PREPARATION AND PERMEABILITY STUDY OF POLYSULFONE MEMBRANE FOR CO2 SEPARATION

IDA NURYANI BINTI IBRAHIM

UNIVERSITI MALAYSIA PAHANG

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PREPARATION AND PERMEABILITY STUDY OF POLYSULFONE MEMBRANE FOR CO2 SEPARATION

IDA NURYANI BINTI IBRAHIM

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering

FACULTY OF CHEMICAL AND NATURAL RESOURCES ENGINEERING
UNIVERSITY MALAYSIA PAHANG

MARCH 2008

I declare that this thesis entitled "Preparation and Permeability Study of Polysulfone Membrane for CO2 Separation" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature: ....
Name: ....
Date: ....

To my beloved father and mother.

May Allah bless you.

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ABSTRACT

Polysulfone membrane is one of the potential candidates to be used as membranes for gas separation. With a nonporous and dense membrane structure, the membrane can be applied in a wide range of temperature and pressure. Polysulfone membrane was prepared by mixing a dope, where polysulfone (PSU) polymer was mixed with N, N-Dimetilacetamide (DMAc). Permeability of the membrane was examined by using the gas permeability unit available in the Gas Lab. Four membrane samples have been produce with different characteristics which were membrane A, membrane B, membrane C and membrane D namely. Membrane A is straight away immersed in water for ten second, membrane B was exposed in air and has an immersion time of 1 minute, membrane C was straightly immersed in water for one day while membrane D was exposed to air for one minute and immersed in water for a day. Measured permeability data in polysulfone (glassy polymer) was consistent with literature studies. In this regard, immersion time of membrane gave impact in membrane performance. This behavior was found from CO2 permeability value for membrane A was the lowest and the membrane D gave the highest permeability value. It showed that the permeability of membrane D was the best compared to the other 3 membranes with the permeability of membrane A, B, C and D was 0.0824, 0.0827, 0.0837 and 0.1015 cm/s.bar respectively. From the data and supported theories by various authors, it can be concluded that different immersion time gave impacts to the performance of polysulfone polymer membrane for CO2 separation.

ABSTRAK

Membran polisulfona ada salah satu membran yang sesuai digunakan sebagai membrane untuk proses pemisahan gas. Mempunyai struktur tepu dan bersifat tidak berongga membuatkan membran ini mampu beroperasi dalam pilihan suhu dan tekanan yang pelbagai. Daya penggerak untuk pemisahan gas adalah tekanan yang dikenakan ke atasnya. Kajian ini adalah untuk meningkatkan mutu kadar serapan partikel yang menembusinya. Membran polisulfona dihasilkan dengan satu proses dimana polimer polisulfona (PSU) disebatikan dengan N, N-Dimetilacetamide (DMAc). Kadar serapan membran diuji dengan set experiment di makmal. Empat membran yang mempunyai ciri-ciri yang berlainan telah dihasilkan iaitu membran A, membran B, membran C and membran D. Membran A tidak dibiarkan dalam udara dan terus direndam dalam air selama sepuluh saat, membran B biarkan dalam udara dan direndam dalam air selama seminit, membran C tidak dibiarkan dalam udara dan direndam dalam air selama sehari manakala membran D dibiarkan dalam udara selama seminit dan direndam dalam air selama sehari. Kajian ini telah membuktikan kadar serapan membran D adalah yang terbaik dibandingkan 3 membran lain dengan kadar serapan membran 0.1015 cm/s.bar. Daripada teori yang disokong oleh pelbagai penulis jurnal, maka dapat disimpulkan bahawa waktu rendaman membran dalam air juga memberi kesan kepada kadar serapan membran polisulfona untuk pemisahan gas.

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LIST OF NOMENCLATURE

Å - Angstrom

Jv - Volume Fluxes

P - Constant of Permeation

l - Thickness of Membrane

R - Retentate

µ - micro

MPa - Mega Pascal

kPa - kilopascal

cm - centimeter

J_i - The rate of transfer of component *i* or flux ($g/cm^2 \cdot s$)

$\frac{dc_i}{dx}$ - The concentration gradient of component *i*

D_i - The diffusion coefficient (cm^2/s) and is the measure of the mobility of the individual molecules

k - Solubility

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

P_{CO2} - Permeability of CO_2

D - Diffusivity

S - Selectivity

ΔP - Trans Membrane Pressure

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The application of membranes in gas separation problems has grown rapidly since the installation of the first industrial plants in the early 1980's. It has been used on a large commercial scale for years, and dramatic improvements in membrane permeability and process designs have been made during that time.

The main purposes on improving the membranes' permeability are to get constant quality upgrades to optimize membrane performance and systems for specific applications besides than to enhance troubleshooting. It is because hydrogen sulfide (H_2S), carbon dioxide (CO_2), mercaptans and other contaminants are often found in natural gas streams. H_2S is a highly toxic gas that is corrosive to carbon steels. CO_2 is also corrosive to equipment and reduces the heating value of gas.

Membranes are reliable and cost effective process solution for CO_2 removal across a wide range of operating conditions. The technologies are reviewed and process parameters have been identified. This efficient and effective process could remove contaminants such as carbon dioxide and hydrogen sulfide by chemical reaction so the gas is suitable for transportation and use.

Carbon dioxide removal natural gas has been practiced using polysulfone membranes. Introduction of more selective and higher flux membranes has begun and, in time, is likely to make membrane processes more competitive with amine absorption which is applied widely in petrochemical and refinery growing applications.

Research on gas processing plants and membrane companies, the CO_2 gas was also being removed by a Benfield (hot potassium carbonate) process and remaining hydrocarbons where processed into sales gas. As production grew, the increase in CO_2 in the return gas was outpacing the Benfield plant's capabilities. To avoid a major capital expansion to the Benfield plant, emerging technologies such as CO_2 membrane separation of the produced gas have to be improved.

The new technology carried some risk initially. To keep cost and technology risks under control, the membrane for CO_2 removal have to be designed, built, own and operated. A major concern at the time was the economics associated with how long each membrane element would last.

This study summarizes the development of flat sheet polysulfone membrane for carbon dioxide separation and studies of CO_2 permeability of polysulfone membrane.

1.2 Problem Statement

CO_2 is corrosive to equipment. In petrochemical plants, CO_2 must be removed to prevent freezing in the low-temperature chillers. It also reduces the energy value of gas and need to be separated from the products. Besides, not many researches on differentiations of permeability value of polysulfone membrane at different immersion times have been done. Other than that, the study on the right preparation method of forming polysulfone membrane is very lack.

As production grew, the increase in CO_2 in natural gas production was outpacing the gas processing plants and membrane companies' capabilities. To avoid a major capital expansion to the plant, emerging technologies such as CO_2 membrane separation of the produced gas have to be improved. Therefore, in order to obtain a cost effective system, membrane with high retation of CO_2 has to be developed.

1.3 Objective of Study

The aims of this study are:-

- To prepare and produce flat sheet polysulfone membrane for CO_2 separation.

1.4 Scope of Study

Several scopes that have been outlined in order to achieve the objectives of this study are as follows:-

- Preparation and development of flat sheet polysulfone membrane for CO_2 separation.

- Permeability test on the produced polysulfone membrane at different immersion time.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Definition

A membrane, comes from Latin word, meaning skin, is regarded generally and macroscopically as a selective barrier between two phases. The membrane is an interphase between the two bulk phases. It is either a homogeneous phase or a heterogeneous collection of phases (Sakai, 1994).

Membranes can selectively separate components over a wide range of particle sizes and molecular weights, from macromolecular materials to monovalents ions (Mattsuura, 1994). The membrane is the important element of every membrane separation process and it can be considered as a perm selective barrier of interface between two phases (Dorgan, 1992).

Membrane separation involves the ability of a membrane to control the permeation rate of a chemical species passing through the membrane. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other component (Baker, 2004).

The particle which is bigger than the other particle in a solution will be blocked and the smaller particle will pass through the membrane which is called permeate. The bigger particle, which blocked by the membrane are called rejection or retentate. The basic principle of membrane separation process is shown in Figure 2.1 (Geankoplis, 2003).

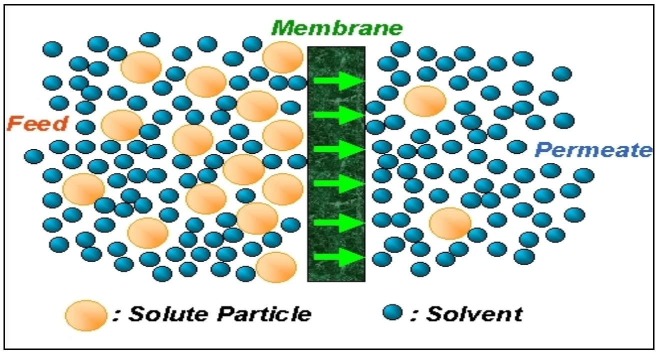


Figure 2.1 Basic Principle of Membrane Separation

2.2 Concept of Membrane Separation

The membrane has the ability to transport one component more readily than the other because of differences in physical or chemical properties between the membrane and the permeating components. The movements of those components across the membrane need a driving force. Figure 2.2 is a schematic diagram showing membrane separation (Dorgan, 1992).

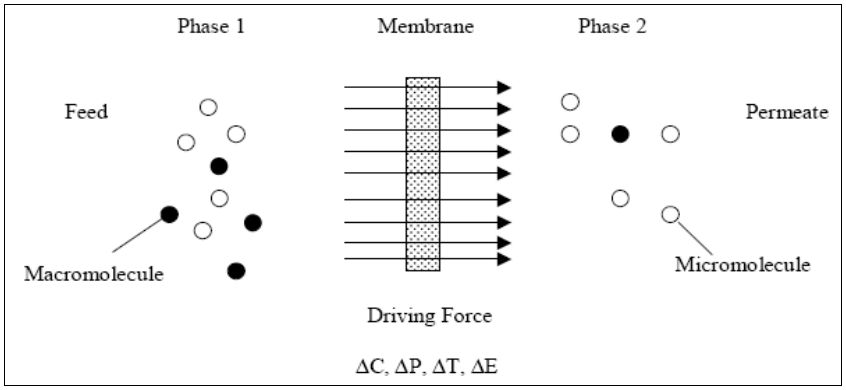


Figure 2.2 Schematic Representation of a Two-Phase System Separated by a Membrane (Setford, 1995)

Phase 1 is usually considered as the feed or upstream side while phase 2 is considered as the permeate or downstream side. Both of the phases could be any combination of miscible or immiscible liquid phases and gaseous phases. Separation occurs due to the ability of membrane to transport one or more selected component from the feed mixture to permeate. The membrane might be thin but does not allow direct contact between the two bulk phases. All these membrane processes are developed individually and used in different industrial field. The development of membrane industries is still expanding in order to fulfill the current needs (Scott, 1998).

There are two factors that determine the performance of a membrane separation process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor. Productivity is expressed as a parameter called flux (expressed by the unit $l/m^2 \cdot h$). Selectivity and productivity is membrane-dependent (Baker, 2004).

Membrane separation processes can be classified into the following groups according to the driving force that causes the flow of the permeate through the membrane (Matsuura, 1994). Table 2.1 illustrates the classification of membrane processes**.**

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

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

2.3 Principle Types of Membranes

The principle types of membrane are shown schematically in Figure 2.3 and are described briefly below. Polymeric membranes can be classified into two main groups according to its morphology, asymmetric and symmetric types.

