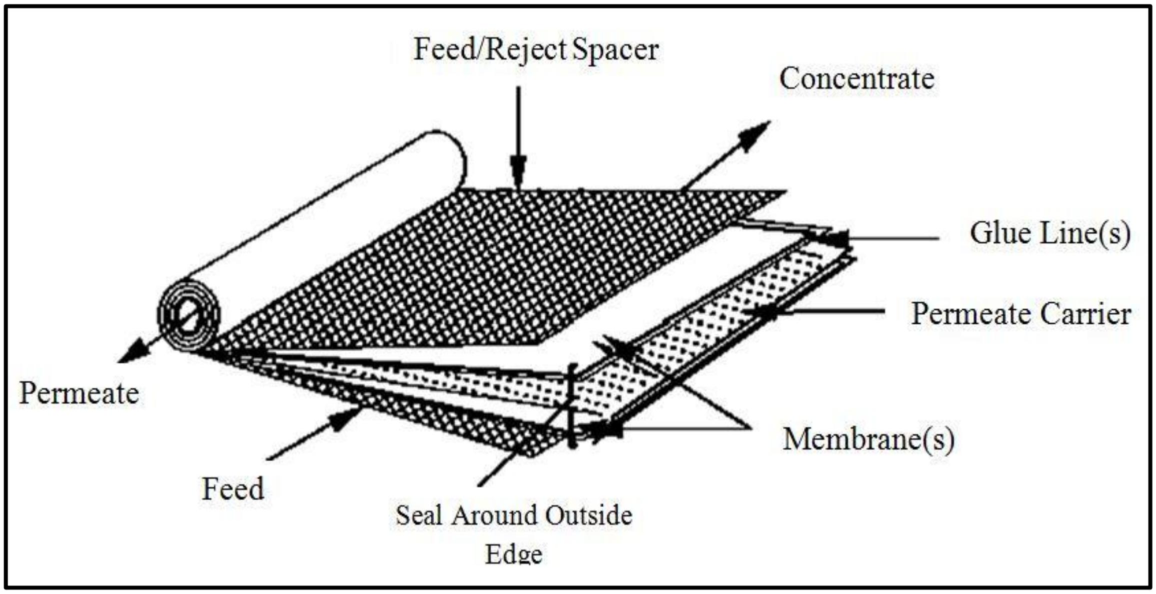


Figure 2.6: Spiral wound membrane module (EPA, 2005)

2.3.3 Tubular Module

The supporting material is placed inside a 5 to 15 mm diameter tubular tube. Its bigger size makes the density quite low and plugging seems not happen. The attachment of the supporting materials is not strong enough and makes the feed flow in the centre of the membrane tube and the permeate flow outside the tubular. Figure 2.7 shows the module for tubular membrane.

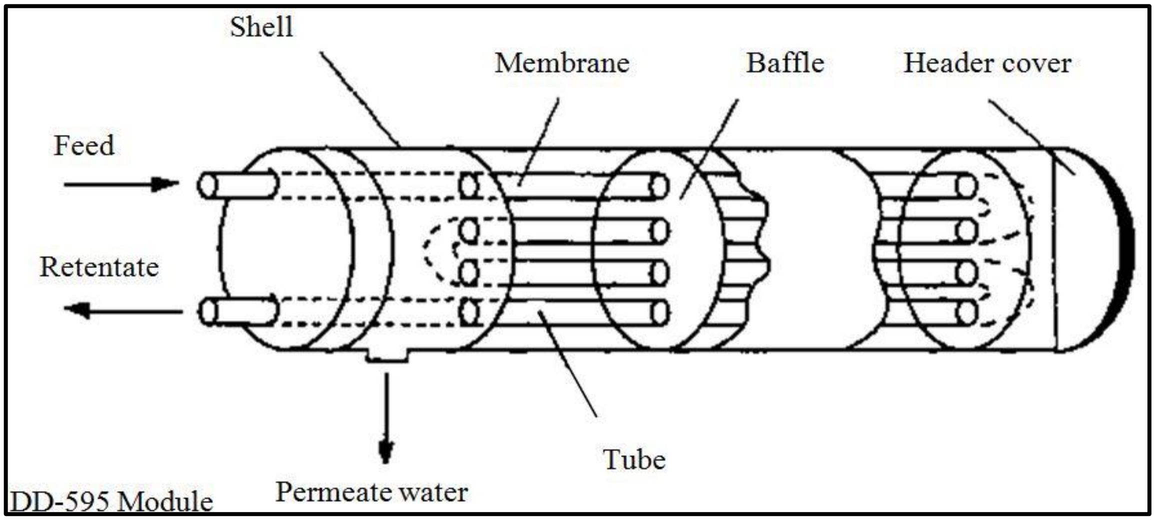


Figure 2.7: Schematic diagram of tubular membrane module (EPA, 2005)

2.3.4 Capillary Module

Capillary module membrane serves as a selective barrier that can resist filtration pressure strongly. At the free ends, the capillary will bound together with agents such as polyurethane or silicon rubber. The flows inside this capillary can be both inside out and outside in flow. With the smaller diameter, 0.5 to 5 mm, the density is much greater but the chance of plugging is higher (Gryta, 2000). Figure 2.8 shows the module for capillary membrane.

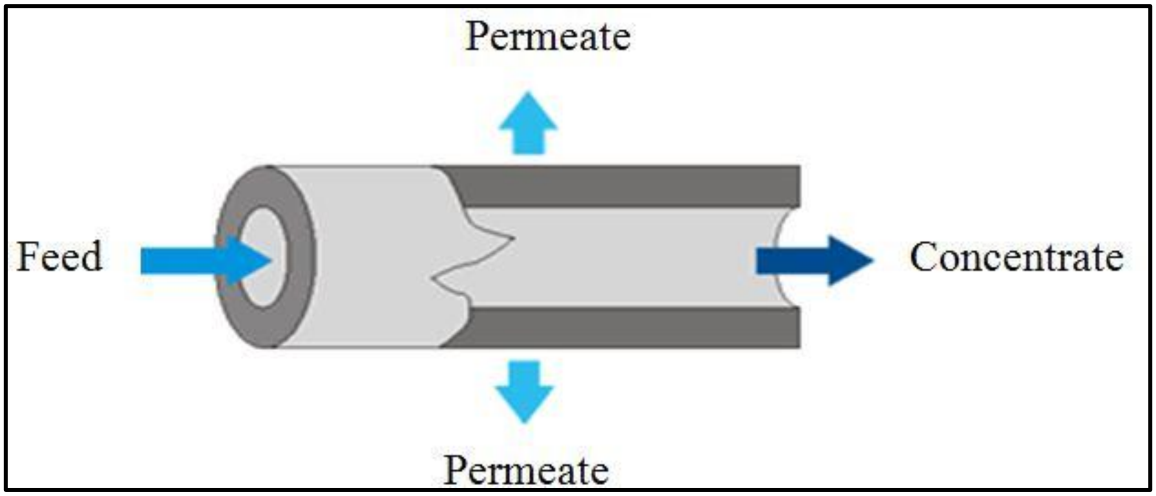


Figure 2.8: Module for capillary membrane (Gryta, 2000)

2.3.5 Hollow Fibre Module

Hollow fibre membrane is merely used for nano filtration and reverse osmosis process. It has a smallest diameter size, below 0.1 µm the chance of plugging is very high and the packing density is 30000 m^2/m^3. The pressure losses are also high and 'outside-in' flow type can reduce the pressure losses and higher membrane area can attain (Zhang, 2010). Figure 2.9 shows the hollow fibre membrane module.

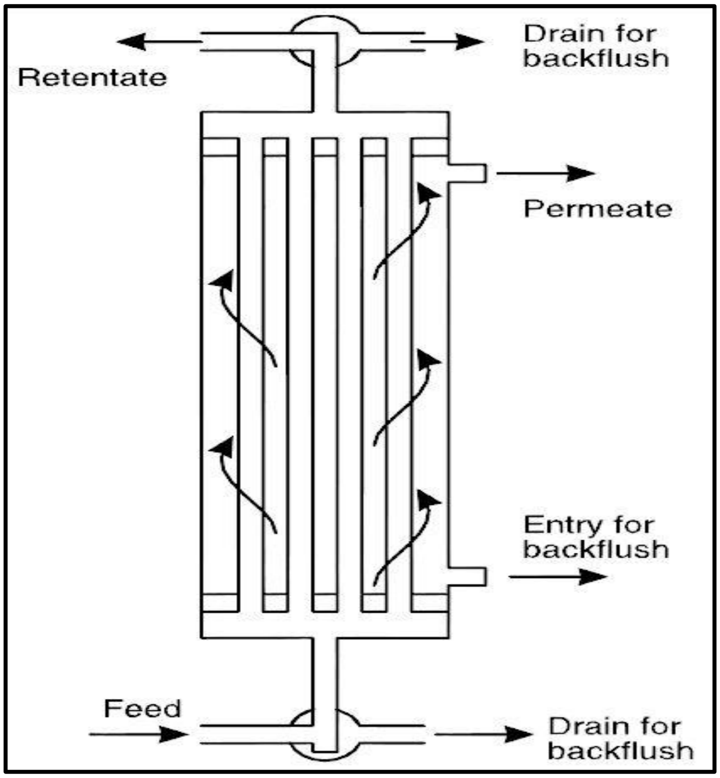


Figure 2.9: Hollow Fibre membrane module (Sharma, 2009)

The characteristics of these major module membranes are summarized in the Table 2.2 below.

Table 2.2: Characteristic of major module membrane (Aizan *et al.*, 2006)

Properties	Hollow Fibres	Capillary Fibres	Spiral Wound	Plate and Frame	Tubular
Packing density	High	Moderate	Moderate	Low	Low
Resistance to fouling	Very poor	Good	Moderate	Good	Very good
Parasitic pressure drop	High	Moderate	Moderate	Moderate	Low
High separation process	Yes	No	Yes	Can be done with difficulty	Can be done with difficulty
Limited to specific types of membrane	Yes	Yes	No	No	No

From the table above, hollow fibres membrane shows the greatest characteristics with high in packing density and pressure drop but very poor in resistance to fouling. Meanwhile tubular membrane has the poorest characteristics. It has low packing density and pressure drop but very well in resistance to fouling. Even it can use to any types of membrane, but it is difficult to perform a high separation process.

2.4 Application of Membrane

Membrane has been widely used in wastewater treatment and in gas separation.

2.4.1 Wastewater Treatment

In wastewater treatment, membrane process can be divided into four which are reverse osmosis, nanofiltration, ultrafiltration and microfiltration process. Table 2.1 below displays the process and the membrane characteristics in wastewater treatment.

Table 2.3: Processes and membrane characteristics in wastewater treatment (Sharma, 2009)

	Reverse osmosis	**Nanofiltration**	**Ultrafiltration**	**Microfiltration**
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Asymmetrical Symmetrical
Thickness thin film	150 μm 1 μm	150 μm 1 μm	150-250 μm 1 μm	10-150 μm
Pore size	< 0.002 μm	< 0.002 μm	0.2 – 0.02 μm	4 – 0.002 μm
Rejection of	HMWC, LMWC sodium chloride, glucose, amino acid	HMWC, mono-, di-,and oligosaccharides polyvalent neg. ions	Macro molecules, proteins, polysaccharides vira	Particles, clay, bacteria
Membrane material(s)	CA Thin film	CA Thin film	Ceramic PSO, PVDF, CA Thin film	Ceramic PP, PSO, PVDF
Membrane Module	Tubular, Spiral wound, plate and frame	Tubular, spiral wound, plate and frame	Tubular, hollow fibre, spiral wound, plate and frame	Tubular, hollow fibre
Operating pressure	15 - 150 bar	5 – 35 bar	1 -10 bar	< 2 bar

Based on the Table 2.3, only microfiltration process that using both asymmetrical and symmetrical membrane whiles the others used asymmetrical membrane. Reverse osmosis and nanofiltration process has the smallest pore size, < 0.002 μm. All process use tubular membrane module and microfiltration process undergoes at the lowest pressure, < 2 bar.

2.4.2 Gas Separation

Membrane has been broadly used in separation of gas mixture or pure gas. Table 2.4 below will summarize the type of gas separation and its application in the industry.

Table 2.4: Gas separation and its application (Peinemann *et al.*, 2001)

Gas separation	**Application**
O_2/N_2	Nitrogen generation, Oxygen enrichment
H_2/Hydrocarbons	Refinery hydrogen, Recovery
H_2/CO	Syngas ratio adjustment
H_2/N_2	Ammonia purge gas
CO_2/Hydrocarbon	Acid gas treating, Enhanced oil recovery, Landfill gas upgrading
H_2S/Hydrocarbon	Sour gas treating
H_2O/Hydrocarbon	Natural gas dehydration
H_2O/Air	Air dehydration
Hydrocarbon/Air	Pollution control, Hydrocarbon recovery
Hydrocarbons from process stream	Organic solvent recovery, Monomer recovery

The advantage of using gas separation membranes is that the equipment is much smaller and there is no solvent involved. The CO_2 passes through this barrier more easily than other gases. The membrane selectivity increased with a decrease in temperature and an increase in the feed pressure (Yuting *et al*., 2006). Both membrane's permeability and selectivity influence the economics of a gas separation membrane process.

2.5 Gas separation system

Gas separation is widely known as a best method to purify gas and to reduce CO_2 emission. Here are the type of systems that generally used is in gas separation.

2.5.1 Water and Polyethylene Glycol Scrubbing

In this counter-currently absorption process, the mixture gas is pressurized and fed to the bottom of the packed column while the water is fed at the top. CO_2 and H_2S can be removed because of they are more soluble than methane in water. The same process goes to the polyethylene glycol scrubbing but the solvent will be Selexol and instead of using air, it will use steam or inert gas. There is no much chemical required but in the water scrubbing, more water will be needed because CO_2 will reduce the pH of solution and H_2S can causes corrosion. According to Hullu (2008), the cost of the water scrubbing method is 0.13 €/Nm biogas. Figure 2.10 shows the flow digram of water scrubbing technology.

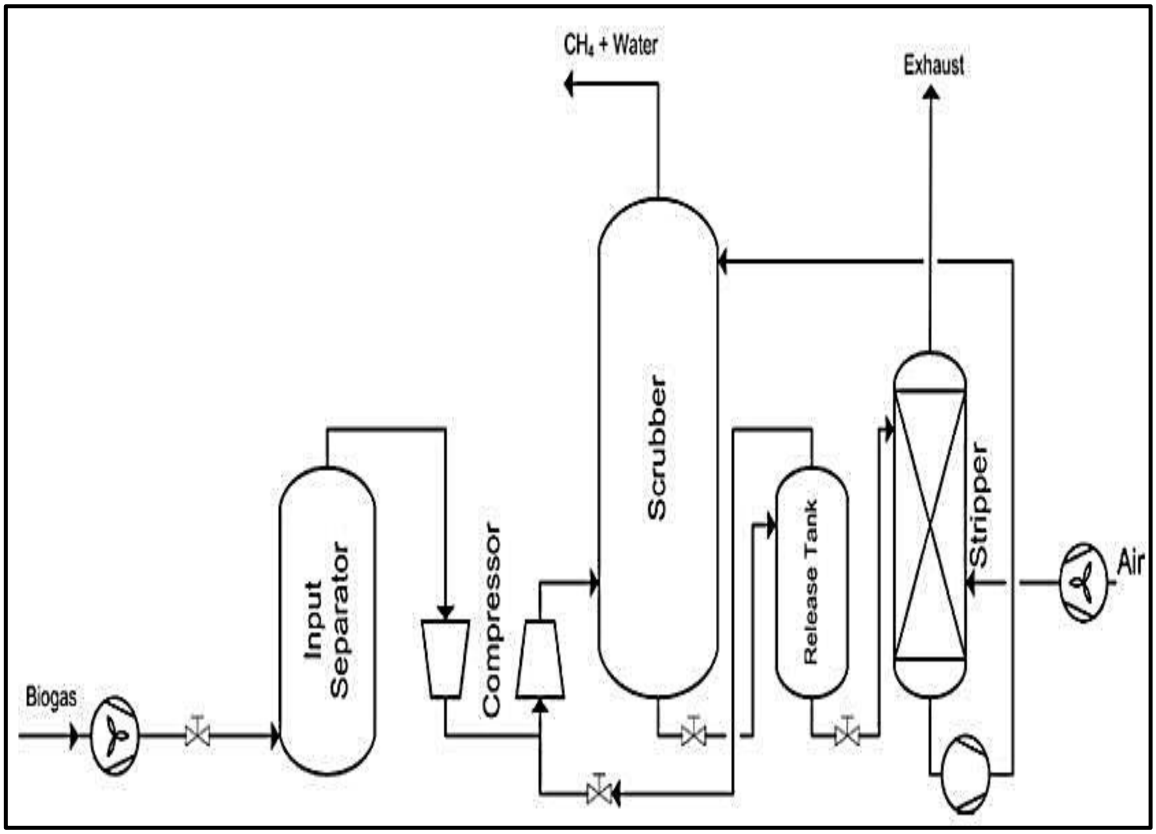


Figure 2.10: Flow diagram of water scrubbing system (Hullu, 2008)

2.5.2 Chemical Absorption

It is a reversible solute and solvent chemical bond formation. The highly energy input will required when the solvent bond is break during the regeneration process. There are two types of solvent used which is aqueous solution of alkaline salts such as sodium, potassium and calcium hydroxide. The other one is an aqueous solution of amine like mono-, di-, and tri-ethanolamine. (Zhao *et al*., 2010) claims that 20 % mono-ethanolamine perform the best as the solvent with 100 % removal of CO_2 as well as H2S. Its high efficiency and reaction rates able the process to happen at low pressure. This method also has been use in the natural gas purification. It also claimed that this is a high cost process with only 0.17 €/Nm biogas (Hullu, 2008). Figure 2.11 displays the flow chart of chemical absorption process.

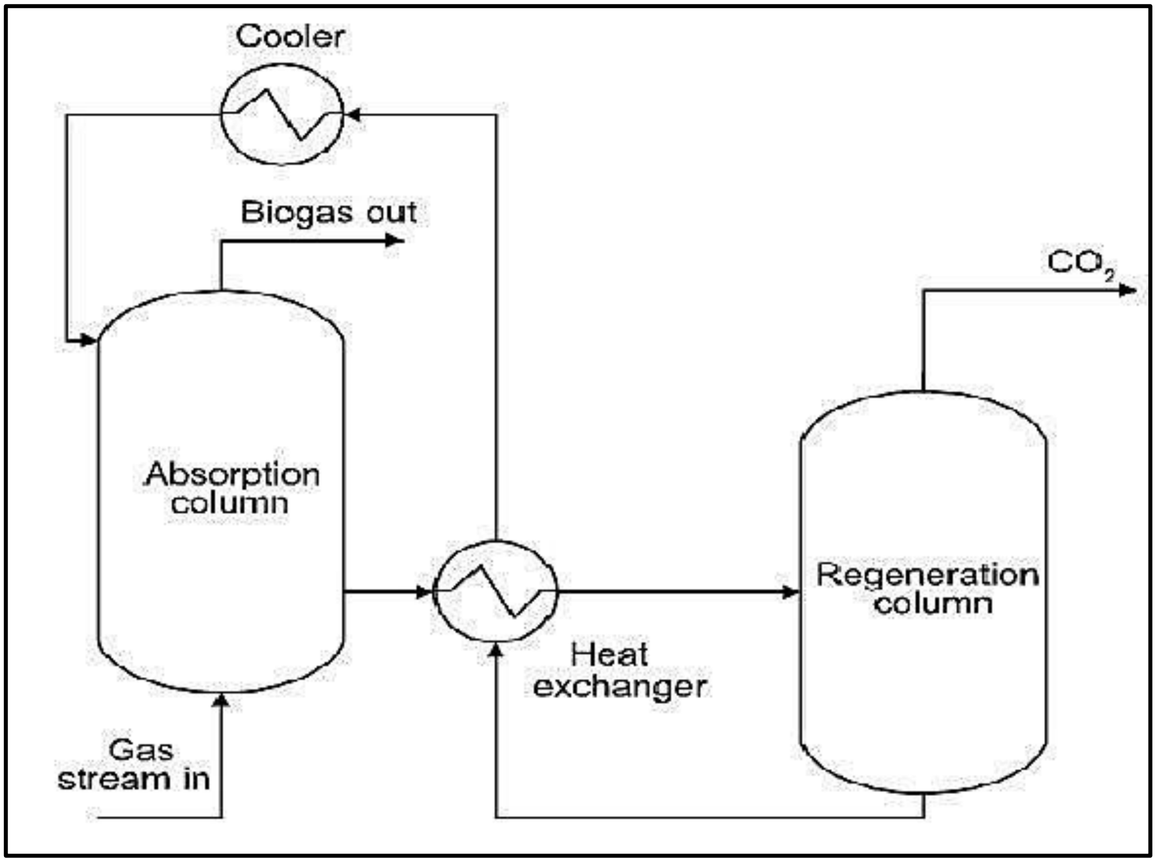


Figure 2.11: Flow diagram of chemical absorption process (Hullu, 2008)

2.5.3 Pressure Swing Adsorption

One of gas component will separate from a mixed gas where the gas is adsorbing at high pressure and will desorb when the pressure is reduced. It is possible because of the ability of different gases to attached at the solid surface is different. Cavenati *et al*., (2005) state that this operation happens at near ambient temperature and high pressure with special materials as a molecular sieve. Zeolite and active carbon are an effective materials to separate CO_2 (Rodrigues *et al*., 2007; Pinto *et al*., 2008). The cost for this method is € 0.4 Nm^3 biogas. Figure 2.12 shows the process flow diagram for pressure swing adsorption process.

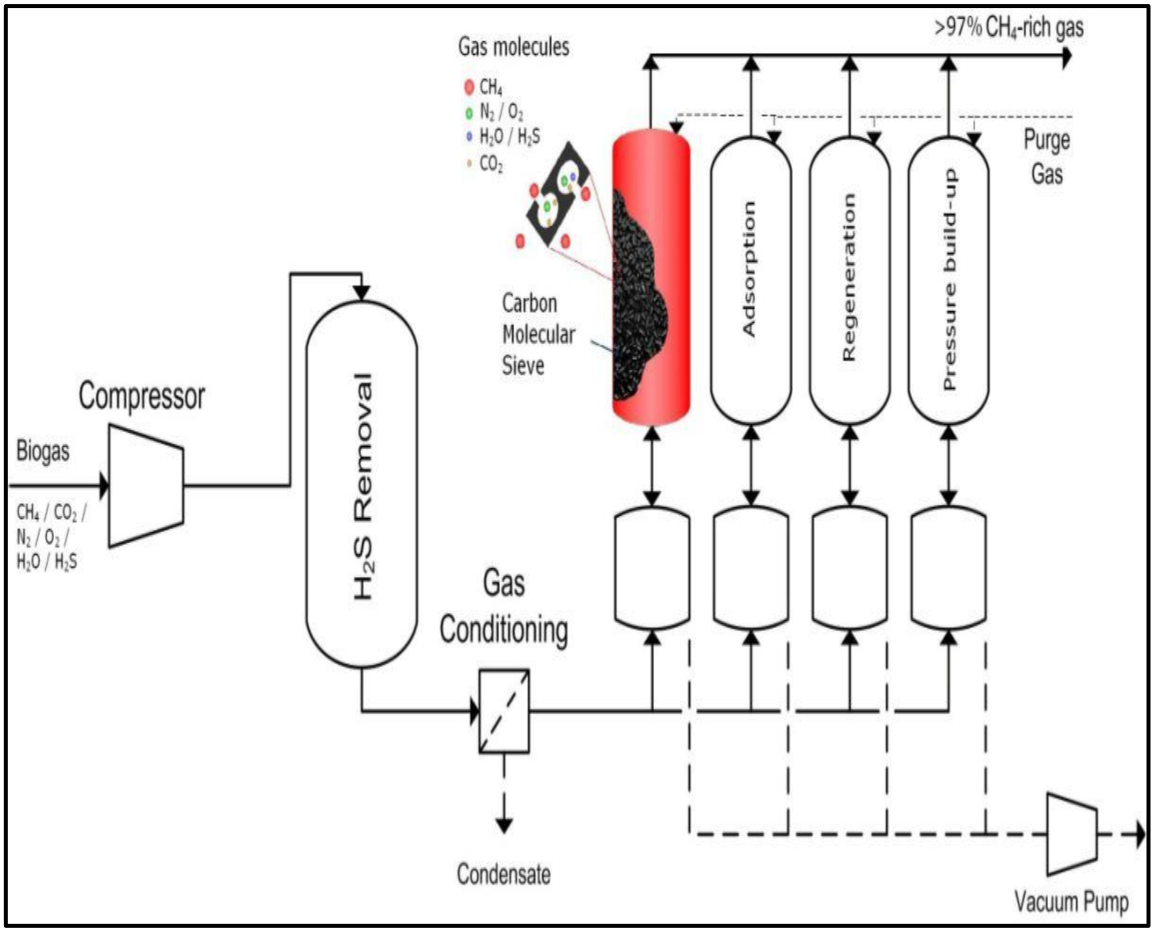


Figure 2.12: Schematic diagram of pressure swing adsorption process (Hullu, 2008)

2.5.4 Cryogenic Separation

This type of separation that operates at 40 bars and -100°C is based on the fact that each biogas contaminant can be separated from CH_4 at different temperature-pressure domain. The first heat exchanger will cool the crude biogas down to -70°C using the product steam before leaving the plant. The next heat exchangers and compressors will cool down the gas to 100°C at 40 bars pressure. Finally, the gas enters the distillation column to separate CO_2 and H_2S from CH_4. The purity of the methane is high but there are much equipment used. Figure 2.13 shows the process flow diagram for cryogenic separation process.