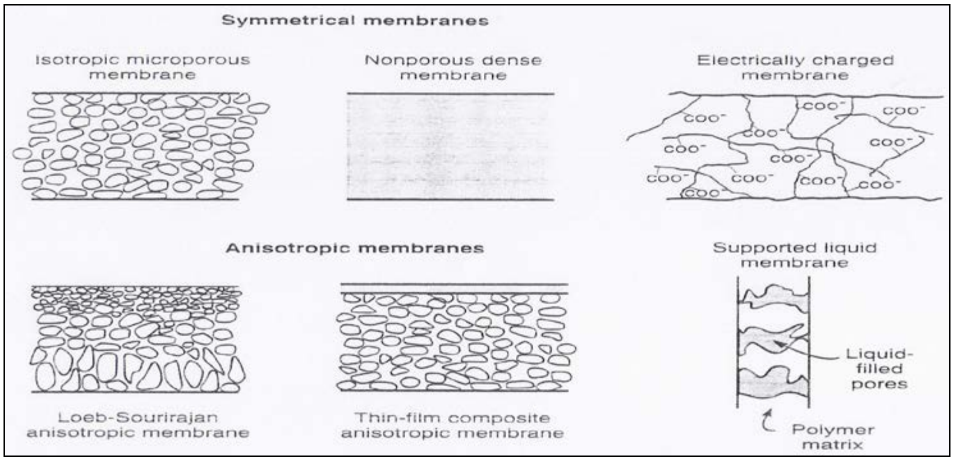


Figure 2.3 Schematic Diagrams of the Principle Type of Membranes (Baker, 2004)

2.3.1 Symmetric Membrane

Symmetric membranes (porous or non porous) have a thickness range from 10 to 200 μm. The diameter of pores is almost constant. The entire membrane thickness acts as a selective barrier, which means the resistances of mass transfer are determined by the whole membrane. A decrease in membrane thickness results in an increased permeation rate (Matsuura, 1994).

2.3.1.1 Microporous Membrane

A microporous membrane is very similar in structure and function to a conventional filter. It has a rigid, highly voided structure with randomly distributed, interconnected pores. However, these pores differ from those in a conventional filter by being extremely small, on the order of 0.01 to 10 µm in diameter.

Separation of solutes by microporous membranes is mainly a function of molecular size and pore size distribution. In general, only molecules that differ considerably in size can be separated effectively by microporous membranes, for example, for ultrafiltration and microfiltration.

All particles larger than the largest pores are completely rejected by membrane. Particles that are smaller than the largest pores, but larger than the smallest pores are partially rejected, according to the pore size distribution of the membrane. Particles that is much smaller than the smallest pores will pass through the membrane (Geankoplis, 2003).

2.3.1.2 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 (Geankoplis, 2003).

2.3.1.3 Electrically Charged Membranes

Electrically charged membranes can be dense or microporous, but are almost commonly very finely microporous, 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 anion 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. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis (Geankoplis, 2003).

2.3.2 Asymmetric Membranes

Asymmetric which is also known as anisotropic membranes consist of an extremely thin surface layer, supported on a much thicker, porous structure. The surface layer and its substructure may be formed in a single operation or separately. The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; the membrane should be as thin as possible. Conventional film fabrication technology limits manufacturer of mechanically strong, defect free films to about 20 μm thickness. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such membranes (Scott, 1998).

Asymmetric membranes are layered structures in which the porosity, pore size, or even membrane composition change from the top to the bottom surface of membrane. It has thin, selective layer supported on a much thicker, highly permeable microporous substrate. Because the selective layer is very thin, membrane fluxes are high (Geankoplis, 2003).

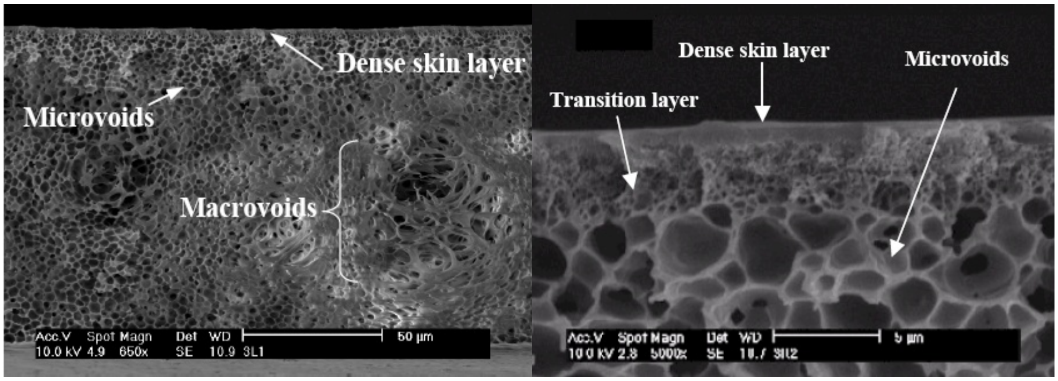


Figure 2.4 Scanning Electron Photomicrographs of a Flat Sheet Polysulfone Asymmetric Membrane Magnification of 650 and 5000 (Ng *et al.*)

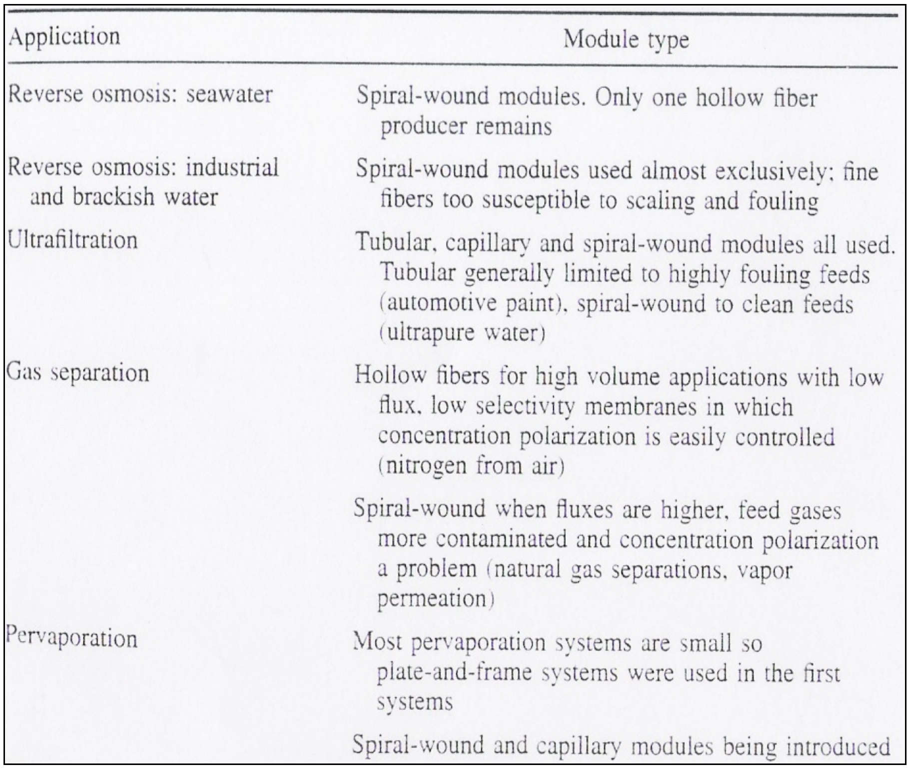
2.3.2.1 Ceramic, Metal and Liquid Membranes

Membrane materials are organic polymers and, in fact, the vast majority of membranes used commercially are polymer based. Ceramic membranes, a special class of microporous membranes, are used in ultrafiltration and microfiltration applications for which solvent resistance and thermal ability are required. Dense metal membranes particularly palladium membranes, is considered for the separation in gas mixtures (Geankoplis, 2003).

2.4 Membrane Modules

Gas separation membranes are manufactured in one of two forms: flat sheet or hollow fiber. The flat sheets are typically combined into a spiral-wound module, and the hollow fibers are combined into a bundle similar to tubular modules (Dortmundt and Doshi). The types of modules generally used in some of the major membrane processes are listed in Table 2.2.

Table 2.2 Module designs Most Commonly Used in the Major Membrane Separation Processes (Baker, 2004)



Application	Module type
Reverse osmosis: seawater	Spiral-wound modules. Only one hollow fiber producer remains
Reverse osmosis: industrial and brackish water	Spiral-wound modules used almost exclusively; fine fibers too susceptible to scaling and fouling
Ultrafiltration	Tubular, capillary and spiral-wound modules all used. Tubular generally limited to highly fouling feeds (automotive paint), spiral-wound to clean feeds (ultrapure water)
Gas separation	Hollow fibers for high volume applications with low flux, low selectivity membranes in which concentration polarization is easily controlled (nitrogen from air)
	Spiral-wound when fluxes are higher, feed gases more contaminated and concentration polarization a problem (natural gas separations, vapor permeation)
Pervaporation	Most pervaporation systems are small so plate-and-frame systems were used in the first systems
	Spiral-wound and capillary modules being introduced

2.4.1 Flat Sheet Modules

2.4.1.1Plate-And-Frame Modules

Plate-and-frame modules were one of the earliest types of membrane system. Figure 2.5 shows the early plate-and-frame designed by Stern et al. for the separation of helium from natural gas (Baker, 2004).

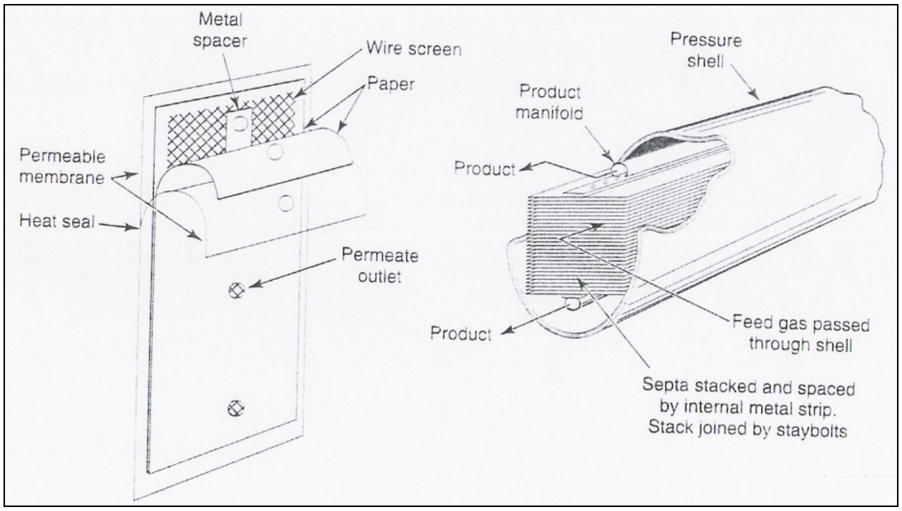


Figure 2.5 Early Plate-And-Frame Designed By Stern *et al.* for the Separation of Helium from Natural Gas (Baker, 2004)

Membrane, speed spacers, and product spacers are layered together between two end plates. The feed mixture is forced across the surface of the membrane. A portion passes through the membrane, enters the permeate channel, and makes its way to a central permeate collection manifold. Plate-and-frame units have been developed for some small-scale application, but these units are expensive compared to the alternatives. Figure 2.6 shows the schematic of a plate-and-frame module. Plate-and-frame modules provide good flow control on both the permeate and the feed side of the membrane, but the large number of spacer plates and seals lead to high module costs. The feed solution is directed across each plate in series. Permeate enters the membrane envelope and is collected trough the central permeate collection channel (Baker, 2004).

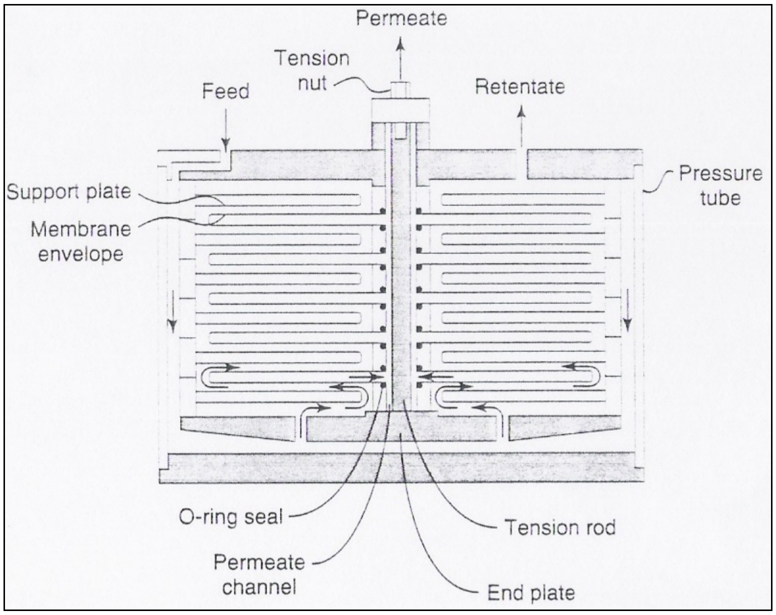


Figure 2.6 Schematic of a Plate-And-Frame Module (Baker, 2004)

2.4.1.2 Spiral Wound

Spiral wound modules were used and fully developed for industrial membrane separations. The design shown in Figure 2.7 is the simplest, consisting of a membrane envelope of spacers and membrane wound around a central collection tube; the module is placed inside a tubular pressure vessel. Feed passes axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals towards the center and exits through the collection tube. (Baker, 2004)

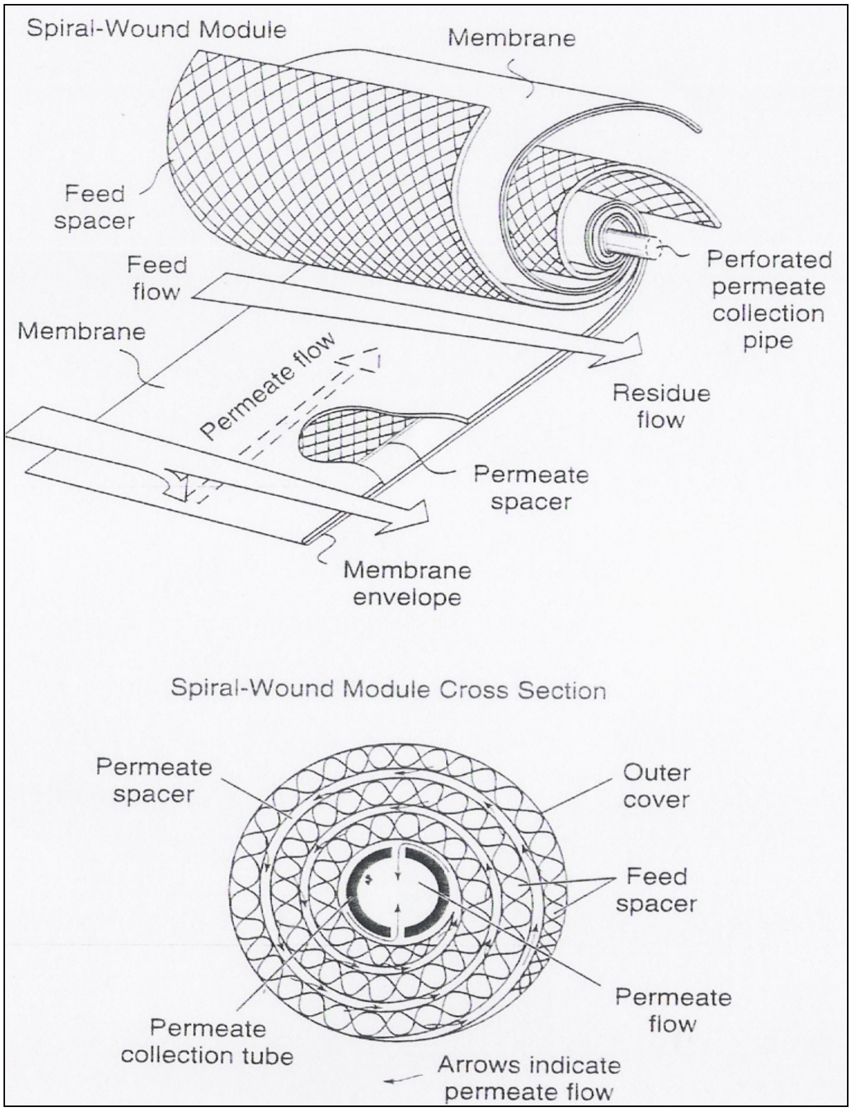


Figure 2.7 Exploded View and Cross-Section Drawings of a Spiral-Wound Module (Baker, 2004)

Feed solution passes through the membrane and enters the membrane where it spirals inward to the central collection pipe. One solution enters the module (the feed) and two solutions leave the residue and permeate. Spiral-wound modules are the most common module design for reverse osmosis and ultrafiltration as well as for high-pressure gas separation applications in the natural gas industry.

Small laboratory spiral-wound modules consist of a single membrane envelope wrapped around the collection tube. The membrane area of these modules is typically 0.2 to 1.0 m^2.

Industrial-scale modules contain several membrane envelopes, each with an area 1-2 m^2, wrapped around the central collection pipe. The multi-envelope design developed at Gulf General Atomic by Bray *et al* is illustrated in Figure 2.8. Multi-envelope designs minimize the pressure drop encountered by the permeate fluid travelling towards the central pipe. By using multiple short envelopes, the pressure drop in any one envelope is kept at a manageable level (Baker, 2004).

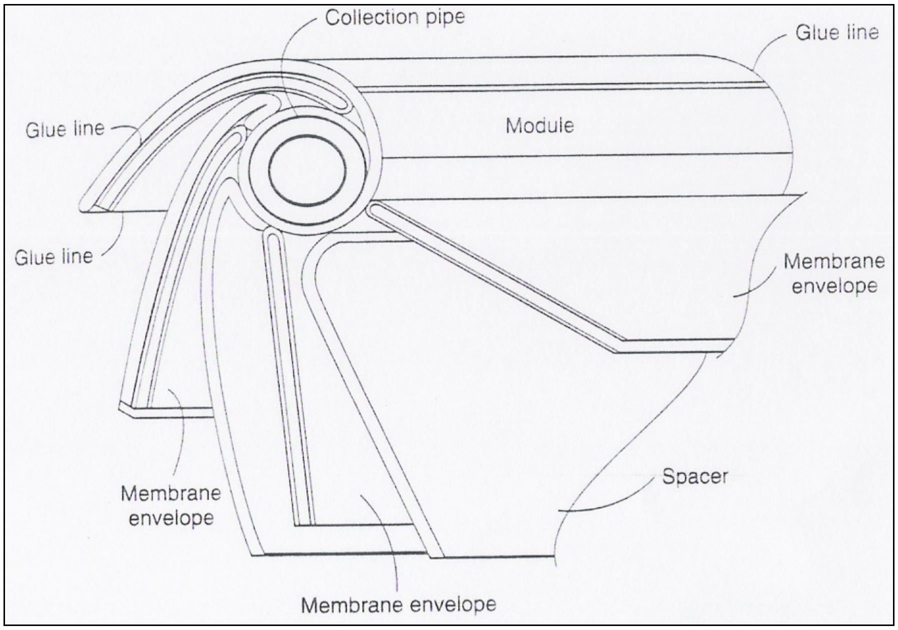


Figure 2.8 Multi-Envelope Spiral-Wound Module, Used to Avoid Excessive Pressure Drops on the Permeate Side of the Membrane. Large Diameter Modules May Have as many as 30 Membrane Envelopes, Each with a Membrane Area of 1-2 m^2 (Baker, 2004)

2.4.2 Hollow Fiber Modules

The schematic of the principle types of hollow fiber membranes are illustrated in Figure 2.9. Fibers of 50- to 200-µm diameter are usually called hollow fine fibers. Such fibers can withstand very hydrostatic pressure applied from the outside, so they are used in high-pressure gas separation or reverse osmosis. When the diameter is greater than 200-500 µm, the technique is used for low-pressure gas separations or ultrafiltration. Fibers with a diameter greater than 500 µm are called capillary fibers.

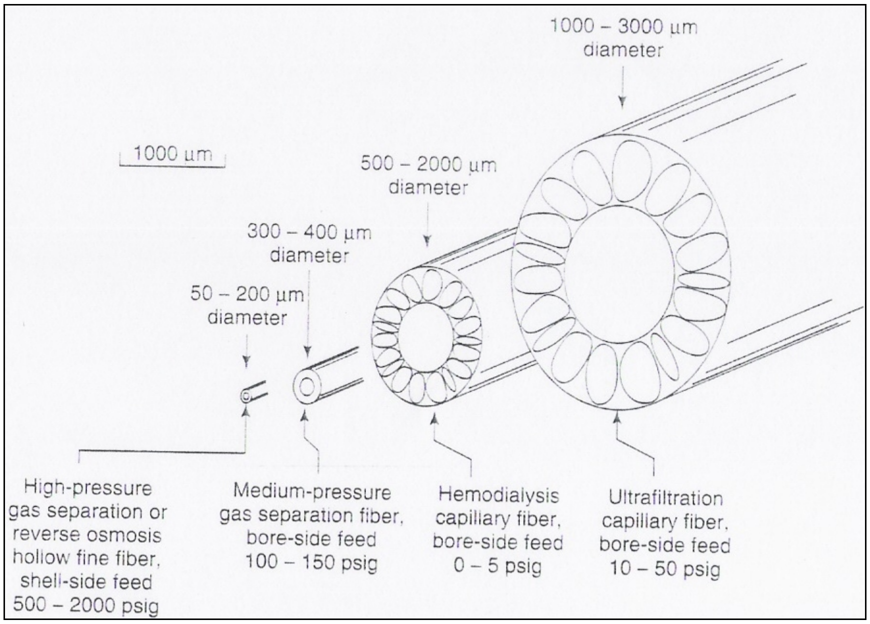
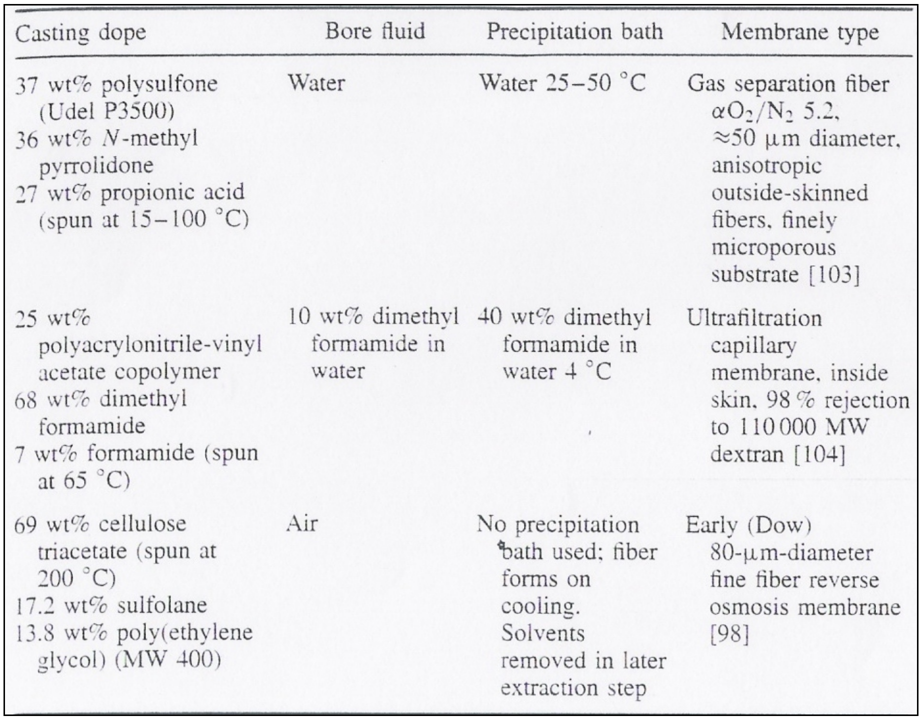


Figure 2.9 Schematic of the Principle Types of Hollow Fiber Membranes (Baker, 2004)

Hollow fiber membranes must be able not only to perform the separation but also to withstand the applied pressure of the process without collapsing. It has a higher polymer concentration and is more viscous than the casting solutions used to form equivalent flat sheet membranes which cause greater thickness of the hollow fiber membranes’ skin layer and usually result lower fluxes. The low cost of producing a large membrane area in hollow fiber form compensates for the poorer performance. The important advantage of high membrane surface areas of hollow fiber membranes also have been offset by the lower fluxes compared to flat sheet membranes made from the same materials (Geankoplis, 2003). Hollow fiber preparation parameters varying over a wide range of applications are given in Table 2.3.