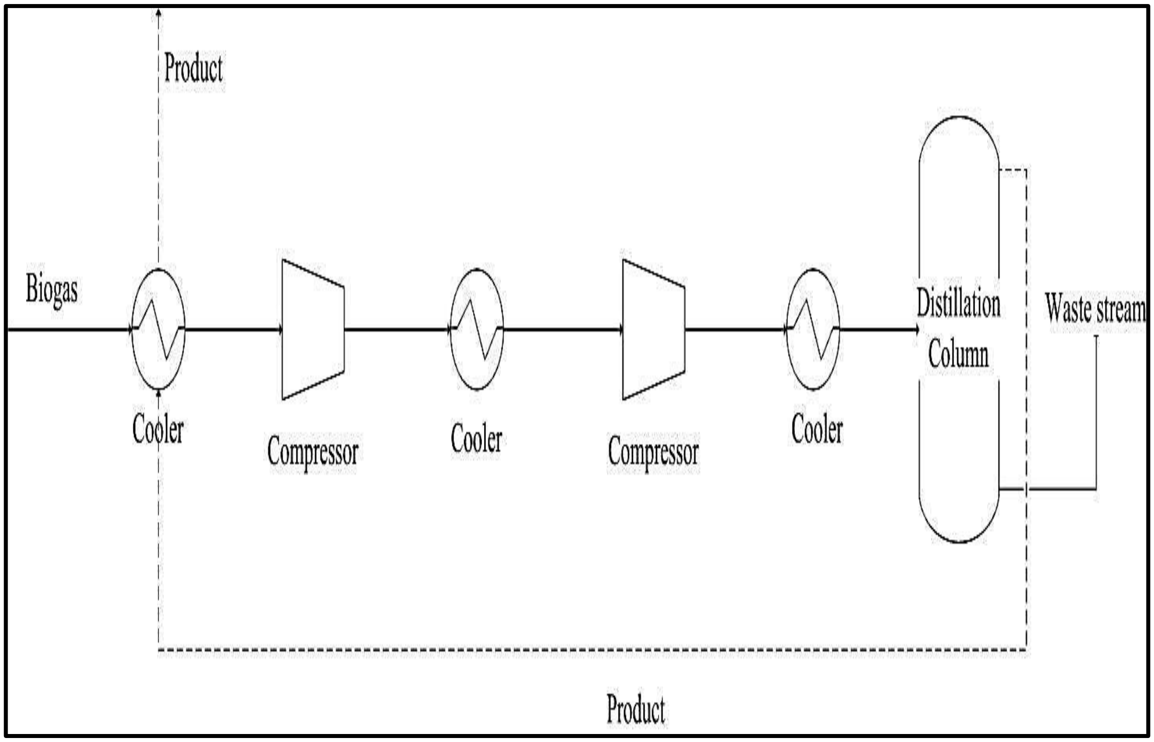


Figure 2.13: Flow diagram for cryogenic separation process (Hullu, 2008)

2.5.5 Membrane Separation

This gas permeation method operates continuously and stable. In the range 25-40 bars pressure, the high methane purity will be trade off with the methane yield. Increasing the size or number of the membrane module is improving the purity of CH_4 but more methane will be lost. It is also light in weight and easy to control. The cost is only 0.12 €/Nm^3 biogas because there is no expensive regeneration or chemicals used. It also claims that the low energy consumed in this process was lowering the CH_4 losses as well. In high pressure separation process, CO_2 and H_2S were separated from CH_4 in three stages and 96 % of CH_4 was produced. Another technique used is a gas liquid separation where a micro-porous hydrophobic membrane used as interface between gas and liquid. CO_2 and H_2S will dissolve into liquid while CH_4 that remained in the gas phase was collected for use. Figure 2.14 shows the principal of gas separation in gas permeation technique (Hullu, 2008).

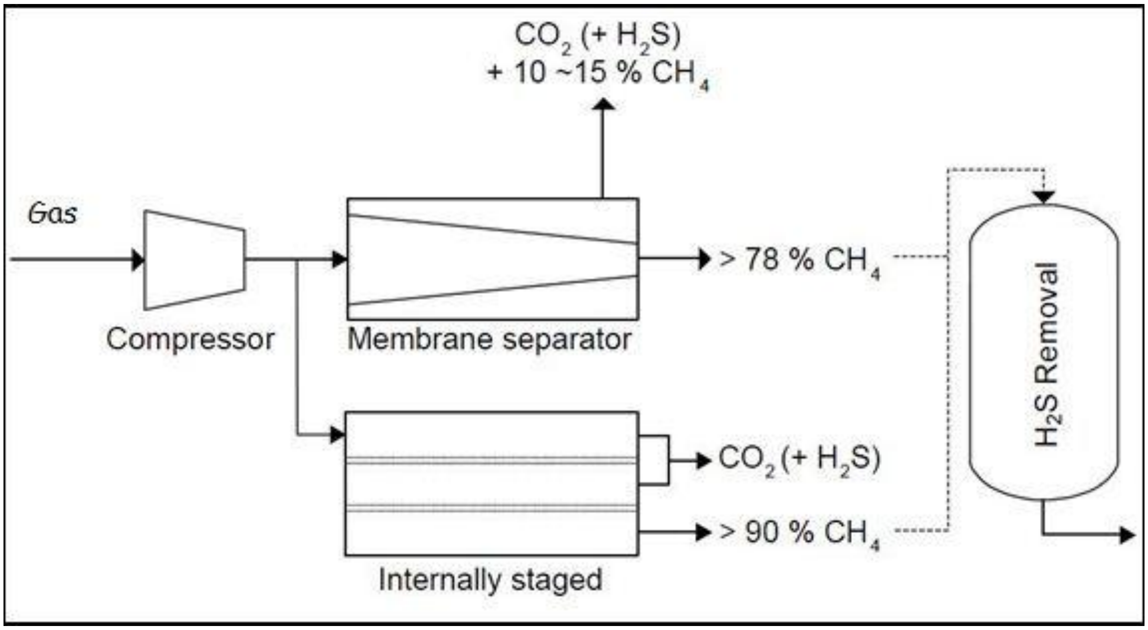


Figure 2.14: Schematic diagram for gas separation using membrane (Hullu, 2008)

These gas separation technologies are summarized with respect to their performance in the Table 2.5 and special attention are given to the product quality and general economic considerations.

Table 2.5 Advantages and disadvantages of gas systems technology

Process	**Advantages**	**Disadvantages**
Cryogenic distillation	• Lower power consumption • Could produce high quality products • Could achieve higher recovery compare to other process	• Unable to economically scale down to very small size • Consist of highly integrated, enclosed system which do not permit easy handling of widely varying feed streams
Adsorption	• Could obtain high purity of products • Can be supplied to remote locations where equipment size is critical	• Lower recovery products • Single relatively pure products
Absorption	• Excellent for CO_2 and H_2S removal	• High partial pressure needed for physical solvents • Low partial pressure needed for chemical solvent slow purity of acid gas
Membrane	• Versatility • Simplicity • Stable at high pressure • Could achieve high purity of product • Could give high recovery • Excellent for separation of hydrogen and hydrocarbon	• Possible recompression of permeate • Medium purity

2.6 Polymeric Membrane

The advantage of using gas separation membranes is that the equipment is much smaller and there is no solvent involved. The CO_2 passes through this barrier more easily than other gases. The membrane selectivity increased with a decrease in temperature and an increase in the feed pressure (Shi *et al*., 2006). Both membrane’s permeability and selectivity influence the economics of a gas separation membrane process.

Polymeric membranes are microporous films which act as semi-permeable barriers to separate two different medium phases. Polymeric membranes come in different pore sizes and filter by retaining particles larger than their pore size primarily by surface capture. They are ideal for both microfiltration and ultrafiltration applications. Two types of materials used in polymeric membranes are glassy polymers and rubbery polymers.

2.6.1 Glassy polymers

Glassy polymers are considered low permeable materials compare to the rubbery one. Its rigid aromatic chain may retard the penetration of gas molecule between intersegment polymer chains. The permeability of gas falls with increasing permeant size and small molecules permeate preferentially. In instance, polystyrene (PS) and polymethyl methacrylate (PMMA) are known to have many attractive properties likes high strength, optical clarity, ease of processing and low cost material.

Yet, glassy membrane operates below glass transition temperature and takes an extraordinary time to able to rearrange the polymer. It polymeric chain is packed imperfectly and it can excess free volume. Plus, it never reach thermodynamic equilibrium (Kentish *et al.*,2008).

2.6.2 Rubbery polymers

Rubbery polymers tend to have much higher permeability than glassy polymers. Its permeability increase with increasing permeates size and large molecules permeate.

Rubbery polymer can operates above glass transition temperature and able to rearrange in the meaningful time scale. Polymeric membrane can usually reach thermodynamic equilibrium (Kentish *et al.*,2008).

In practice almost all plants use rubbery membrane and a preferred membrane used in gas separation is polydimethylsiloxane, PDMS. Another example of rubbery polymer is styrene-butadiene, polybutadiene and polyisoprene.

2.7 Membrane material

Membrane that high in permeability and selectivity will shows a good performance. Therefore several criteria should be well-thought-out in order to create the high quality membrane. Aizan *et al*,2008 claimed that the criteria for a high quality membrane is:

- High in selectivity
- High in permeability
- Mechanical strength
- Temperature stability
- Chemical resistance

2.7.1 Polydimethyl siloxane (PDMS)

Polydimethylsiloxane (PDMS) in general is inert, non-toxic and non-flammable and optically clear. It belongs to a polymeric organosilicon compounds or referred as silicon. Its chemical formula is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$, with n referred to the number of repeating monomer $[SiO(CH_3)_2]$ units. PDMS molecules have quite flexible polymer chains due to their siloxane linkages, which are analogous to the ether linkages used to impart rubberiness to polyurethanes. Such flexible chains become loosely entangled when molecular weight is high, which results in PDMS unusually high level of viscoelasticity. Due to its viscoelasticity, PDMS tend to acts like a viscous liquid at high temperature while at low temperature it acts like an elastic solid/rubber.

As PDMS is a good viscoelastic material, it always used as a material in membrane. The separation factor and the permeation flux of the PDMS membrane is increase with the increasing of the membrane layer thickness.
PDMS is high-performance materials with excellent oxidative and thermal stability. It is most permeable rubbery polymer because of its chain flexibility, rotational flexibility, large free volume and low glass transition temperature.

However, pure PDMS has low gas selectivity. Pihnan et al., (2004) claims that the permeability and selectivity for hydrocarbon/methane and hydrocarbon/hydrogen separation can be improved by vapour-induced swelling of PDMS. Decreasing the temperature will increase the selectivity of PDMS. PDMS that been embedded with zeolite particles also shows an improvement in permeation. Zhan *et al*., (2008) once claim that the separation factor and selectivity and total flux of multi-layer PDMS/PDVF membrane maintain a high level. Table 2.6 below shows the properties of PDMS.

Table 2.6: Properties of PDMS

Property	Value	Reference
Mass density, kg/m^3	0.97	Polymer Data Handbook, Mark J.,Oxford Univ. Press,New York (1999)
Young's modulus, kPa	360-870	Re-configurable Fluid Circuits by PDMS ElastomerMicromachining
Poisson ratio	0.5	Polymer Data Handbook
Tensile or fracture strength, MPa	2.24	Polymer Data Handbook
Specific heat , kJ/kg.K	1.46	Polymer Data Handbook
Thermal conductivity, W/m.K	0.15	Polymer Data Handbook
Dielectric constant	2.3-2.8	Polymer Data Handbook
Index of refraction	1.4	Polymer Data Handbook
Electrical conductivity, Ωm	4x10^{13}	Polymer Data Handbook
Magnetic permeability, cm^3/g	0.6 x 10^6	Polymer Data Handbook
Melting point, ^{o}F	-49.9 – 40	Knovel Critical Tables

Some polymer have been tested by Nunes *et al.*,(2008) in order to know their permeability limit for gas separation at 30°C. The results is simplify in the Table 2.7 below:

Table 2.7: Gas permeabilities of gas separation polymers

Polymers	Permeability at 30°C (Barrer*)				
	H_2	N_2	O_2	CH_4	CO_2
Cellulose acetate	2.63	0.21	0.59	0.21	6.3
Ethyl cellulose	87	8.4	26.5	19	26.5
Polycarbonate, brominated		0.18	1.36	0.13	4.23
Polydimethylsiloxane	550	250	500	800	2700
Polymide (Matrimid)	28.1	0.32	2.13	0.25	10.7
Polymethylpentane	125	6.7	27	14.9	84.6
Polyphenyleneoxide	113	3.81	16.8	11	75.8
Polysulfone	14	0.25	1.4	0.25	5.6

* 1 Barrrer = 10^{-10} $cm^3.cm/cm^2.s.cmHg$

Source: Peinemann *et al.*, 2008

The table 2.7 shows that permeance for N_2 through PDMS is 250 Barrer CO_2 shows the highest permeance with PDMS which is 2700 Barrer. it is proved that PDMS has high permeability.

2.7.2 Polyvinilidene fluoride

Polyvinylidene Fluoride (PVDF) is a pure and non-reactive thermoplastic fluoropolymer with plastic material speciality. In general, PVDF is used in the application that required highest purity, strength and resistance to solvents, acids, bases and heat and low smoke generation during a fire event. PVDF has a low melting point, 177^0C, low density; 1.78 g/m^3 and low cost material compared to other fluoropolymers. PVDF also will not soluble in water.

The use of PVDF membrane as a support substrate layer for making a polyamide thin-film composite has been hindered by the hydrophobic nature of PVDF. These PVDF membranes are more resistant to discoloration than other commercially available PVDF membranes and have better retention of adsorbed proteins than other types of transfer membranes used. The excellent mechanical properties and resistance to severe environmental stress makes PVDF is suitable as a membrane support layer. The general properties of PVDF are shown in Table 2.8.

Table 2.8: General properties of PVDF (Polymer Data Handbook, 1999)

Properties	ASTM or Unit	PVDF
MECHANICAL PROPERTIES		
Specific Gravity	D792	1.77
Elongation%	D638	300~450
Tensile Strength (psi)	D638	4500-6200
Flexural Strength (psi)	D790	8600-9500
Compressive Strength	D695	11,600
Tensile Elastic Modulus (Young's Modulus) (psi)	D638	160,000
Flexural Modulus (psi)	D790	90,000~168,000
Flex Life (MIT cycles)	D2176	n.a
Hardness Durometer Shore D	D636	D75~85
Coefficient of Friction on steel	D1984	0.4
Abrasion Resistance 1000 revs.	Taber	5~15
Impact Strength IZOD 73°F/23°C, notched ft/lbs/in	D256	4
THERMAL PROPERTIES		
Melting Point	°C (°F)	171 (340)
Upper Service Temperature(20,000h)	°C (°F)	129 (264)
Thermal Conductivity	BTU/hr/ft2/deg F in	1.3
	cal/sec/cm2,ºC/cm	3.0x10-4
Linear Coefficient of Thermal Expansion	D696	4.2 10-5 °C
Heat of Fusion	BTU/LB	n.a
Heat of Combustion	BTU/LB	n.a
Low Temperature Embitterment	°C (°F)	-62 (-80)
ELECTRICAL PROPERTIES		
Dielectric Constant	D150/103Hz	7.72
	D150/106Hz	6.43
Dielectric Strength 10 mil film	D149	>1080
Volume Resistivity ohm-cm	D257	2 x 1014
Surface Resistivity ohm/sq.	D257	5 x 1014
GENERAL PROPERTIES		
Chemical/Solvent Resistance	D543	Very Good
Water Absorption, 24h,%	D570	<0.04
Refractive Index		1.42
Limiting Oxygen Index %	D2863	43

2.8 Thin Film Composite (TFC)

Thin film composite (TFC) membrane is a composite membrane consists of at least two different materials. A selective membrane material is deposited as a thin layer upon a porous sublayer, which serves as support. The support or porous layer has high porosity, no selectivity and a thickness of 50 to 150 mm. The skin or top layer is very thin (0.1 to 5 mm) and it is responsible for the membrane selectivity.