Table 2.3 Preparation Parameters for Various Hollow Fiber Membranes (Baker, 2004)



Casting dope	Bore fluid	Precipitation bath	Membrane type
37 wt% polysulfone (Udel P3500) 36 wt% *N*-methyl pyrrolidone 27 wt% propionic acid (spun at 15–100 °C)	Water	Water 25–50 °C	Gas separation fiber $\alpha O_2/N_2$ 5.2, ≈50 μm diameter, anisotropic outside-skinned fibers, finely microporous substrate [103]
25 wt% polyacrylonitrile-vinyl acetate copolymer 68 wt% dimethyl formamide 7 wt% formamide (spun at 65 °C)	10 wt% dimethyl formamide in water	40 wt% dimethyl formamide in water 4 °C	Ultrafiltration capillary membrane, inside skin, 98 % rejection to 110 000 MW dextran [104]
69 wt% cellulose triacetate (spun at 200 °C) 17.2 wt% sulfolane 13.8 wt% poly(ethylene glycol) (MW 400)	Air	No precipitation bath used; fiber forms on cooling. Solvents removed in later extraction step	Early (Dow) 80-μm-diameter fine fiber reverse osmosis membrane [98]

2.4.2.1 Tubular Modules

Tubular modules are now generally limited to ultrafiltration applications, for which the benefit of resistance to membrane fouling due to good fluid hydrodynamics outweighs their high cost. Typically, the tubes consist of a porous paper or fiberglass support with the membrane formed on the inside of the inside of the tubes, as shown in Figure 2.10. It is then nested inside a plastic or steel support tube. In the past, each plastic housing contained a single 2- to 3-cm-diameter tube. More recently, as many as five to seven smaller tubes, each 0.5- to 1.0-cm-diameter, nested inside single larger tube (Geankoplis, 2003).

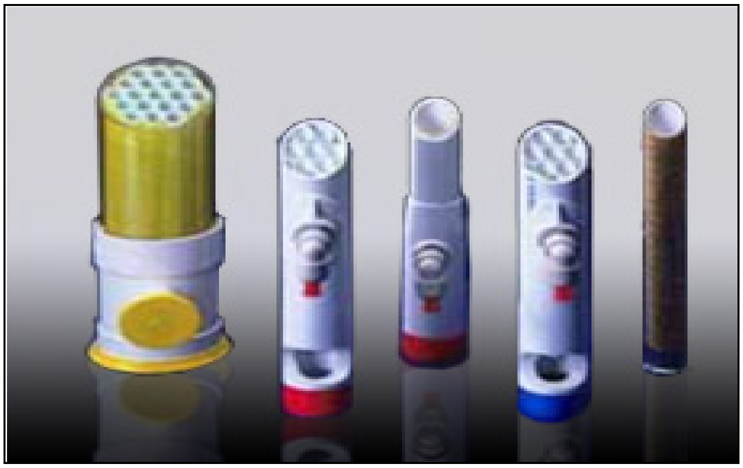


Figure 2.10 Typical Tubular Ultrafiltration module Design (Courtesy of Koch Membrane Systems)

In a typical tubular membrane system a large number of tubes are manifolded in series. The permeate is removed from each tube and sent to a permeate collection header. A drawing of 30-tube system is shown in Figure 2.11. The feed solution is pumped through all 30 tubes connected in series (Baker, 2004).

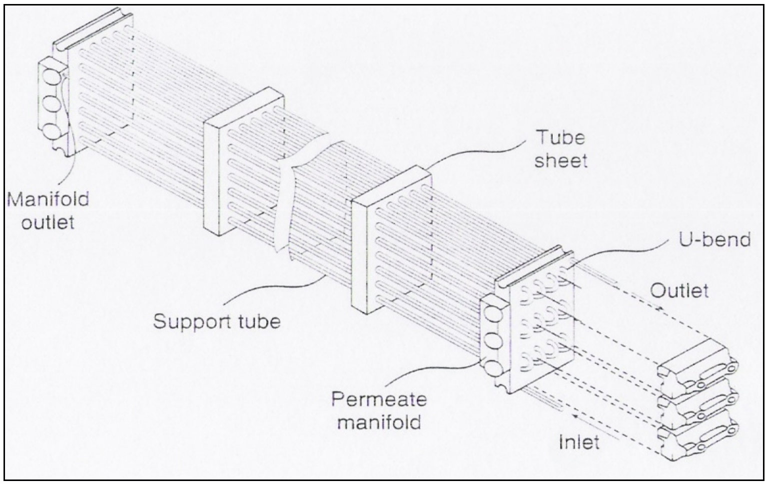


Figure 2.11 Exploded view of a tubular ultrafiltration system in which 30 tubes are connected in series (Baker, 2004)

2.5 Advantages and Disadvantages of Membrane Technology

2.5.1 Advantages

The technology of membrane separation has been developing to be the top of gas separation. It is because there are a lot of advantages by using membrane for separation. The advantages of membrane are:

a) Save energy

The separation of membrane is used for saving energy because it is no change phases happen during the separation process. As we know, the change phase's process needs more and extra energy. So, in separation process using membrane, the energy can be saved and it seems to be more economical to be used by industrial.

b) Easy to operate

The separation process of membrane do not use large or complex machine, which have to move from a part of plant to another part of plant. It only consist some instrument that is very easy to handle and operate. This process can be use continuously.

c) Keep the product quality

The separation process by using membrane can be operating in room temperature. Thus, it no needs to increase or decrease the temperature during separation process. It is suitable for separate the product that will change easily with the changing of temperature. From that, it can keep the product quality. Membranes can also be "tailor-made" so that their properties can be adjusted to a specific separation task or based on costumer's need.

d) Environment friendly

This separation process of membrane is the technology, which not polluted the environment. In this process, the pH of solution or product will not change because it does not use any chemical matter. That means, it will not effect to the environment and some process, separation product can be reused.

e) Save operation cost and place

The separation process of membrane is only using small instrument that is low cost and only need some place.

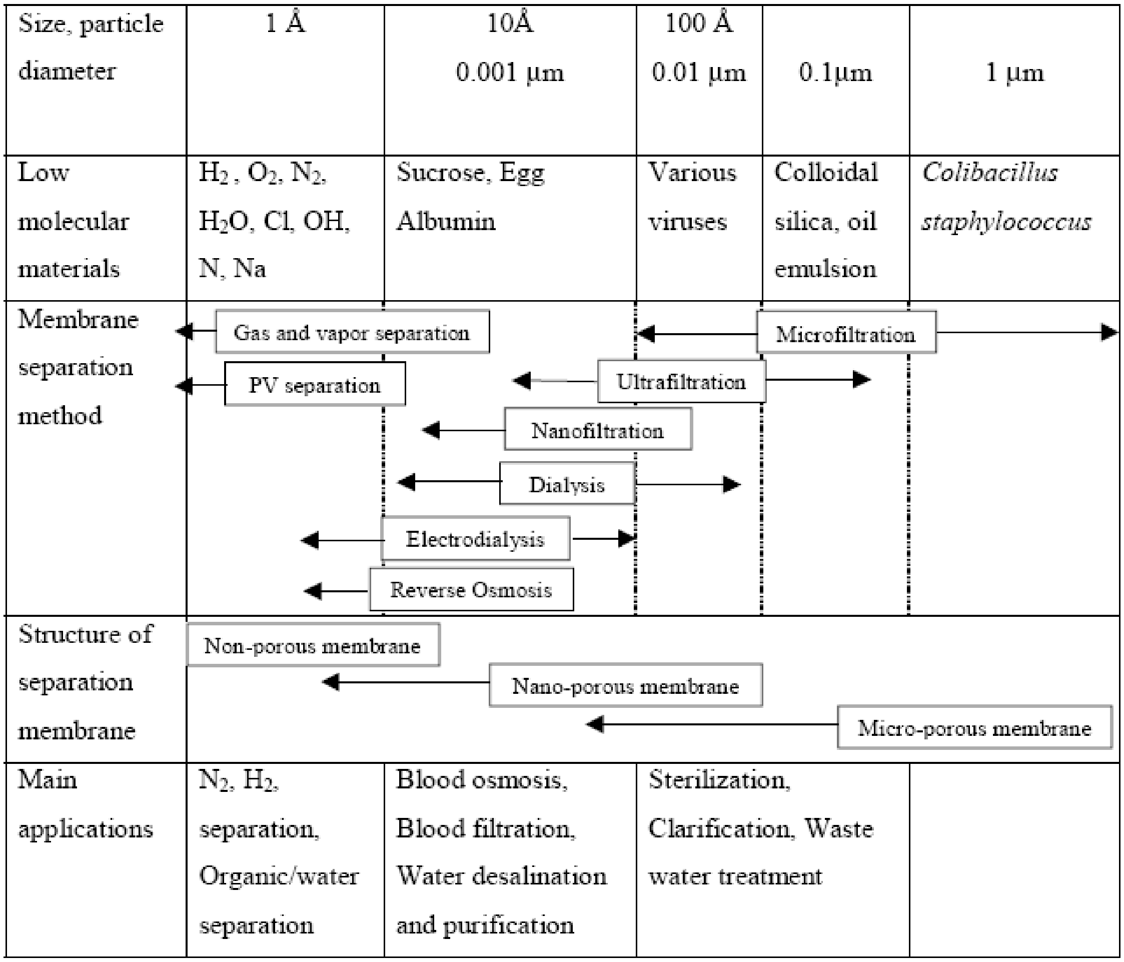
2.5.2 Disadvantages

The technology of membrane filtration cannot be used for long term because the membrane fouling will block the pores of membrane. Thus, it must be clean in short term to avoid clog.

2.6 Membrane Processes

Generally, there are five major membrane separation processes. They are reverse osmosis separation, ultrafiltration, microfiltration, pervaporation, and gas separation membrane technology. All these membrane processes are developed individually and used in different industrial field. The development of membrane industries is still expanding in order to fulfill the current needs. Table 2.4 shown below is the overview of membrane separation technology (Scott, 1998).

Table 2.4 Overview of Membrane Separation Technology (Scott, 1998)



Size, particle diameter	1 Å	10Å 0.001 µm	100 Å 0.01 µm	0.1µm	1 µm
Low molecular materials	H_2, O_2, N_2, H_2O, Cl, OH, N, Na	Sucrose, Egg Albumin	Various viruses	Colloidal silica, oil emulsion	*Colibacillus staphylococcus*
Membrane separation method	Gas and vapor separation PV separation	Nanofiltration Dialysis Electrodialysis Reverse Osmosis	Ultrafiltration	Microfiltration	
Structure of separation membrane	Non-porous membrane	Nano-porous membrane		Micro-porous membrane	
Main applications	N_2, H_2, separation, Organic/water separation	Blood osmosis, Blood filtration, Water desalination and purification	Sterilization, Clarification, Waste water treatment		

2.7 Overview of CO_2 Separation

Carbon dioxide, which falls into the category of acid gases (as does hydrogen sulfide, for example) is commonly found in natural gas streams at levels as high as 80%. In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO_2 must be removed to prevent freezing in the low-temperature chillers.

A wide variety of acid gas removal technologies are available. They include absorption processes, such as the Benfield process (hot potassium carbonate solutions) and Amine process (formulated solvents); cryogenic processes; adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA) and membranes. Membranes are increasingly being selected for newer projects, especially for applications that have large flows, have high CO_2 contents, or are in remote locations (Dortmundt and Doshi).

2.8. Gas Separation

Gas separation has become a major industrial application of membrane technology only during the past 20 years, but the study of gas separation has a long history. Systematic studies began with Thomas Graham who, over a period of 20 years, measured the permeation rates of all the gases then known through every diaphragm. The separation plant, constructed in Knoxville, Tennessee, represented the first large-scale use of gas separation plant membranes and remained the world’s largest membrane separation plant for the next 40 years.

The development of high-flux membranes and large-surface-area membrane modules for reverse osmosis applications in the late 1960’s and early 1970’s provided the basis for modern membrane gas separation technology. The first company to establish a commercial presence was Mosanto, which launched its hydrogen-separating Prism ® membrane in 1980. By the mid 1980’s, Cynara, Separex and Grace Membrane Systems were producing membrane plants to remove carbon dioxide from methane in natural gas.

Gas separation membranes are used for a wide variety of other, smaller applications ranging from dehydration of air and natural gas to organic vapor removal from air and nitrogen streams. Application of the technology is expanding rapidly and further growth is likely to continue. Figure 2.12 shows a summary of the milestone of gas separation technology.

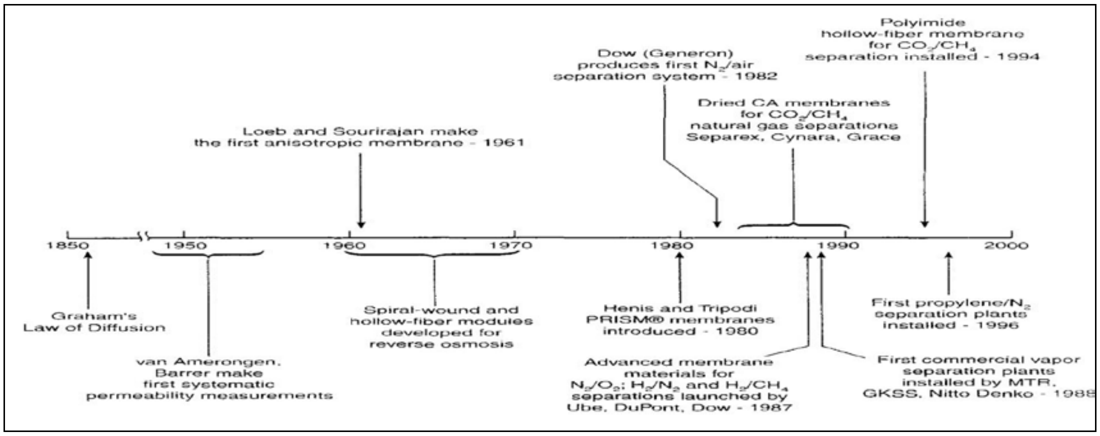


Figure 2.12 Milestone of Gas Separation Technology (Baker, 2004)

2.9 Types of Gas Separation Membrane

There are many types of gas separation membrane. Each of these types has different characteristics and use. Generally, there are three main types of gas separation membrane. These are Metal Membrane, Polymeric Membrane and Ceramic and Zeolite Membrane.

2.9.1 Polymeric Membrane

Most gas separation processes require that the selective membrane layer be extremely thin to achieve economical fluxes. Typical membrane thicknesses are less than 0.5 µm and often less than 0.1 µm.

Gas separation membranes are far more sensitive to minor defects, such as pinholes in the selective membrane layer, than membranes used in reverse osmosis or ultrafiltration. Even a single small membrane defect can dramatically decrease the selectivity of gas separation membranes, especially with relatively selective membranes such as those used to separate hydrogen from nitrogen.

The sensitivity of gas separation membranes to defects posed a serious problem to early developers. Generation of a few defects is very difficult to avoid during membrane preparation and module formation (Geankoplis, 2003).

2.9.2 Metal Membrane

Although almost all industrial gas separation processes use polymeric membranes, interest in metal membranes continues, mostly for the high-temperature membrane reactor applications and for the preparation of pure hydrogen for fuel cells. Hydrogen-permeable metal membranes are extra ordinarily selective, being extremely permeable to hydrogen but essentially impermeable to all other gases.

2.9.3 Ceramic and Zeolite Membrane

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

2.10 Membrane Preparation Method

Membrane can be prepared by various methods to form different variety of characteristics and properties. A significant step toward the efficient application of membrane was the development of asymmetric skin type membranes, which are capable of very high filtration rates, developed by Loeb and Sourirajan (1962). Various techniques to prepare membranes will result in different membrane structures. The membrane preparation method used in this study is discussed below.

2.10.1 Phase inversion technique

The most widely used method to produce asymmetric polymeric membrane is phase inversion technique. Phase inversion is a process whereby a polymer solution inverts into a swollen three-dimensional macro molecular complex or gel. It soon became apparent that asymmetric membrane can be prepared from almost any polymer that can be brought into a homogeneous solution by an appropriate solvent or solvent system and that can be precipitated from the solution in a continuous phase (So *et al.*, 1973). The usual method of phase inversion is to dissolve the polymer in a solvent solution, which may contain additives. This solution is spread directly onto a suitable inert support, such as glass.

The thickness casting membrane can typically vary from 50 to 500 μm (Scott, 1998). The cast film is then transferred to a non-solvent bath where exchange occurs between solvent and non-solvent, which lead to polymer precipitation. Many variables during membrane preparation have an influence on the resulting membrane structure and properties. The variables are related to the composition of the polymer solution and the composition of the coagulation bath (Bokhorst *et al*. 1981). Membranes produces under apparently identical conditions may vary appreciable in properties (Grethlein, 1973).

2.11 Phase Inversion Mechanism

Synthetic asymmetric skin type membrane was first developed by Loeb and Sourirajan (1962) from cellulose acetate for water desalination. Phase inversion method had been widely used to produce asymmetric membranes by immersed a casting film consisting polymer and solvent into a non-solvent coagulation bath. In order to understand the asymmetric membrane formation mechanism, it is convenient to analyze the membrane as a two-layer structure: the dense top layer and the porous sublayer (Young and Chen, 1991). The three components phase diagram of polymer-solvent-non solvent can conveniently be used as a tool to discuss the asymmetric membrane formation mechanism via phase inversion method. Figure 2.12 shows a basic schematic phase diagram of the ternary system and the precipitation pathway.

Once the casting film is immersed into the non-solvent coagulation bath, represented by point A, phase exchanges immediately occur. Solvent from the homogenous casting solution diffuses out into the coagulation bath rapidly, resulting the polymer concentration at the surface of the film increase (Strathmann and Kock, 1977; Bokhorst *et al*., 1981; Chuang *et al.*, 2000). The point B along the path is the concentration at which the first polymer precipitates. As the precipitation proceeds, more solvent is lost and large amount of polymer molecules aggregate at the surface of the film resulting a polymer rich phase occur. Consequently, cumulative of high polymer molecules produce a dense skin layer.

As soon as the skin layer has formed, the diffusion of solvent out of the layers beneath will be hindered. The skin thus becomes a barrier that delays the outflow of the solvent from membrane film into the coagulation bath. Here, membrane formation mechanism has reach into the liquid-liquid phase separation region, denoted as II in Figure 2.13. Thus, the non-solvent from the coagulation bath diffused through the top layer into the membrane film and the precipitation process continues (Chuang *et al*., 2000). The coagulant medium will cause a nucleus of polymer-poor phase that inducing the neighboring solvent to diffuse into it and the nucleus grow bigger becomes a space that consisting the solvent and non-solvent. This process continues and resulting the polymer concentration surrounding the nucleus space increase and thus until a stage that solidify to produce a permanent macrovoid space. This results the formation of porous sublayer in the asymmetric membrane.

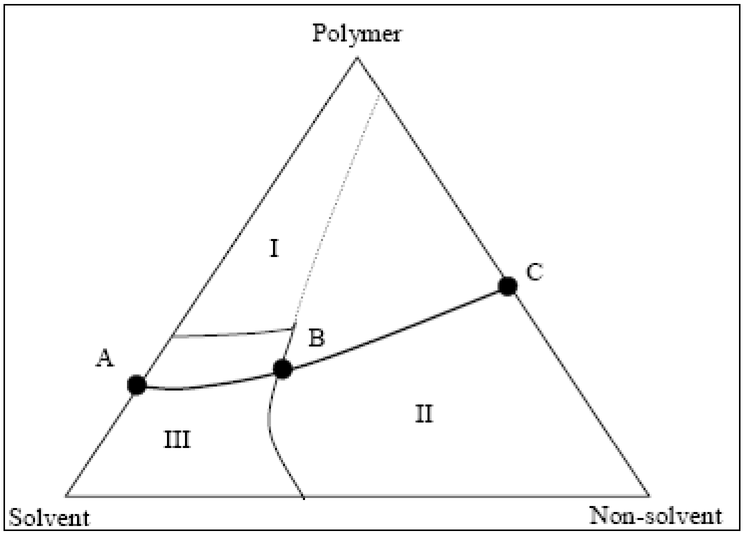
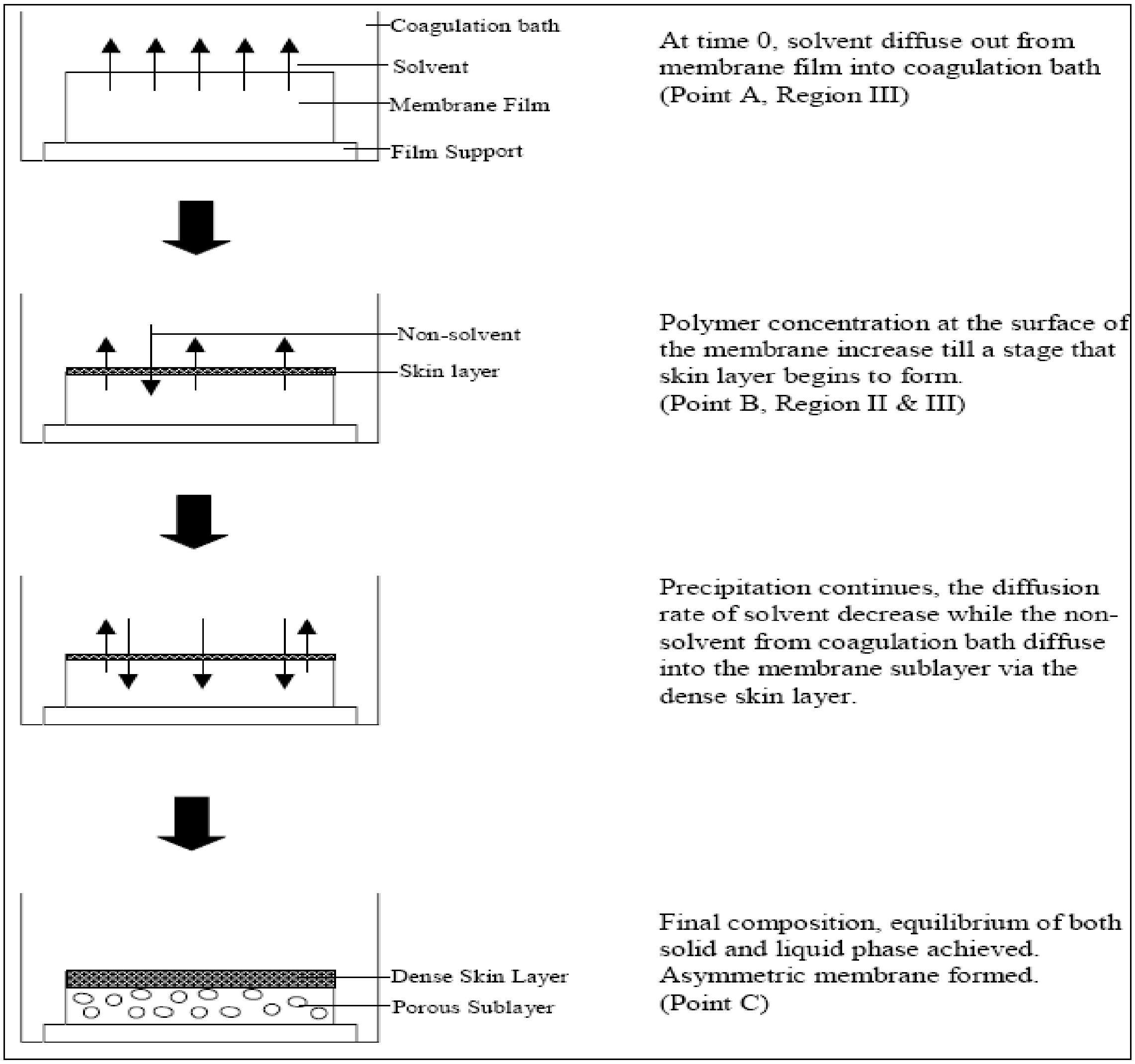


Figure 2.13 Schematic Ternary Phase Diagram Showing the Precipitation Pathway Of The Casting Solution during Membrane Formation; I Gelation Region, II Liquid Liquid Phase Separation Region and III Homogeneous Region

The precipitation continue till it reaches the point C, which is the two phase are in equilibrium, a solid (polymer-rich) phase that forms the membrane structure; liquid (polymer-poor) phase that constitutes the membrane pores filled with nonsolvent. Hence, asymmetric membrane with a dense top layer with porous sublayer was formed. Figure 2.14 briefly shows the phase inversion mechanism discussed (Strathmann and Kock, 1977; Bokhorst *et al.*, 1981; Chuang *et al.*, 2000).