The theory of TFC has been stated in the research by Stookey, (2001). It states that, the trans-membrane flux is inversely proportional to membrane thickness and directly proportional to the membrane area and applied pressure. So, it is needed to produce the thinnest possible membrane in structural form that will accommodate the applied pressure while maximizing membrane surface area. However, the structural and mechanical strength of the membrane is important. A polymer which is the gas permeable membrane has poor mechanical strength. It requires underlying support material that can erect the applied pressure load. The best support layer is the porous polymer because it enables to reduce a few microns of the selective layer.

The advantage of this membrane is that each layer can optimized independently to achieve desired membrane performance. The roles of the active, separating layer and the support can be separated and each part made from the optimum polymer, rather than relying upon a single polymer to provide both good separating characteristic and mechanical strength (Naylor, 1996). TFC membrane with PVDF had higher permeances without losing selectivity (Ashwani *et al*., 2008). Jianfu Ding, (2008) claims that TFC membrane with PDMS/PEG based PU coating layer shows higher selectivity for O_2/N_2 separation. There are many technique used in applying the support layer such as polymerization. Figure 2.15 illustrate the thin film composite membrane structure.

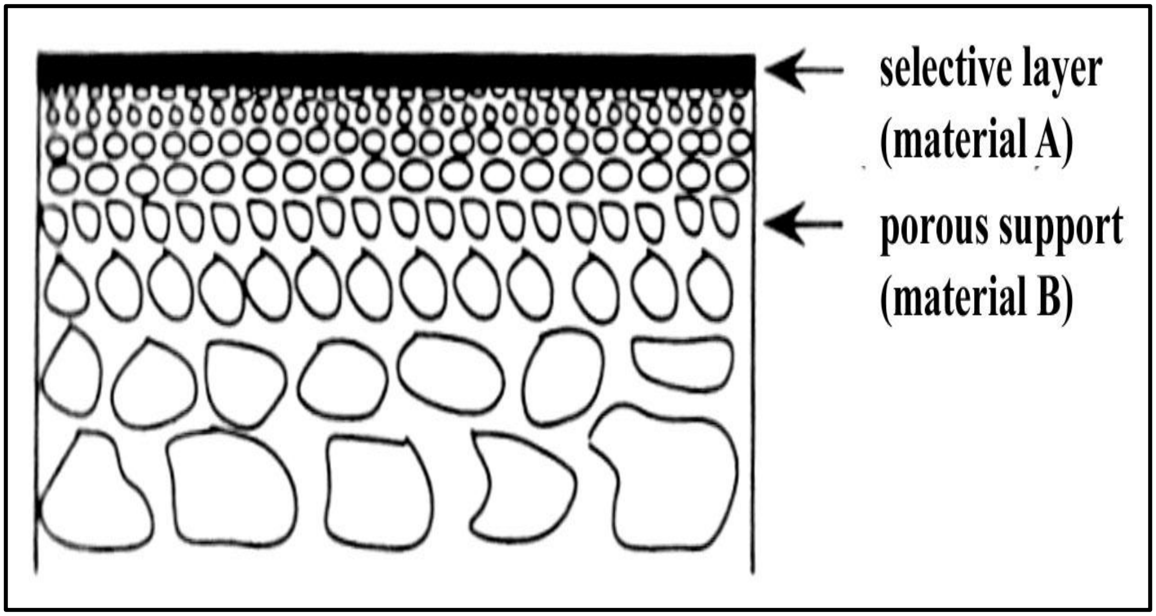


Figure 2.15 Thin film composite (TFC) membrane structure

CHAPTER 3

METHODOLOGY

3.1 Research Design

This chapter will cover the materials that will be used and steps in the formation of thin film composite membrane. Basically, two main steps are involved in the formation of thin film composite membrane. A first step is the preparation of the polymer-sieve slurry and the second step is casting the polymer-sieve mixture to form a thin film membrane. A performance of the membrane is highly depends on the materials chosen. The flow chart for experiment shows in Figure 3.1.

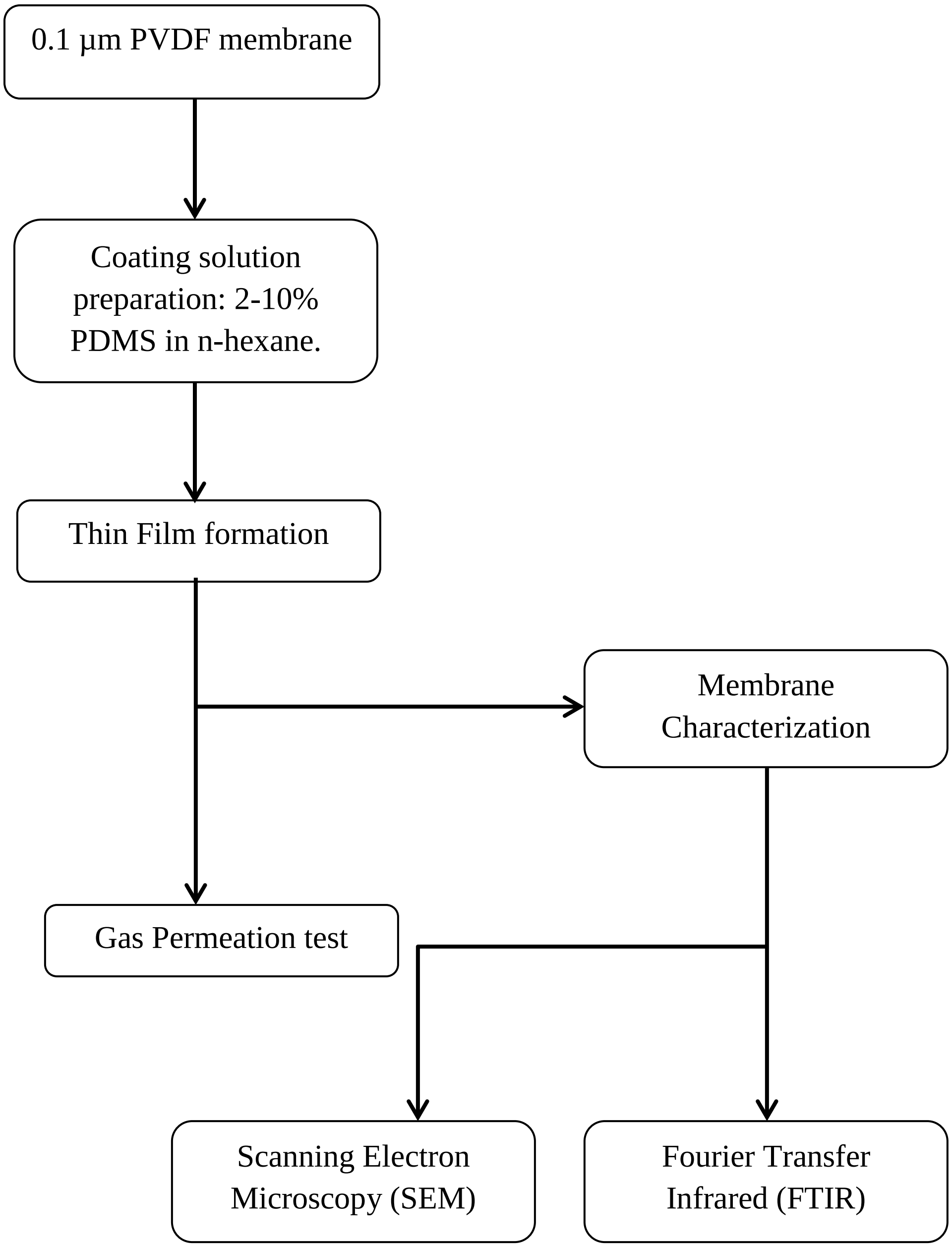


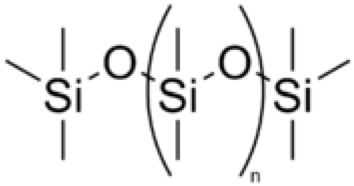
Figure 3.1: Research design flowchart

3.2 Coating layer selection

3.2.1 Polydimethyl siloxane (PDMS)

PDMS is chosen to be a silicone rubber in this study. In general, is considered to be inert, non-toxic and non-flammable silicone. PDMS molecules have quite flexible polymer backbones (or chains) that cause it become loosely entangled when molecular weight is high, which results in high level of viscoelasticity. A solid PDMS samples will present an external hydrophobic surface after polymerization and cross-linking. This surface chemistry makes it difficult for polar solvents to wet the PDMS surface, and may lead to adsorption of hydrophobic contaminants. Table 3.1 shows the characteristics of PDMS.

Table 3.1: Characteristics of PDMS (Polymer Data Handbook, 1999)

Characteristics	
	
IUPAC name	poly(dimethylsiloxane)
Molecular formula	$(C_2H_6OSi)_n$
Density, kg/m^3	965

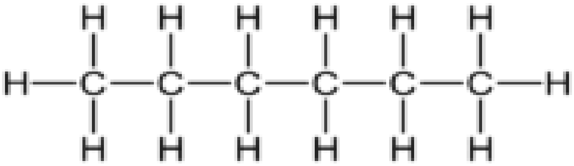
PDMS is a grade of silicone rubber which contains Si-O-Si in the backbone. Because of Si-O band energy (88-117 kcal/mol), this polymer is a heat resistance polymer, while C-C band energy is about (83-85 cal.mol). Therefore silicone rubber can be used at high temperatures for a long time (Madaeni *et al.*, 2009).

3.3 Solvent selection

3.3.1 n-hexane

n-hexane or hexane is an unbranched isomers with six carbon atoms. It appears as colourless liquids at room temperature, with boiling points between 50 and 70 °C, with gasoline-like odour. They are widely used as cheap, relatively safe, largely unreactive, and easily evaporated non-polar solvents. Table 3.2 shows the general properties of n-hexane.

Table 3.2: Properties of n-hexane (Wolfram, 2010)

Properties	
	
IUPAC name	Hexane
Molecular weight	C_6H_{14}
Molar mass, g/mol	86.18
Density, g/mL	0.6548
Melting point, ^{o}C	-95
Boiling point, ^{o}C	69

Chendake *et al.* once claimed that PDMS membrane that prepared with n-hexane in pores exhibited better selectivity of a particular gas pair. This is attributable to the better miscibility of PDMS solution with n-hexane (Chendake *et al.*, 2010).

3.4 Penetrants

Pure CO_2 and N_2 will be the penetrants for this study. The properties of these penetrants are shown in the Table 3.3.

Table 3.3: Properties of methane and carbon dioxide (Wolfram, 2010)

	Nitrogen	Carbon dioxide
Formula	N_2	CO_2
Molecular weight, g/mol	14.0067	44.0l2
Melting point, ^oC	-210	-78
Boiling point, ^oC	-195.8	-57

3.5 Thin film composite (TFC) formation

Thin film composite (TFC) membrane was primed by coating a ready-made membrane with the coating solutions. The coating solution was prepared by added PDMS liquid to n-hexane solvent to obtain a homogeneous solution of 3 wt. %, 5 wt. %, 8 wt. % and 10 wt. %. Then, the coating process was done by using the dip coating method. This simple and low cost method was performed in five key stages; immersion, withdrawal, film formation, solvent evaporation and continued drainage of the excess solution. After the coating process, the membrane is further dried in the vacuum oven to remove residual solvent for 15 minutes at temperature of 60 ^oC.

3.6 Gas Permeation Test

This test is done in order to examine the separation ability of this new membrane under ideal condition by using the pure gases; CO_2 and N_2. Figure 3.2 shows the schematic diagram of gas permeation test.

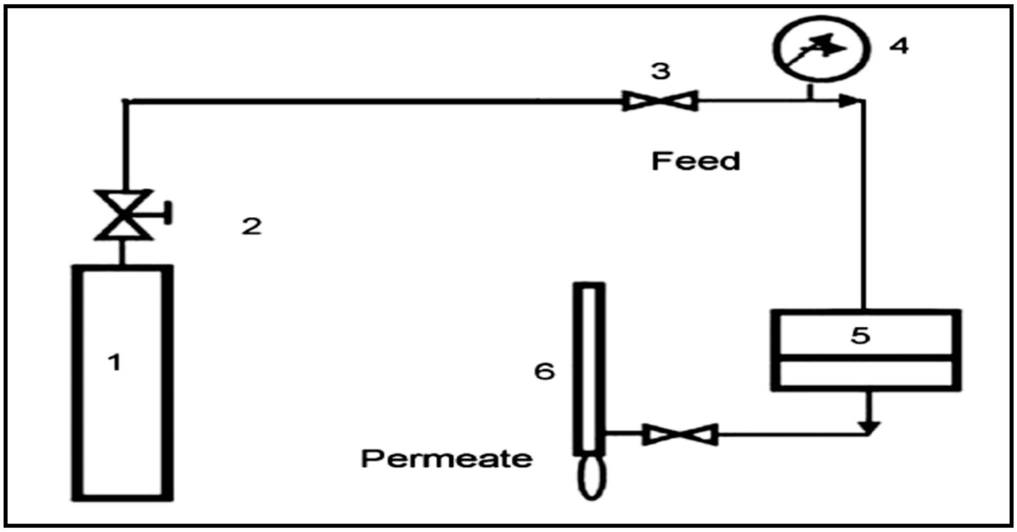


Figure 3.2: Schematic diagram of experimental setup for gas permeation: (1) gas cylinder, (2) pressure regulator, (3) valve, (4) pressure gauge, (5) membrane cell and (6) bubble flow meter (Madaeni *et al.,* 2009)

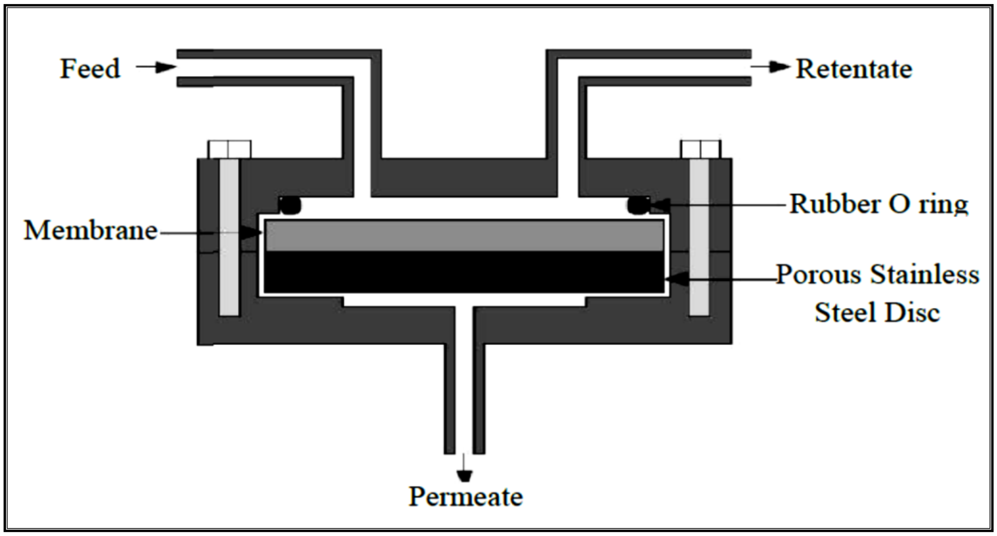


Figure 3.3: Schematic diagram of membrane cell (Nurhana, 2010)

This test is done at room temperature and at pressure around 1 bar to 2 bars. The membrane was firstly folded around the membrane cell. The fitting of the gas hose and permeability unit is ensured to be suiting each other to avoid gas leakage. The last step is let the CO_2 gas flow through the membrane fitted in it. The time of the first bubble formed and volume difference of the soap water by the membrane was taken.

From this test, permeability and selectivity of the membrane can be determined. Permeation of one gas was calculated using the formula shown in the Eq. (3.1) below:

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

where P_i is permeability coefficient in cm^3(STP).cm/cm^2.s.cmHg of gas i, l is effective layer of separation in cm, Q_i is gas flow in cm^3(STP)/s of gas i, A is effective membrane area in cm^2 and Δp is trans membrane pressure, where $P_{us} - P_{ds}$ in cmHg. Common unit for permeability coefficient is Barrer, which known

$$1\ \text{Barrer} = 1 \text{ x } 10^{-10}\ cm^3.(STP)\ cm/cm^2\ .s.cmHg \qquad (3.2)$$

Meanwhile the permeance which is the normalized flux with pressure can be measured based on the permeability of the membrane using Eq (3.3).

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{A\,\Delta p} \qquad (3.3)$$

The effective separation layer of the membrane is unknown and cannot be measured using present method. Therefore, (Madeani, 2009) stated that $(P/l)_i$ can be defined as the permeance of gas i in unit GPU. Q_i is gas flow in cm^3(STP)/s of gas i, A is effective membrane area in cm^2 and Δp is transmembrane pressure, where $P_{us} - P_{ds}$ in cmHg. The conversion unit of GPU is

$$GPU = 1 \text{ x } 10^{-6}\ cm^3.(STP)/cm^2\ .s.cmHg \tag{3.4}$$

The ideal selectivity (α) of one gas, i, over another gas, j, is defined as in the Eq. (3.5):

$$\alpha_{ij} = \frac{P_i}{P_j} \tag{3.5}$$

The gas selectivity, $\alpha_{CO_2/N_2}$of the membrane with 3 wt. % PDMS as coating layer was much lower compare to membrane with coating layer of 7 wt. % PDMS. This result was due to the low viscosity of the 3 wt. % PDMS solution that cause defect to the coating layer.

3.7 Membrane Characterizations

In this process, the thin film membrane will be characterized using Scanning Electron Microscopy (SEM) and Fourier Transforms Infrared (FTIR).

3.7.1 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope, or SEM, is an incredible tool for seeing the unseen worlds of microspace. It used to study the surface and cross sectional morphology of the thin film composite PDMS membrane and to measure the thickness of the skin layer. It creates the magnified images by using electrons instead of light waves. Figure 3.4 below illustrate the schematic diagram of SEM.

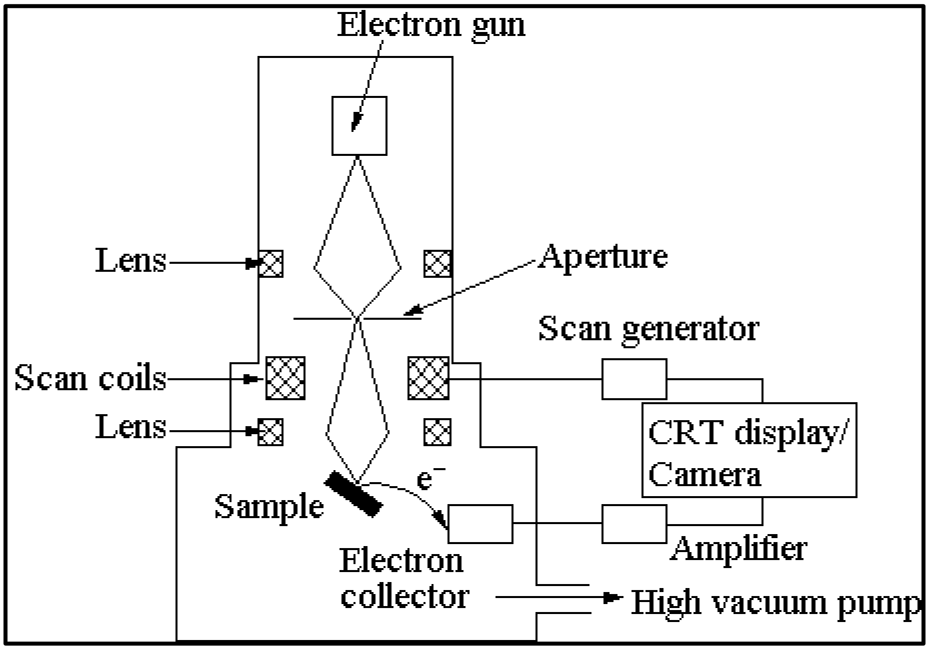


Figure 3.4: Schematic diagram of Scanning Electron Microscope (SEM) (Mauppasant, 1887)

The SEM shows very detailed 3-dimensional images at much higher magnifications than is possible with a light microscope. The images created without light waves are rendered black and white. Samples have to be prepared carefully to withstand the vacuum inside the microscope and placed inside the microscope's vacuum column through an air-tight door. After the air is pumped out of the column, an electron gun emits a beam of high energy electrons.

This beam travels downward through a series of magnetic lenses that designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample.

3.7.2 Fourier Transfer Infrared (FTIR) Spectroscopy

FTIR (Fourier Transform Infrared) Spectroscopy, or simply FTIR Analysis, is an analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used to identify unknown materials present in a specimen. Figure 3.5 below shows the example of an FTIR spectrometer.

Figure 3.5: Image of FTIR Spectroscopy (Maupassant, 1887)

The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analysed and matched with known signatures of identified materials in the FTIR library.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Polydymethylsiloxane-polyvinyl fluoride (PDMS-PVDF) thin composite membrane was prepared in this experiment by coating a readymade PVDF membrane using a dip coating method. A various concentration of PDMS used as coating layer on the membrane which were 3%, 5%, 8% and 10% (w/w). n-hexane which is easily vaporized has been used as solvent in preparing the coat solution. After coating, the membrane was dried in the oven at 60^{o}C for 15 minutes.

In this chapter, each membrane with different concentration of PDMS was tested for its permeation and selectivity of pure gas carbon dioxide (CO_2) and nitrogen (N_2). Besides, the membrane also was characterized using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR).

4.2 Gas Permeation Result

The permeation test was performed by letting carbon dioxide, CO_2 gas pass through the membrane cell. Then, the time the first bubble formed was taken until the required volume. After all pressure tested for CO_2, then nitrogen, N_2 gas was used to pass through the membrane. The main purposed of this experiment was to calculate the pressure normalized flux (permeance) of carbon dioxide, CO_2 and nitrogen, N_2. The selectivity of the membrane then can be calculated based on the permeance value. This permeance and selectivity value is shown on the Table 4.1 below.

Table 4.1: Pressure normalized flux and selectivity of each membrane from Gas Permeation Test

Pressure, (bar)	**Concentration of membrane coating layer, (%)**	**Pressure normalized flux CO_2, (GPU)**	**Pressure normalized flux N_2, (GPU)**	**Selectivity $\alpha_{CO_2}/\alpha_{N_2}$**
1	3	437	313	1.40
	5	377	225	1.68
	8	358	175	2.05
	10	338	150	2.25
2	3	800	528	1.52
	5	729	332	2.20
	8	609	218	2.79
	10	540	190	2.84

*1 GPU = 1 x 10^{-6} $cm^3/cmHg.s.cm^2$

From Table 4.1 above, it shows that the pressure normalized pressure of the membrane is the highest for CO_2 gas with 3 wt% PDMS which is 800 GPU. Meanwhile the lowest pressure normalized flux is 150 GPU which is the membrane with 10 wt% PDMS for N_2 gas. This result shows that the concentration of the coating layer affected the permeability of each membrane.

The increasing and decreasing of the permeance values also depend on the pressure applied. At 1 bar, the permeance of each membrane much smaller compare to when the permeance value when 2 bars pressured applied. The relationship between the permeance value and the coating layer concentration and the pressure applied for carbon dioxide (CO_2) presented in the Figure 4.1 below.

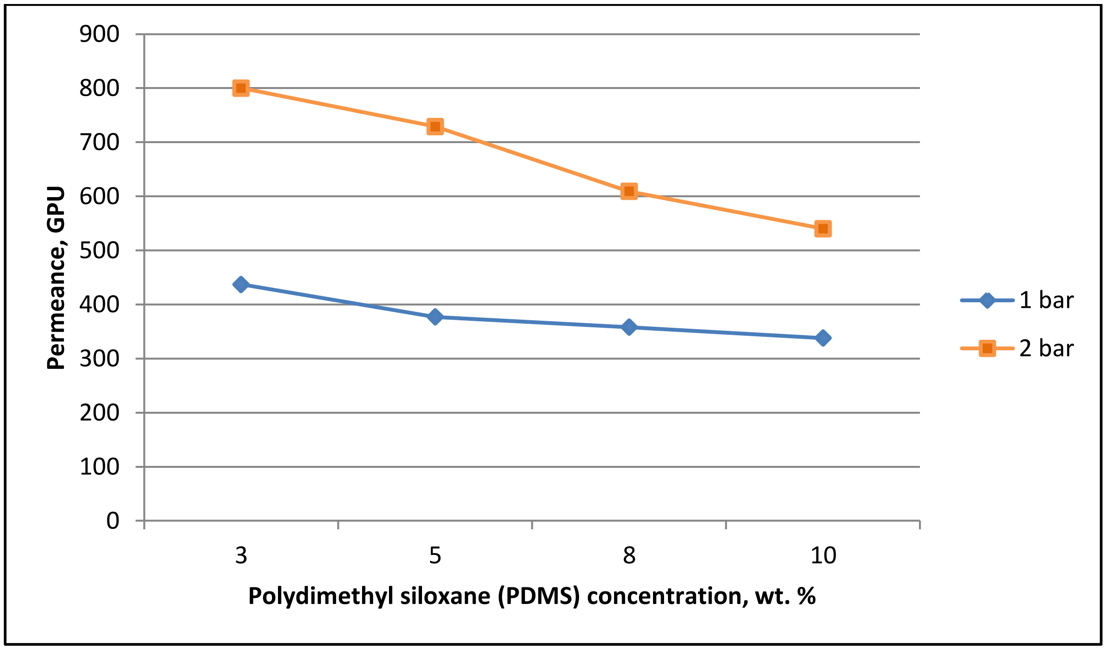


Figure 4.1: Relationship between permeance, GPU and coating layer concentration, wt. % at different pressure applied for carbon dioxide (CO_2)

From the graph, it can be clearly seen that the permeance of CO_2 gas is decrease as the concentration of PDMS increase. However, enhancing the pressure will increase the permeance for CO_2. Meanwhile, Figure 4.2 below display the relationship of pressure normalized flux nitrogen (N_2).