At time 0, solvent diffuse out from membrane film into coagulation bath (Point A, Region III)

Polymer concentration at the surface of the membrane increase till a stage that skin layer begins to form.
(Point B, Region II & III)

Precipitation continues, the diffusion rate of solvent decrease while the non-solvent from coagulation bath diffuse into the membrane sublayer via the dense skin layer.

Final composition, equilibrium of both solid and liquid phase achieved. Asymmetric membrane formed.
(Point C)

Figure 2.14 Phase Inversion Mechanism Process for Different Points in the Casting Film at Different Stage

2.12 Gas Permeation

The most important property of membrane is their ability to control the rate of permeation of different species. They are the pore flow and solution diffusion model. The two models used to describe the mechanism of permeation are illustrated in Figure 2.15.

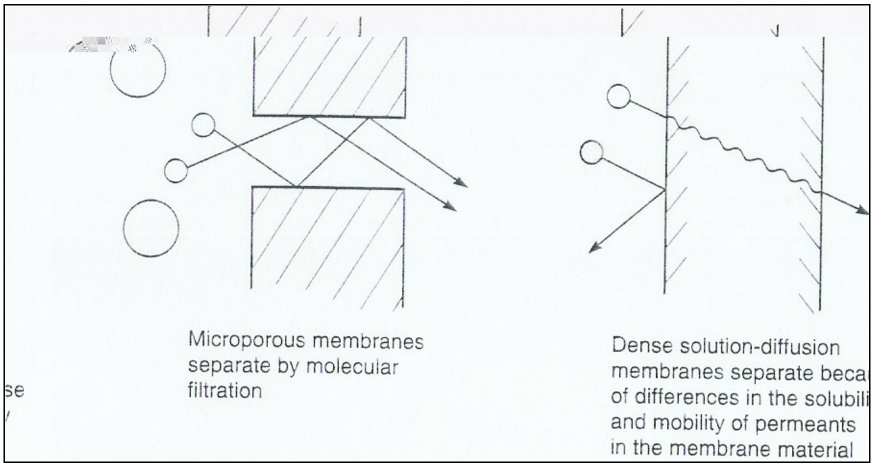


Figure 2.15 Molecular Transport through Membranes can be described by a Flow Through Permanent Pores or by the Solution-Diffusion Mechanism (Baker, 2004)

2.12.1 Pore Flow Model

In pore flow model, the permeants are transported by pressure driven convective flow through through tiny pores. Separation occurs because one of the permeants is excluded (filtered) from some of the pores in the membrane through which other permeants move.

2.12.2 Solution Diffusion Model

In solution-diffusion model, the permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient (from high to low concentration region). It is used to explain the transport of gases through polymeric films. Baker (2004) stated that the permeants are separated because of the differences in the solubility of the materials in the membrane and the differences in the rates at which the material diffuse through the membrane.

When two adjacent volume elements wit slightly different permeant concentrations are separated by an interface, simply because of the different in the number of molecules in each volume element, more molecules will move from the concentrated side to the less concentrated side of the interface than will move in the other direction. This concept was recognized by Fick theoretically and experimentally as the equation now is called Fick's law of diffusion, which states:-

$$\boxed{J_i = -D_i \frac{dc_i}{dx}} \tag{2.1}$$

where:-

J_i = the rate of transfer of component i or flux (g/cm^2•s)

$\frac{dc_i}{dx}$ = is the concentration gradient of component i.

D_i = the diffusion coefficient (cm^2/s) and is the measure of the mobility of the individual molecules.

The minus sign shows that the direction of diffusion is down the concentration gradient.

Integrating over the thickness then gives

$$\boxed{J_i = \frac{D_i\left(c_{io} - c_{il}\right)}{l}} \tag{2.2}$$

From above relationship, we can relate it to equation 2.3

$$\boxed{J = k \times D \times \Delta p / l} \tag{2.3}$$

where:-

J = flux

k = solubility

D = diffusion of the CO_2

Δp = difference of CO_2 and permeate low pressure between flow in phase and the filtrate, and l is the thickness of membrane.

2.13 General Groups of Membrane Transport Theory

Based on the solution-diffusion and the Pore Flow Model discussed above, membranes can be organized into three general groups and is briefly discussed below.

a) Ultrafiltration, microfiltration and microporous Knudsen-flow gas separation membranes are all clearly microporous, and transport occurs by pore flow.

b) Polymeric gas separation, reverse osmosis, and pervaporation membranes which have a dense polymer layer with no visible pores, in which separation occur. The fluxes of permeants through these membranes are much lower than through the microporous membranes. Transport is best described in solution-diffusion model.

c) Nanofiltration membranes which the membranes are intermediate between microporous and solution-diffusion membranes. It is an intermediate between ultrafiltration membranes and reverse osmosis membranes at which, these kinds of membranes have high rejections.

These three general groups are shown in Figure 2.16.

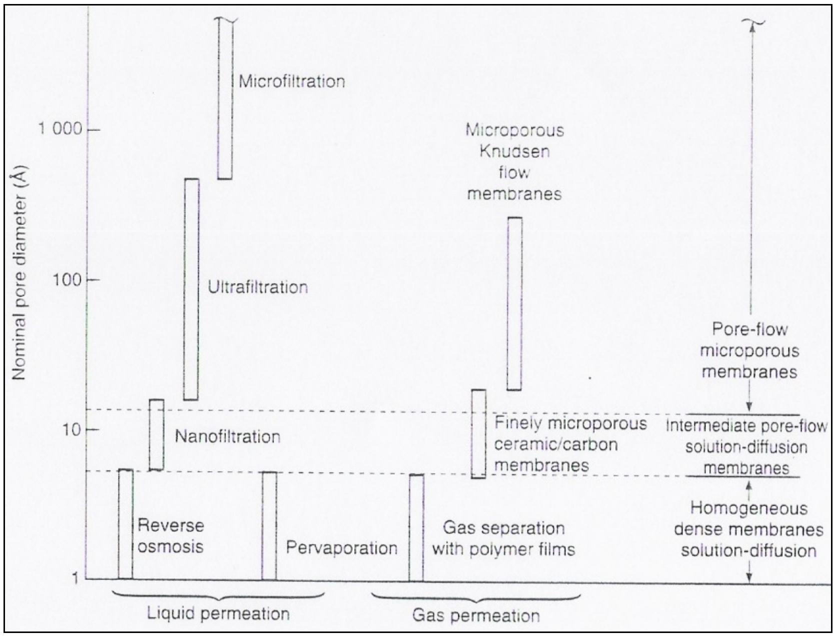


Figure 2.16 Schematic Representation of Theoretical Model for the Principle Membrane Transport Processes (Baker, 2004)

From the figure above, permeation through dense nonporous membranes is covered first; this includes permeation in gas separation membranes, reverse osmosis, and pervaporation membranes. Transport occurs by molecular diffusion and is described by the solution-diffusion model. The transport in microporous ultrafiltration and microfiltration membranes occurs by convective flow with some form of sieving mechanism producing the separation.

2.14 Mechanism of Gas Permeation

Both porous and dense membranes can be used as selective gas separation barriers. Figure 2.17 illustrates the mechanism of gas permeation. Three types of porous membranes differing in pore size are briefly explained below.

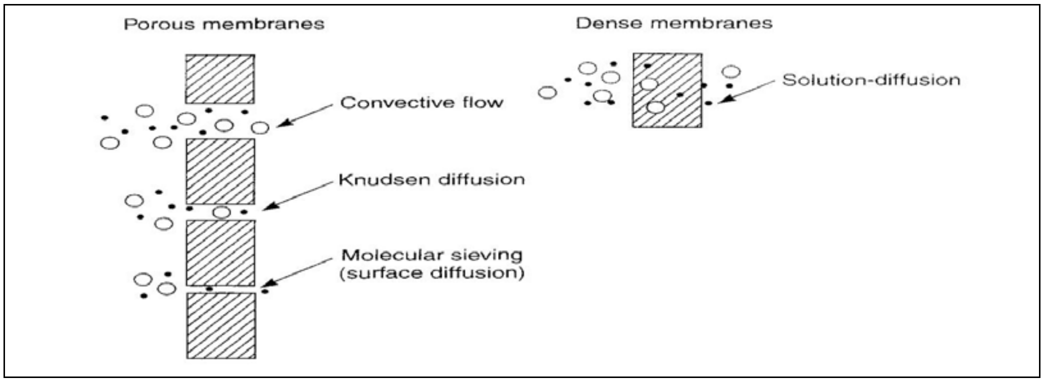


Figure 2.17 Mechanisms for Permeation of Gases through Porous and Dense Gas Separation Membranes (Baker, 2004)

If the pores are relatively large - from 0.1 to 10 µm – gases permeate the membrane by convective flow, and n separation occurs.

If the pores are smaller than 0.1 µm, then the pore diameter is the same size as or smaller than the mean free path of the gas molecules. Diffusion through such pore is governed by Knudsen diffusion, and the transport rate of any gas is inversely proportional to the square root of its molecular weight. This relationship is called Graham's Law of diffusion.

If the membrane pores are extremely small, of the order 5-20 Å, then gases are separated by molecular sieving. Transport through this type of membrane is complex and includes both diffusion in the gas phase and diffusion of adsorbed species on the surface of the pores which also know as surface diffusion (Geankoplis, 2003).

2.15 Definition of Parameters in Membrane Separation System

2.15.1 Fluxes

Volume fluxes can be defined as the volume of filtrate divided by the area of membrane and time. The relationship between pressure ratio and membrane selectivity can be derived from the Fick's Law expression as show below:-

$$\boxed{J = k \times D \times \Delta p / l} \qquad (2.3)$$

where:-

J = flux

k = solubility

D = diffusion of the CO_2

Δp = difference of CO_2 and permeate low pressure between flow in phase and the filtrate, and l is the thickness of membrane.

During the polar concentrate at the control range, fluxes will be influence by the concentrate of solute, liquid flow rate and temperature. The fluxes will be linear increasing with log concentrate of solute, and modified by polar controllable. Basically, each membrane will achieve the maximum flow rate at different pressure and interchange flow rate.

2.15.2 Permeability

Permeability is the flowrate of the supplied gas (CO_2) over the area of the membrane. The unit is cm/s. It can be related with equation 2.4:-

$$\boxed{P_{CO_2} = Q / A \bullet P} \qquad (2.4)$$

where:-

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

A = Area (cm^2)

P = Trans Membrane Pressure, TMP (bar)

2.15.3 Selectivity

Selectivity, is the ratio of the permeabilities of CO_2 to other components in the stream. This paramaeter has no unit. It can be related with the equation below:-

$$\boxed{Selectivity, S = \frac{P_{\mathrm{CO_2}}}{P_{\mathrm{CH_4}}}} \qquad (2.5)$$

2.16 Membrane Material Selection

2.16.1 Choice of Polymer

The ideal polymer is a tough, amorphorous, but not too brittle thermoplastic with a glass transition temperature more than 50 ^{0}C above the expected use temperature. A high molecular weight is important. Commercial polymers made for injection molding have molecular weights in the 30,000 to 40,000 Dalton range, but for solution precipitation, polymers with higher molecular weights are preferable. If the polymer is crystalline or a rigid glass the resulting membrane may be too brittle and will break if bent during handling. The polymer must also be soluble in a suitable water-miscible solvent. Polymers that meet these specifications include polysulfone, cellulose acetate, poly (vinylidine fluoride), polyetherimide and aromatic polyamides. So, in this study, polysulfone pellets are used as the polymer.

2.16.2 Choice of Casting Solution Solvent

Generally, the best casting solution solvents are aprotic solvents such as Dimethyl Formamide, N-Methyl Pyrrolidone and Dimethyl Acetamide. These solvents dissolve a wide variety of polymers, and casting solutions based on these solvents precipitate rapidly when immerse in water to give porous, very anisotropic membranes. Generally, polymer casting solution concentrations for gas separation and reverse osmosis membranes are higher than other membranes. So, in this study, Dimethyl Acetamide (DMAc) is used as the solvent.