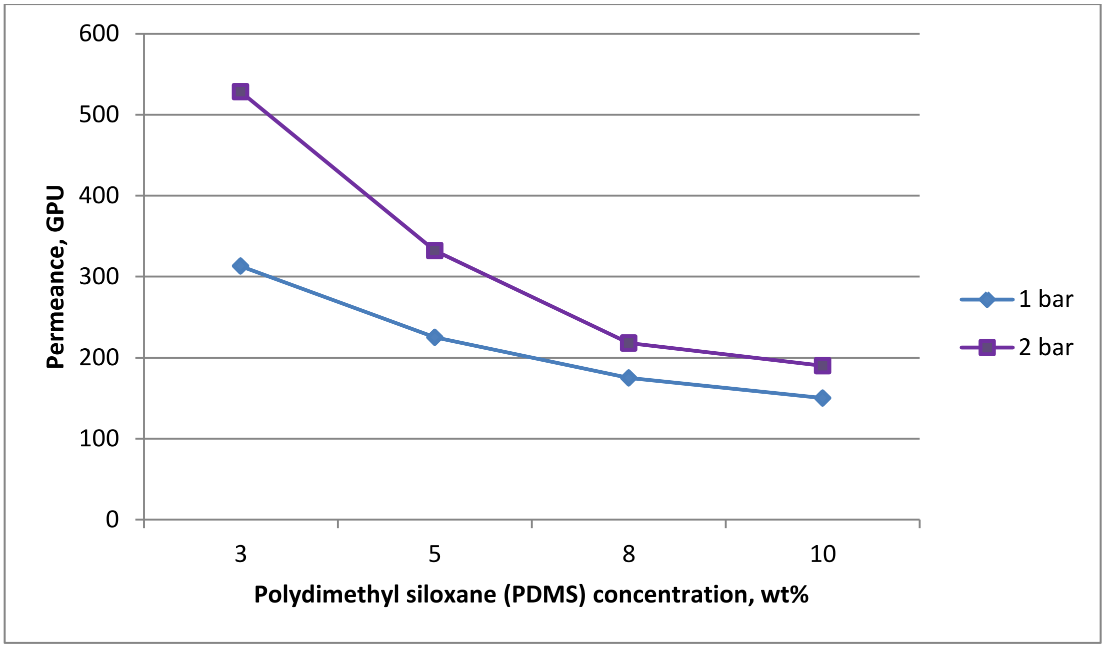


Figure 4.2: Relationship between permeance, GPU and coating layer concentration, wt. % at different pressure for Nitrogen (N_2)

The graphs from figure above shows that the permeance values for N_2 gas was depend to the feed pressure applied. Increment on the feed pressure is increasing the membrane permeance for N_2. Increasing in PDMS concentration shows decrement in permeance for N_2. Then, the selectivity for CO_2/N_2 is calculated by divide the permeance of CO_2 with permeance of N_2. The relationship between the selectivity of the membrane and the membrane coating layer concentration with different pressure applied can be seen on the graph display in Figure 4.3 below.

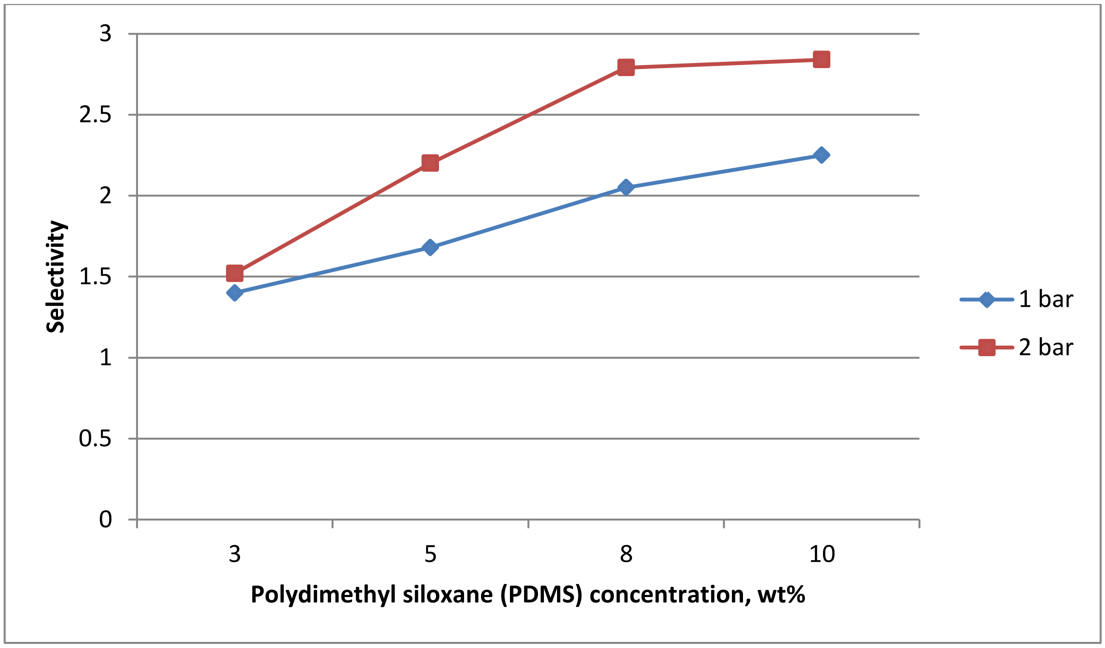
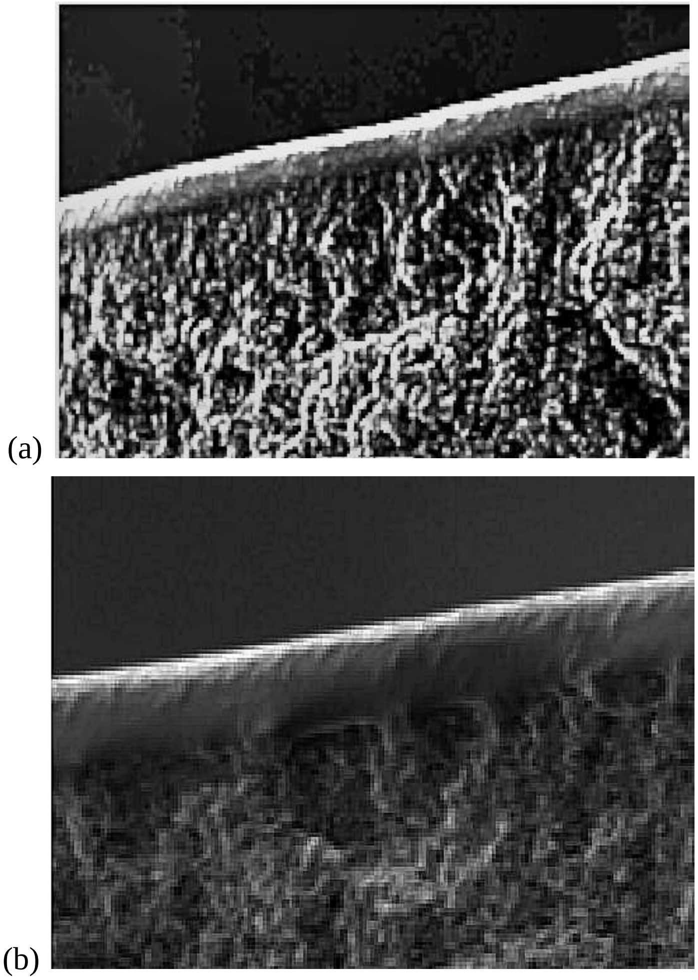


Figure 4.3: Relationship between selectivity and coating layer concentration at different pressure

The figure above indicates that the selectivity of CO_2/N_2 is increase with the increment of the polydimethyl siloxane (PDMS) concentration. The graph also shows that increasing the feed pressure can enhanced the selectivity of the membrane. Membrane with the highest concentration of PDMS higher feed pressure shows the higher selectivity. It can be concluding that, increment the feed pressure and PDMS concentration will enhancing its selectivity.

4.3 Scanning electron microscopy (SEM) Analysis

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. Then, the sample can be tested. The cross sections of each membrane are shown in the Figure 4.4 below.



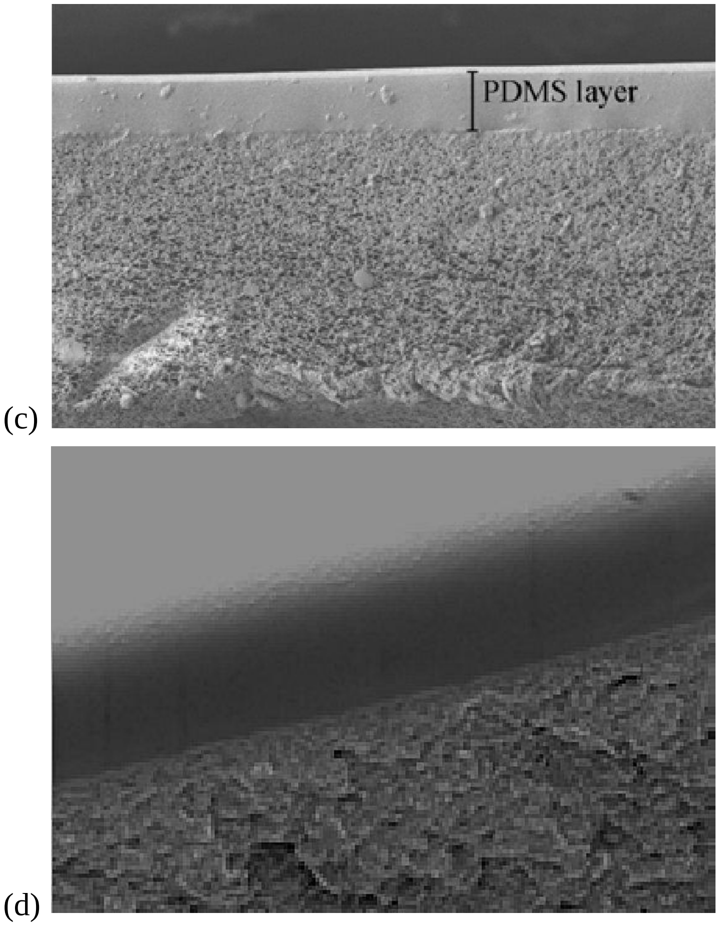
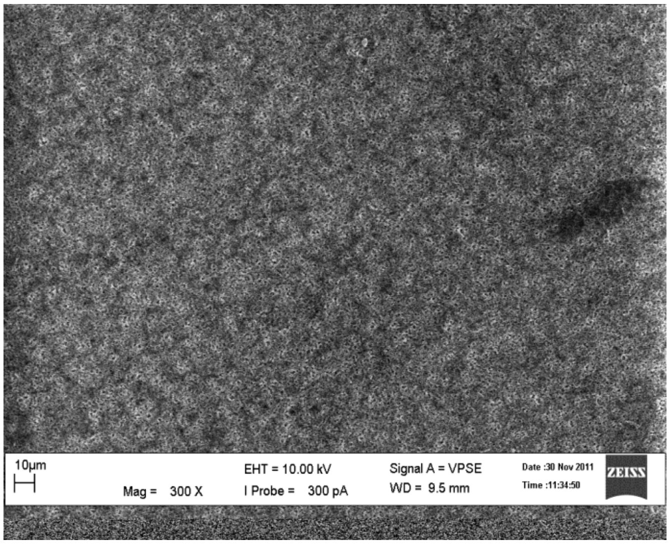
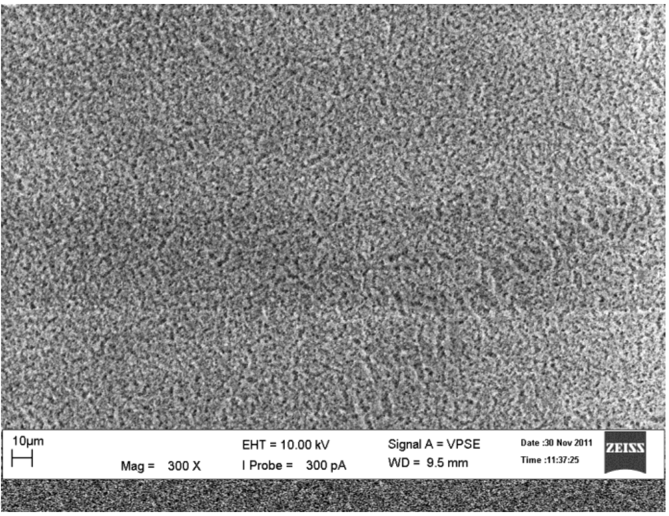


Figure 4.4: Cross Section of membrane with different concentration; (a) 3 wt. %, (b) 5 wt. %, (c) 8 wt. %, (d) 10 wt.%

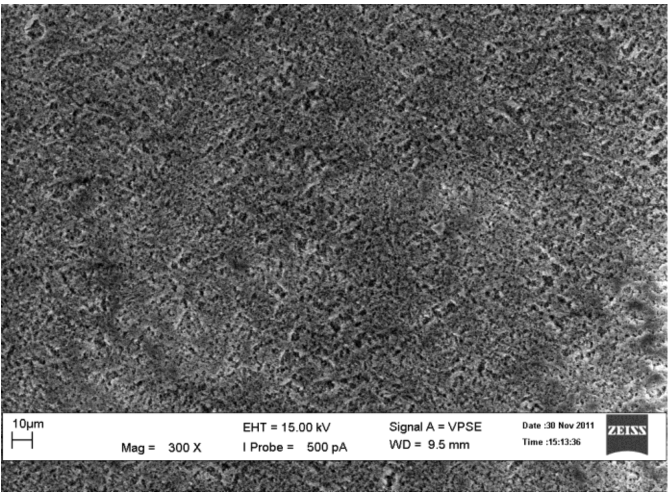
It is clearly shown in the figure above that the membranes consist of two layers where the top layer is a dense layer while the bottom is the porous support layer. The characteristics shown in the figure above proved that the membrane is the thin film composite membrane. For figure 4.4(a) and figure 4.4(b), the thicknesses of the coating layer are merely the same and figure 4.4(d) have the less thick of dense layer. Meanwhile Figure 4.5 below displays the surface of each membrane with different concentration of PDMS.