2.16.3 Choice of Precipitation Medium

Water is the common solution used for precipitation medium. Organic solvent are particularly used to form hollow fiber membranes for which the mechanical and safety problems of handling an organic solvent precipitation bath is more easily controlled than in flat sheet casting. Organic-based solvent precipitation media such as methanol or isopropanol almost always precipitate the casting solution more slowly than water, and the resulting membranes are usually denser, less anisotropic and lower flux than membranes precipitated in water (Geankoplis, 2003). So, in this study, water is chosen as the precipitation medium.

2.17 Current R & D in Membrane for Gas Separation

The study findings in membrane for gas separation by various authors are shown in Table 2.5.

Table 2.5 Current R & D in Membrane for Gas Separation

No.	Author	Membrane / gas separation properties	Study findings
1.	Ettouney, and Majeed, JMS 135, 1997	Silicone rubber and polysulfone membrane CO_2, N_2, O_2, and CH_4	-Feed flow rates used are 3.33 x 10^{-5}, 6.67 x 10^{-5}, 1 x 10^{-4} and 1.33 x 10^{-4}. -The absolute pressures used in the experiment are 239.2, 377, 514.9, and 790.6 kPa. -The highest permeability is in CO_2 mixture, followed by the pure gas, and the lowest is found in the air gas mixture. -Permeability of the polysulfone membrane, faster species is reduced in mixtures with slower species (CO_2 against O_2, N_2, or CH_4) and (O_2 against N_2 or CH_4). -Permeability of species is only affected by presence of faster permeating species such as CO_2 or O_2. -P_{CO2} PSU = 1.1x 10^{-6} to 3.3x10^{-7}. -P_{CH4} PSU = 1.4 x 10^{-8} to 3.5x10^{-8}. -$S_{CO2/CH4}$ = 23 to 32.4.
2.	Xu *et al.*, JMS 202, 2002	-Advanced polymer membrane, pyromellitic dianhydride (PMDA)/ oxydianiline (ODA) polyimide (PI) memrbanesfilling with polystyrene (PS) and poly(styrene-4-vinylpyridine) (PSVP)- nanoparticles - CO_2/N_2, CO_2/CH_4 and O_2/N_2 (at	- Gas permeability coefficient, α and selectivity values for PI/PS-nanoparticle composite membranes decrease in diffusion selectivities. -PI/PSVP-nanoparticle composite membranes increase in gas permeabilities,P and selectivities when the PSVP – nanoparticles increase from 10 to 20wt% in the membranes, while the diffusion coefficients and diffusion selectivities show both decrease. - P_{CO2} for all the membranes = 0.86

		temperature of 35 ^{0}C and 10 atm)	(PI) to 6.55 (PI/25PSVP) -P_{CH4} for all the membranes = 0.018 (PI) to 2.19 (PI/25PSVP) - P_{CO2}/P_{CH4} for all the membranes = 0.083 (PI) to 0.85 (PI/25PSVP) - D_{CH4} for all the membranes = 0.013 (PI) to 0.73 (PI/25PS) - D_{CO2}/D_{CH4} for all the membranes = 1.04 to 10.8
3.	Wang and Kamiya, JMS 98, 1995	Polysulfone membrane / CO_2	-The sorption equilibrium obeys the dual-mode model. -The diffusion coefficient is concentration dependent and its temperature dependence can be well expressed by the Arrhenius equation. -the partial molar volume of CO_2 is smaller than in rubbery polymers and no appreciable temperature dependence in the range of 15-75 ^{0}C
4.	Xu *et al.*, JMS 205, 2002.	-Poly(arylene ether)s (PAEs), one containing the 2,6-bis(trifluoromethylphe-nylene)pyridine unit (6Fppy series) and the other, containing 2,5-bis(3-trifluoromethyl-phenylene)thiophene unit (6FPT series) in the polymer backbone. -H_2, CO_2, O_2, N_2, and CH_4 (measured using time-lag method at 1 atm and 35 ^{0}C)	The –CF_3 groups into the bisphenol unit increases the gas permeability and decreases the selectivity for both series of membranes. (consistent with the observed phenomenon for polyimide membranes) - The 6FPPy membranes show higher gas permeability coefficient than the 6FPT membranes and show similar selectivity. -The effect of temperature on the gas transport properties was measured between 30 - 75 ^{0}C and the activation energies for gas permeation and diffusion were calculated from Arrhenius calculation. - P_{CO2} 6FPT/6FBPA = 25.29 to 29.46, while in 6FPT/BPA = 18.53 to 21.44 - P_{CH4} 6FPT/6FBPA = 1.58 to 1.92, while in 6FPT/BPA = 1.41 to 1.78 - D_{CO2} 6FPT/6FBPA = 3.88 to 4.03, while in 6FPT/BPA =3.33 to 3.65 - D_{CH4} 6FPT/6FBPA= 1.12 to 1.27, while in 6FPT/BPA = 1.04 to 1.41 - Solubility, S_{CO2} 6FPT/6FBPA= 4.95

			to 5.56, while in 6FPT/BPA = 4.17 to 4.46 - Solubility, S_{CH4} 6FPT/6FBPA = 1.07 to 1.15, while in 6FPT/BPA = 0.96 to 1.03 - P_{CO2}/P_{CH4} 6FPT/6FBPA = 15.32 to 16.01, while in 6FPT/BPA = 12.04 to 13.11 - D_{CO2}/D_{CH4} 6FPT/6FBPA = 3.16 to 3.46, while in 6FPT/BPA = 2.56 to 3.20 -Solubility coefficient, S_{CO2}/S_{CH4} 6FPT/6FBPA = 4.63 to 4.83, while in 6FPT/BPA = 4.05 to 4.64
5.	Xu *et al.*, Polymer Vol. 38, No. 7	-Poly(phenylene thioether imides)s (PPTI), 2,2-bis(3,4-decarboxyphenyl) hexafluoropropane dianhydride (6FDA), poly(1,4-phenylene thioether) (PPT) or poly (1,4-phenylene sulfide) -CO_2, O_2, N_2 and CH_4 (at temperature of 35 ^{0}C and 10 atm)	- 6FDA/PPTI-4 polyimide shows higher permeabilities and selectivity toward CO_2/CH_4 system than PPT. - P_{CO2} 6FDA/PPTI = 6.62 to 23.11 - P_{CH4} 6FDA/PPTI = 0.22 to 0.66 - D_{CO2} 6FDA/PPTI = 1.53 to 3.54 - D_{CH4} 6FDA/PPTI = 0.19 to 0.39 -Solubility, S_{CO2} 6FDA/PPTI = 2.98 to 4.96 -Solubility, S_{CH4} 6FDA/PPTI = 0.71 to 0.71 to 1.29 - P_{CO2}/P_{CH4} 6FDA/PPTI = 25.42 to 34.79 - D_{CO2}/D_{CH4} 6FDA/PPTI = 6.09 to 9.07 -Solubility coefficient, S_{CO2}/S_{CH4} 6FDA/PPTI = 3.84 to 4.18
6.	Krishna and Baten, Chemical Engineering Journal 133, 2007	Twelve different zeolites (AFI, MOR, TON , FER, LTL, MFI, ISV, BEA, FAU, LTA, CHA, and DDR)	-CO_2/CH_4 membrane permeation selectivity for all the zeolites = 1 to 1000 roughly. -The sorption selectivity CO_2/N_2 for all the zeolites = 0.5 to 800 -The self diffusivity between CO_2 and N_2 = 0.1 to 1.0 -CO_2/N_2 membrane permeation selectivity for CH_4 = 10 to 100

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

3.1.1 N, N-dimethylacetamide

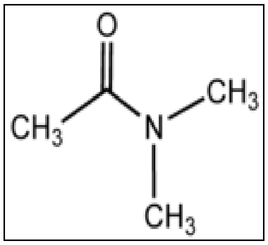


Figure 3.1 Structure of N, N-Dimethylacetamide (DMAc)

N, N-dimethylacetamide (DMAc) is an organic compound with the formula $CH_3C(O)N(CH_3)_2$ and a chemical formula of C_4H_9NO. This colorless, water miscible, high boiling liquid is commonly used as a polar solvent in organic chemistry. DMAc is miscible with most other solvents although it is poorly soluble in aliphatic hydrocarbons. The boiling point is 164-166 ^{0}C and the melting point is -20 ^{0}C. Figure 3.1 shows the structure of N, N-dimethylacetamide (DMAc) and Table 3.1 shows the table of properties for DMAc.

Table 3.1 Table of Properties of DMAc

Chemical Properties		Unit (SI)
IUPAC name		Dimethylacetamide
Other names		DMAc, DMA, acetic acid-dimethylamide, N,Ndimethylacetamide, acetyldimethylamine
CAS number		[127-19-5]
RTECS number		AB7700000
SMILE		O=C(C)N(C)C
Molecular formula		C_4H_9NO
Appearance		Colorless liquid with faint ammonia odor
Molar mass		87.12 g/mol
Density-Liquid (20°C)		0.94 g/cm^3
Boiling point (760 mm Hg)		164-166 °C
Freezing point (760 mm Hg)		-20 °C
Viscosity	(25°C)	1.956 mPa-s
	(50°C)	1.279 mPa-s
	(75°C)	0.896 mPa-s
	(100°C)	0.661 mPa-s
Flash point		70 °C
Ignition Temperature		490 °C

3.1.2 Polysulfone

Polysulfone has many advantages compare to the other polymers. Polysulfone (PSF) was used for this study since the transport behavior of carbon dioxide (CO_2) in this polymer is typical and well studied (Wang and Kamiya, 1994).

As much of the fouling in water comes from hydrophobic organic particles, they were not attracted to the polysulfone. Polysulfone also has the wide range of pH and temperature. It has good temperature stability allowing operation up to 80°C, and tolerated a pH from 1.5 to 12 for cleaning (Scott and Hughes, 1996).

This kind of membranes found wide application in various separation processes, such as membrane gas separation, pervaporation, reverse osmosis, micro filtration and ultra filtration, depend on the pore size (Matsuura *et al*, 2004).

Polysulfone has many advantages compared to the other polymers. Polysulfone was supplied by BP Amoco Company in Singapore. The sulfur atoms in polysulfone's structure made this polymer have high affinity to the water. These atoms also made this polymer polar and thus hydrophilic. Figure 3.2 shows the structure of polysulfone (Ulbricht, 2006).

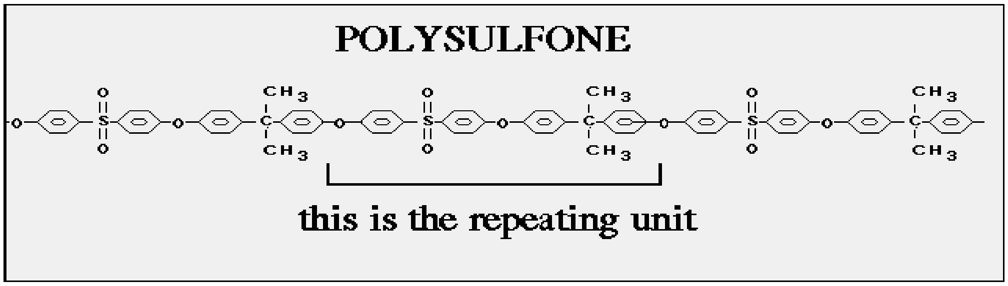


Figure 3.2 Structure of Polysulfone (Moon *et al*, 2006)

Engineering polymers from the classes of polysulfone showed interesting facts as membrane materials for gas separation. The potential application of a polymer as a separation membrane depends on the possible throughput and the purity of the product. This means that both the permeability coefficient for the gas that was transported more rapidly and the permeability should be as large as possible (Dannenberg *et al*, 2002).

The sulfur atoms in this oxidation state make the polymer quite polar and thus hydrophilic. As much of the fouling in water comes from hydrophobic organic particles, they are not attracted to the polysulfone. The pH and temperature ranges were wide for using this polymer (Ulbricht, 2006). Table 3.2 shows the table of properties of polysulfone.