10µm
EHT = 10.00 kV
Signal A = VPSE
Date :30 Nov 2011
Mag = 300 X
I Probe = 300 pA
WD = 9.5 mm
Time :11:34:50
ZEISS

(a)


10µm
EHT = 10.00 kV
Signal A = VPSE
Date :30 Nov 2011
Mag = 300 X
I Probe = 300 pA
WD = 9.5 mm
Time :11:37:25
ZEISS

(b)


10µm
EHT = 15.00 kV
Signal A = VPSE
Date :30 Nov 2011
Mag = 300 X
I Probe = 500 pA
WD = 9.5 mm
Time :15:13:36
ZEISS

(c)

(d)

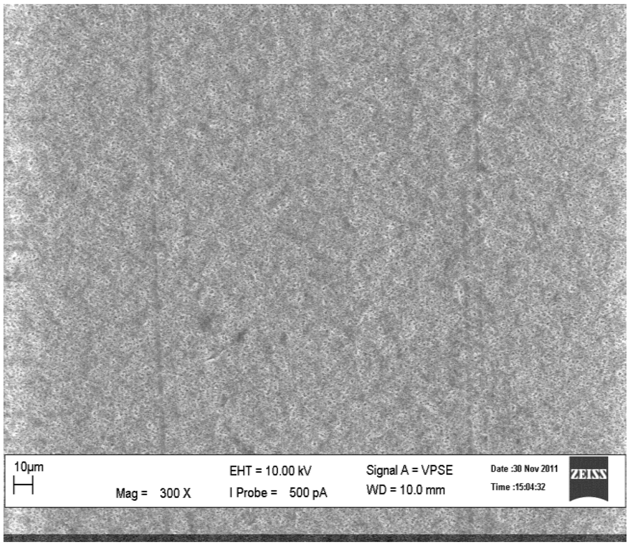


Figure 4.5: Surface view for different concentration of PDMS; (a) 3 wt. %, (b) 5 wt. %, (c) 8 wt. %, (d) 10 wt. %

From the figures above, it shows that the membrane surface became smoother as the concentration of PDMS increase. All of the membranes also have fewer defects on the surface and this analysis is supporting the membrane high performance.

4.4 Relationship of Membrane Performance with Membrane morphology

The performance of the membrane from the gas permeation test can be correlated to the membrane characteristics. The characteristics of the membranes are shown from the Scanning Electron Microscopy (SEM) analysis. Based on the concentration of polydimethylsiloxane (PDMS) and the result from permeation test and SEM analysis, several parameters that correlated to the membrane performance can be discussed.

First is the dense layer form on the membrane. Based on the SEM analysis, Figure 4.4 shows that the dense layer is formed on the top of the membrane. The silicon rubber dense layer will provide a resistance against the gas flow through the membrane. The resistance of the dense layer is depend on the concentration of the polydimethyl siloxane (PDMS) used. The higher the concentration, the higher the resistance will be. The formation of the dense layer is the reason of the decreasing of the membrane permeability as shown on the Table 4.1 Thus, increment in PDMS concentration will increase the resistance of the dense layer and the selectivity of CO_2/N_2 but decreasing the pressure normalized flux.

Figure 4.4 also shows that the membrane is the thin film composite membrane which consists of dense layer at the top and porous support layer at the bottom. The concentration of PDMS is affected the pore size of the support layer which is polyvinylidene fluoride (PVDF). Figure 4.5 shows that the surface of the membrane becomes smoother when the PDMS concentration increases. This analysis indicates that the pore size of the porous layer is smaller as the concentration of PDMS increase. Decrement in pore size is decreasing the gas permeability but increasing the selectivity of CO_2/N_2 in the permeation test.

The results of permeation test in Table 4.1 shows that the permeability of CO_2 is higher compare to permeability of N_2. This is due to the differences of the kinetic diameter for both gases. Kinetic diameter of CO_2 is 3.3 $\check{A}$ while the kinetic diameter of N_2 3.64 $\check{A}$. The small kinetic diameter of CO_2 makes it easy to permeate through the membrane and give high permeability compare to N_2. As discussed before, the pore size of the membrane is decrease with the increment of the concentration of PDMS disregarding the kinetic diameter of the gases. So, the permeability and the selectivity of the gases also correspond to the kinetic diameter of the gases and the membrane pore size.

The performance of the membrane also related to the feed pressure. Table 4.1 shows that the higher the feed pressure, the higher the permeability and selectivity of CO_2/N_2 be. This is related to the gas kinetic diameter, the pore size of the membrane and the pressure applied. The strong pressure that applied to the small kinetic diameter and large pore size will obtain the high gas permeability and low selectivity. Meanwhile, a small feed pressure that applied to the small kinetic diameter and large pore size will acquire a low permeability and low selectivity compare to the one with high feed pressure. This is due to the small force applied to drive the gas molecule to permeate from the membrane. Increment in the pressure applied will enhance the force to drive the gas molecule.

4.5 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transform Infrared (FTIR) spectroscopy was used in order to identify the unknown materials in the membrane. Every peak of the result will show different frequency (cm^{-1}) with different characteristic. The frequency and its characteristic of polydimethylsiloxane (PDMS) are shown in the Table 4.2 below.

Frequency (cm^{-1})	**Characteristic**
2905-2960 1020 1090	$-Si(CH_3)_2-O-Si(CH_3)_2$
2905-2960 1250 840 765	$Si(CH_3)_3$
2905-2960 1260 855 805	$Si(CH_3)_2$
2905-2960 1245-1275 760-845	$Si-CH_3$
2100 -2300 760-910	Si-H
3695 3200-3400 810-960	Si-OH
1590-1610 1410 990-1020 940-980	$Si-CH=CH_2$

Table 4.2: Infrared characteristic absorption of PDMS

Result from FTIR spectroscopy can be seen in the Figure 4.6-Figure 4.9. The figure shows that the frequency reading of each membrane merely same and some of the peaks have the same value and functional group.

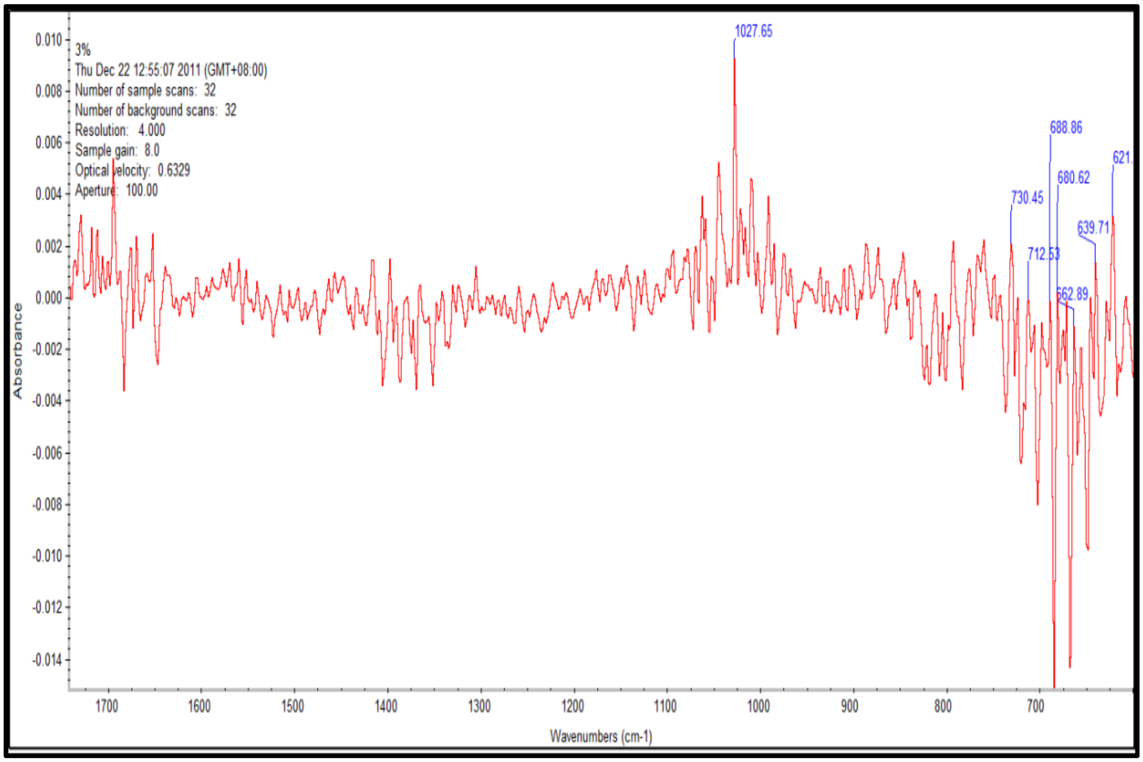


Figure 4.6.: Infrared spectrum of 3 wt. % PDMS membrane

Figure above displays the absorption peak for membrane with 3 wt% PDMS in the range of 600 cm^{-1} to 1700 cm^{-1}.The peak of 680 cm^{-1} and 688 cm^{-1} indicates the strong C-H bond deformation. The strong aromatic bond which is the strongest bond is shown with the frequency of 712 cm^{-1} and 730 cm^{-1}. Meanwhile, the 1027 cm^{-1} frequency is point to one of the infrared spectrum of PDMS which is the strong and broad Si-OR bond. Figure 4.7 below displays the infrared spectrum of membrane with 5 wt% of PDMS.

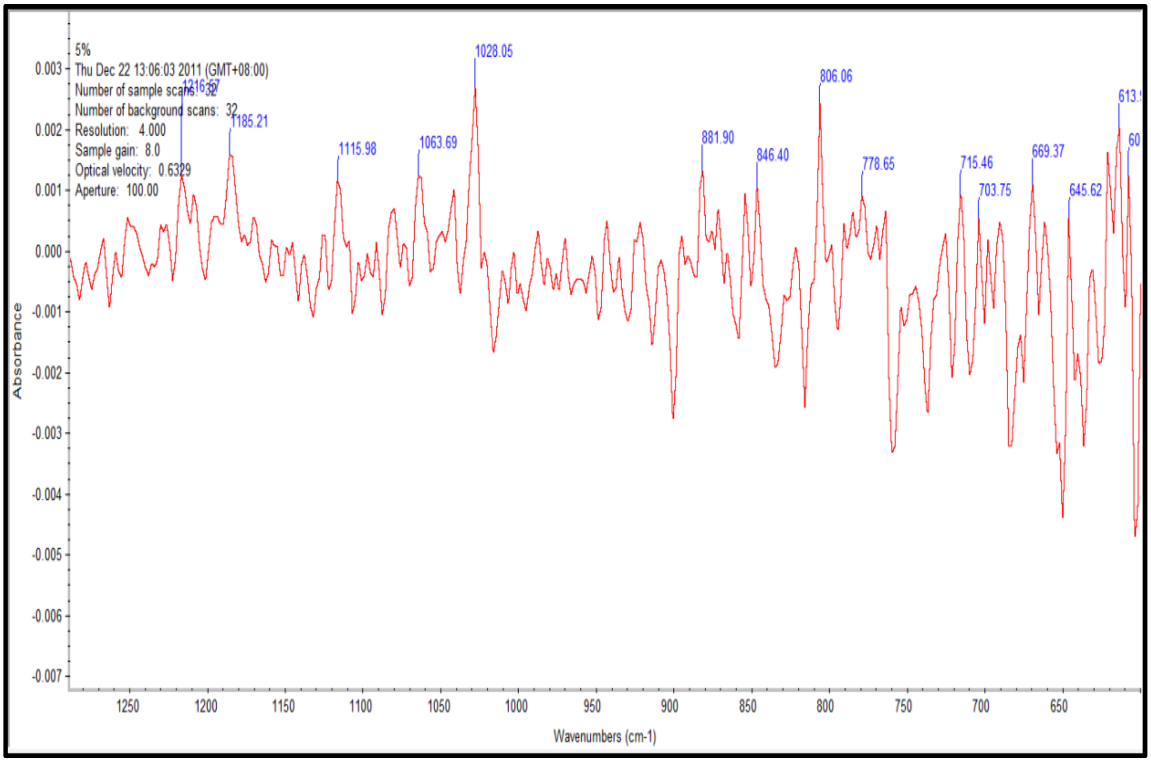


Figure 4.7.: Infrared spectrum of 5 wt. % PDMS membrane

In the figure above, the chemical bond of the membrane is investigated in the range of 600 cm^{-1} to 1300 cm^{-1}. The strong aromatic bond also can be point out from the frequency of 613, 646, 669 and 703 cm^{-1}. The 778, 806 and 846 $^{cm-1}$ frequencies indicate the strong Si-CH_3 bond and 881 cm^{-1} frequency indicate the strong Si-OH bond. The strong and broad Si-OR bond is point out from the frequency of 1063 cm^{-1}. For membrane with 8 wt% of PDMS, the analysis is shown in the Figure 4.8 below.

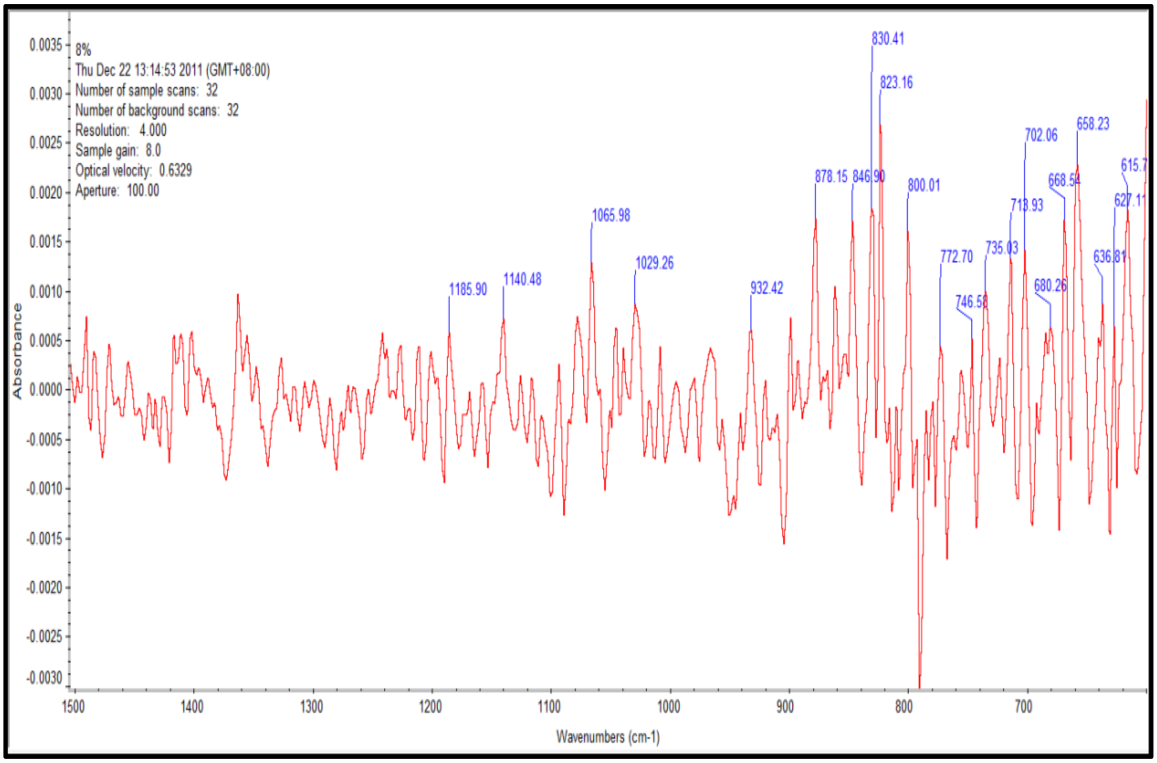


Figure 4.8.: Infrared spectrum of 8 wt. % PDMS membrane

The chemical bond analysis for this membrane is in the range of 600 cm^{-1} to 1500 cm^{-1}. Like the other membranes, this membrane also shows the strong C-H bonding in the frequency of 615 cm^{-1}, 627 cm^{-1}, 636 cm^{-1}, 668 cm^{-1} and 680 cm^{-1}. The peak of 800 cm^{-1} is related to the strong S-OR ester bond from the sulphur class. Silicon bonding is point out from the membrane in the frequency of 1029 cm^{-1} and 1065 cm^{-1}. Strong O-C bond also form and is indicated from the peak of 1185 cm^{-1}. The analysis of the highest concentration of PDMS membrane is depicted in the Figure 4.9 below.

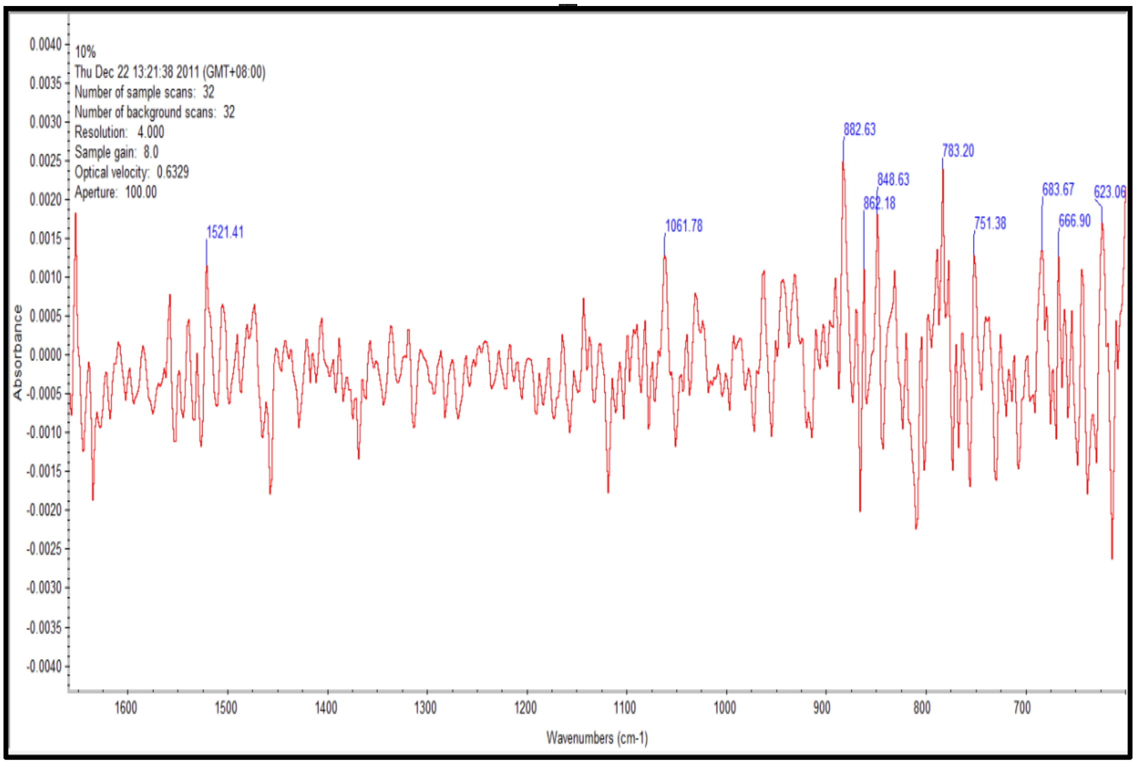


Figure 4.9.: Infrared spectrum of 10 wt. % PDMS membrane

The analysis shows that the strong bond of C-H is shows from the peak of 623 cm^{-1}, 666 cm^{-1} and 683 cm^{-1}. The 751 cm^{-1}, 783 cm^{-1}, 843 cm^{-1} and 882 cm^{-1} frequencies is related to the strong Si-OH bond from the silicon group. Silicon group with strong Si-OR bond is point out from the frequency of 1061 cm^{-1}. The CH_3 asymmetric deformation of Si-CH_3 is indicated from the frequency of 1621.

From the FTIR analysis, it can be conclude that four of the membranes have a strong C-H bond and aromatic bond. Silicon group infrared spectrum like strong Si-OH, Si-OR, Si-H and Si-CH_3 also indicated in the membrane. These strong bond that fomed in the membrane shows that the membrane produced is stable and high strengthness. The silicon bond perform in the membrane shows that the membrane has higer selectivity and permeabilty. So, the chemical bonding performed in the membrane based on the FTIR analysis is supporting the performance of the membrane shows in the permeation test.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Result and discussion from previous chapter will be summarized in this chapter. As we know, the performance of the membrane is depend on its permeability and selectivity. A good membrane must be high in permeability and selectivity. In this study, the thin film composite membrane based on PDMS/PVDF have been produced to separate CO_2/N_2. The characteristics of the membrane is characterize using SEM and FTIR and the performance of the membrane in term of permeability and selectivity is tested using permeation test. Based on the results, a number of conclusion can be made.

This study indicate that the membrane performance is vastly depend on the concentration of the coating layer, polydimethyl siloxane (PDMS). Membrane with the lowest concentration shows the highest permeablity while membrane in higest concentration shows the best selectivity. In term of permeability, the membrane shows the declining graph when the concentration increase. In contrast, increasing the coating concentration shows an escalation to the selectivity of CO_2/N_2.

It is also indicate that feed pressure applied is a significant parameters in tailoring the membrane performance in term of permeability and selectivity. At 2 bar feed pressure, the graph display an increasing result on the permeability and the selectivity of the membrane. Increment in feed pressure applied will enhance the permeability and selectivity of the membrane.

5.2 Recommendation

Some recommendations can be recommend here in order to improve the performance of the membrane in separation of CO_2/N_2.

1. This study only applied up to 2 bar feed pressure in the permeation test. So, the permeation test should be continued using higher pressure. Higher pressure normalized flux and selectivity can be predict with the higher pressure applied.
2. The permeation test also should continued by using gas mixture. Different results may be obtain since this study used only pure gas.
3. The performance of the membrane also can be improved by increasing the thickness of the membrane and the coating layer. Different in thickness may pronounced a different performance of the membrane.
4. Polymer concentration is a significant parameter for modifying the membrane in term of its structure and separation properties. So, decreasing the concentration of the support layer may results in higher permeances membrane.
5. The characterization of the membrane could be expande to include other technique like Atomic Force Microscopy (AFM) in order to imaging and measuring membrane stucture at the nanoscale.

REFERENCES

Naylor T. D, (1996). *Polymer Membranes- Materials, Structures and Separation Performance.* Shawbury, UK: iSmithers Rapra Publishing.

Wolframa Alpha, (2010). Chemical & GasesProperties (online). Retrieved from http://www.wolframalpha.com/entities/chemical_thermodynamic_properties/n-hexane/8f/kg/hu/. (20 August 2011)

Guy de Maupassant, 'The Horla' (1887). *Film Characterization Technique* (online). Retrieved from http://www.chm.bris.ac.uk/pt/diamond/stuthesis/chapter2.htm. (20 December 2011)

Eric Favre, Roda Bounaceur, Denis Roizard (2009). '*Biogas, membranes and carbon dioxide capture'*. Journal of Membrane Science, 328(2009), 11-14.

Eun-Sik Kim, Young Jo Kim, Qingsong Yu, Baolin Deng (2009), '*Preparation and characterization of polyamide thin-film composite (TFC) membranes on plasma-modified polyvinylidene fluoride (PVDF)*'. Journal of Membrane Science 344 (2009) 71–81.

Inge De Bo, Herman Van Langenhove, Peter Pruuost et al., (2003). '*Investigation of the permeability and selectivity of gases and volatile organic compounds for polydimethylsiloxane membranes'.* Journal of Membrane Science 215 (2003) 303–319.

Jiang, Xin; Ding, Jianfu; Kumar, Ashwani (2008) '*Polyurethane-poly(vinylidenefluoride) (PU-PVDF) thin film composite membranes for gas separation'*. Journal of Membrane Science, 323, 2, pp. 371-378, 2008.

Mathias Ulbricht (2007), '*Advanced functional polymer membranes'*. Journal of Polymer 47 (2006) 2217–2262.

M. Harasimowicz, P. Orluk, G. Zakrzewska-Trznadel, A.G. Chmielewski (2007) '*Application of polyimide membranes for biogas purification and enrichment'*. Journal of Hazardous Materials, 144 (2007), 698-702.

Q. Zhao, E. Leonhardt, C. MacConnell, C. Frear and S. Chen, '*Purification Technologies for Biogas Generated by Anaerobic Digestion'*. CSANR Research Report 2010 – 001.

S.P. Nunes and K.-V. Peinemann (2001). '*Gas Separation with Membranes'*. Journal of Membrane Technology in Chemical Industry, WILEY-VCH Verlag GmbH, D-69469 Weinheim (Federal Republic of Germany), 2001.

Shingjiang Jessie Lue*, Su Yu Wu, Shao Fan Wang, Li Ding Wang, Chen Luen Tsai (2008), '*Modeling multi-component vapor sorption in a poly(dimethyl siloxane) membrane*'. Jounal of Desalination 233 (2008) 286–294

Sirkar, Kamalesh K.(1997). *'Membrane Separation Technologies: Current Developments'*. Chemical Engineering Communications, 157: 1, 145 -184.

Xia Zhan, Jiding Li, Junqi Huang, Cuixian Chen (2008) *'Enhanced Pervaporation Performance of Multi-layer PDMS/PVDF Composite Membrane for Ethanol Recovery from Aqueous Solution'*. Journal of Applied Biochemistry and Biotechnology (2008), 160:632–642. doi: 10.1007/s12010-008-8510-y.

Yuting Shi, Charles M. Burns, Xianshe Feng (2006). *'Poly(dimethyl siloxane) thin film composite membranes for propylene separation from nitrogen.'*. Journal of Membrane Science 282 (2006) 115–123.

Sandra E. Kentish *et al.,* (2008). '*Carbon Dioxide Separation through Polymeric Membrane Systems for Flue Gas Applications'*. Recent Patents on Chemical Engineering, 2008, 1, 52-66.

Aizan *et al.,* (2006). *'Formation and Characterization of Mixed Matrix Composite Materials for Efficient Energy Gas Separation'.* Faculty of Chemical and Natural Resources, UMP. Vot no.: 75126.

Mulder, M. 2000. *Basic Principles of Membrane Technology (2nd Ed).* The
Netherlands: Kluwer Academic Publisher.

Nath, K.2008. *Membrane Separation Process*. New Delhi: Prentice-Hall of
India Private Limited

Nunes, S. P. and Peinemann, K. V. 2006. *Membrane Technology in theChemical Industry (2nd Ed).* Weinheim: WILEY-VCH Verlag Gmbh & Co. KGaA.

Pabby, A.K., Rizvi, S.S.H., and Sastre, A.M. 2009. *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications*. US: Taylor & Francis Group.

Park, H.B., Kim, Y.K., Lee, J.M., Lee, S.Y., Lee, Y.M. Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes . J Membr Sci 2004; 229: 117-27

Paul, D.R., and Yampol'skii Y.P. 1994. *Polymeric Gas Separation Membranes*. US: CRC Press. Inc. Porter, M. C. 1990. *Handbook of Industrial Membrane Technology*. United State: Noyes Publications.

Sharma Ranjan, (2009). '*Membrane Filtration'.* (online). Retrieved from www.(online). Retrieved from www.OzScientific.com. (23 August 2011).

Richardson, J.F., Harker, J.H. and Backhurst, J.R. (2002). *Coulson & Richardson's Chemical engineering (2nd Ed): Particle Technology & Separation Processes vol 2*. UK: Elservier.

Madaeni *et al.*, (2009). '*PDMS Coated Polyethersulphone Composite Membranes for Separation of Propylene and Nitrogen Gas Mixtures'*. Membrane Research Center, Chemical Engineering Department, Razi University, Kermanshah-67149, Iran. Iranian Polymer Journal 18 (11), 2009, 873-879

Bhagat *et al.*, (1991). *'A Novel, Self-Correcting Membrane Coating Technique'*. Pharmaceutical Research, Vol.8, No. 5, 1991.

Nurhana (2010). *'Effect of Different Types of Coagulation Medium on Asymmetric Polysulfone Membrane for* CO_2/CH_4 *Gas Separation'*. Faculty of Chemical & Natural Resources Engineering Universiti Malaysia Pahang.

Hullu *et al.*, (2008). *'Purification Technologies for Biogas Generated by Anaerobic Digestion'*. CSANR Research Report 2008-001. Climate Friendly Farming.

Chendake *et al.*, (2010). *Polymeric Gas Separation Membranes*. US: CRC Press. Inc. Porter, M. C. 1990. *Handbook of Industrial Membrane Technology*. United State: Noyes Publications.