Table 3.2 Physical Properties of Polysulfone Polymer

Physical Properties	Unit (SI)
Density	1.24 - 1.25 g/cc
Water Absorption	0.2 - 0.8 %
Tensile Strength, Ultimate	70 - 76 MPa
Tensile Strength, Yield	69 - 80 MPa
Shear Strength	62 MPa
Specific Heat Capacity	1.2 J/g-°C
Thermal Conductivity	0.12 - 0.26 W/m-K
Maximum Service Temperature, Air	149 - 180 °C
Glass Temperature	188 - 190 °C
Oxygen Index	30 - 32 %

3.1.3 Tetrahydrofuran (THF)

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

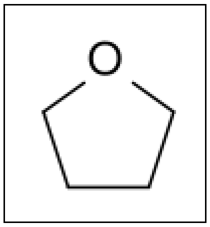


Figure 3.3 Structure of Tetrahydrofuran (THF)

THF was an aprotic solvent with a dielectric constant of 7.6. It is a moderately polar, aprotic solvent that dissolved a wide range of nonpolar and polar compounds. THF was often used in polymer science. For example, it is used to dissolve rubber prior to determining its molecular mass using gel permeation chromatography. THF tends to form peroxides on storage in air. As a result, THF should not be distilled to dryness, which can leave a residue of highly-explosive peroxides. Commercial THF was therefore often inhibited with 2, 6-di-tertbutyl-4-methylphenol, BHT (Dreyfuss *et al.*, 1996).

THF was stable. It was incompatible with halogens, strong oxidizing agents, strong reducing agents, strong bases, oxygen. THF generated explosive peroxides in storage if in contact with air and was highly flammable. It was stored at room temperature under nitrogen. Hazardous polymerization occured. THF was light sensitive and contained BHT as a stabilizer. Table 3.3 shows the table of properties of Tetrahydrofuran.

Table 3.3 Table of Properties for Tetrahydrofuran

Chemical Properties	**Unit (SI)**
IUPAC name	Oxacyclopentane
Other names	THF, tetrahydrofuran, 1,4-epoxybutane, butylene oxide, cyclotetramethylene oxide, oxacyclopentane, diethylene oxide, oxolane, furanidine, hydrofuran, tetra-methylene oxide
CAS number	[109-99-9]
RTECS number	LU5950000
SMILE	C1CCCO1
Molecular formula	C_4H_8O
Appearance	Colorless liquid with ether-like odor
Molar mass	72.11 g/mol
Density-Liquid (20°C)	0.8892 g/cm^3
Boiling point (760 mm Hg)	66 °C (339.15 K)
Melting point (760 mm Hg)	-108.4 °C (164.75K)
Solubility in water	Miscible
Viscosity (25°C)	0.48 mPa-s
Flash point	-14 °C

3.1.4 Methanol

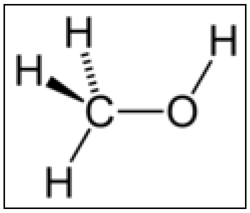


Figure 3.4 Structure of Methanol

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

Table 3.4 Physical Properties for Methanol

Chemical Properties	**Unit (SI)**
IUPAC name	Methanol
Other names	methyl alcohol, hydroxymethane, methyl hydrate carbinol, wood alcohol, wood naphtha or wood spirits
CAS number	[67-56-1]
Molecular formula	CH_3OH
Appearance	Clear, colorless liquid
Molar mass	32.04 g/mol
Density-Liquid (20°C)	0.7918 g/cm^3
Boiling point (760 mm Hg)	64.7 °C (337.8 K)
Melting point (760 mm Hg)	–97 °C (176 K)

3.2 Research Design

The flowchart of the membrane preparation and testing are shown in Figure 3.5.

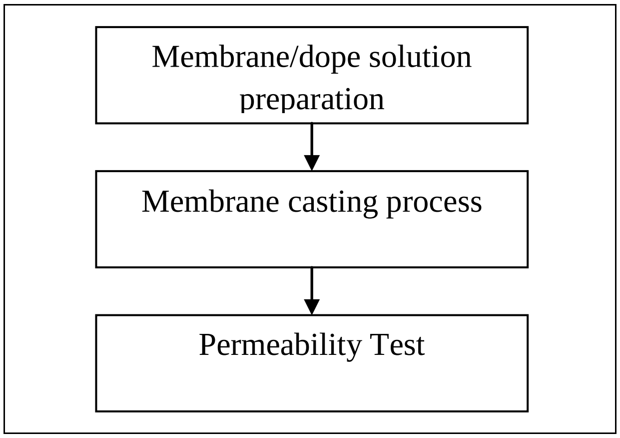


Figure 3.5 Flowchart of The Membrane Preparation and Testing

3.3 Preparation of Polysulfone Membrane

Apparatus for preparing the casting solution is shown in Figure 3.6.

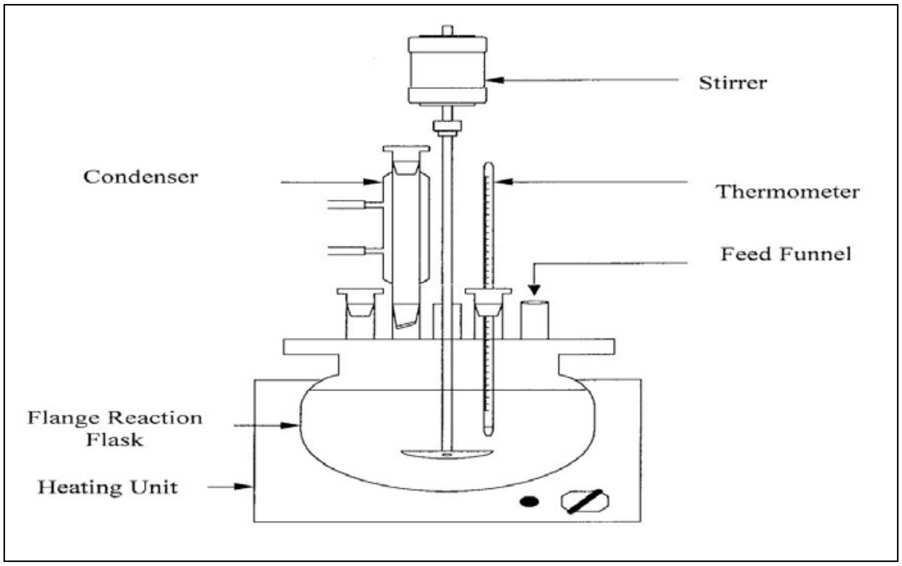


Figure 3.6 Setup for Casting Solution Preparation

Briefly, polysulfone polymer was dried for at least 2 hours in a vacuum oven at a temperature of about 80 ± 2 ^{0}C in order to remove all absorbed water vapor. The polymer was then dissolved in DMAc (solvent) and various nonsolvent additives. The casting solution was heated at 58-63 ^{0}C and stirred for about 4 to 6 hours to achieve complete homogeneity. Finally, the casting solution was kept in a storage bottle and was degassed by using ultrasonic bath to remove any traces of micro bubbles inside the casting solution. The continued sections elaborated the steps of preparing the polysulfone membrane.

3.3.1 Membrane Solution / Dope Preparation

Solution preparation was the first stage of experiment. It has been very careful in preparing the chemicals because the weight percentage of each chemical affected the result during the fabrication process of membrane. Polysulfone pellet was a main chemical in fabricate polysulfone membrane. N, N-dimethylacetamide was used as a solvent to dissolve polysulfone.

Polysulfone was dissolved into a solvent N, N-dimethylacetamide at different composition of weight percent. Polysulfone was mixed well in the flask with N, N-dimethylacetamide organic solvent by using a stainless steel stirrer. After 8 to 9 hours, a solution like honey was formed.

After the process of membrane fabrication, the membrane has immersed into the water bath. The solvent, N, N-dimethylacetamide dissolved in the water. From this phase inversion method, the membrane was produced.

3.3.2 Membrane Casting Process

Solution casting was commonly used to prepare small samples of membrane for laboratory characterization experiments. An even film of a polysulfone polymer solution was spread across a flat plate with a casting knife. The casting knife consisted a steel blade, resting on two runners, arranged to form a precise gap between the blade and the plate onto which the film was cast. A typical hand-held casting knife is shown in Figure 3.7. After casting, the solution was left to stand, and the solvent evaporated to leave a thin, uniform polymer film.

Figure 3.7 Membrane Fabrication by Using Casting Knife

The polymer solution used for solution casting should be sufficiently viscous to prevent it from running over the casting plate. During an extended solvent evaporation time, the cast film absorbed sufficient atmospheric water to precipitate the polymer producing a hazy surface. Rapid evaporation of the solvent cools the casting solution, causing rapid gelation of the polymer. When the solvent has completely evaporated, the dry film is lifted from the glass plate. If the cast film adheres to the plate, soaking in a swelling non-solvent such as water had loosened the film.

The difference of membrane thickness gave different performance. The reason of this was when a thin membrane was used, the pressure given can be low, and when a thicker membrane was used, the pressure given was high to press on the solution to pass through the membrane.

3.3.3 Permeability Test

Figure 3.8 shows the apparatus setup for carbon dioxide gas separation of polysulfone membrane.

Figure 3.8 Apparatus Setup for Carbon Dioxide Gas Separation of Polysulfone Membrane

In this experiment setup, the membrane was firstly cut into a small circle to be pleated and folded around the permeate core. The fittings of the gas hose and permeability unit was ensured to be suiting each other to avoid gas leakage. The gas flow rate to the permeability unit was set to be 0.5 L/min as the initial flow rate and fixed variable. The cartridge fitted inside a specially designed housing into which the feed solution enters at a pressure 1 – 10 bar. The CO_2 permeability test was being conducted once the permeability unit was ready by flowing the CO_2 gas through the polysulfone membrane fitted in it. The time of the first bubble formed and volume difference of the soap water by each membrane was taken. Permeability test was being done when all readings for each membrane A to D was completed.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result and Discussion

Four different membrane samples were prepared with four different characteristics samples are shown in Table 4.1. All of the membranes were hung to dry for 2 days.

Table 4.1 Membrane characteristics for CO_2 performance determination

Characteristics	Membrane A	Membrane B	Membrane C	Membrane D
Exposure to Air	Straight away immerse in water	1 min	Straight away immerse in water	1 min
Immersion Time	10 s	1 min	1 day	1 day

Figure 4.1 shows a graph of the difference of initial and final soap water volume versus time of the first CO_2 gas or bubble formation for membrane A. it can be seen that the volume difference is at the range of 3.00 to 3.70 ml and the time range of the first CO_2 gas or bubble formation is at the range of 782.40 to 841.20 seconds.

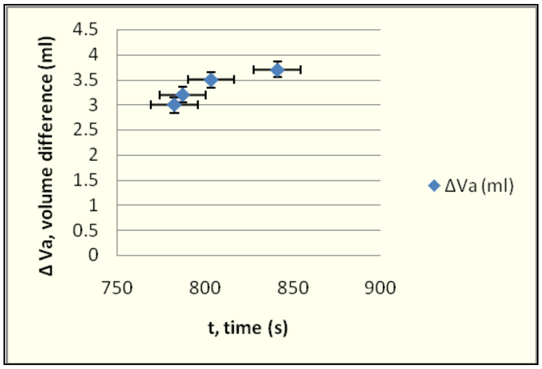


Figure 4.1 Graph of the volume difference versus time of the first CO_2 gas or bubble formed for membrane A

Figure 4.2 shows the graph of the difference of initial and final soap water volume versus time of the first CO_2 gas or bubble formed for membrane B. Note that the volume difference and the time readings are in the range of 3.2 to 5.3 ml and 181.2 to 241.2 seconds respectively.

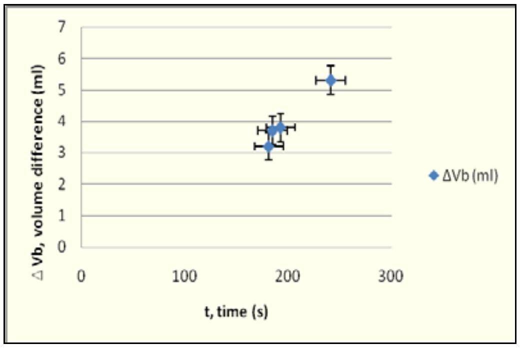


Figure 4.2 Graph of the volume difference versus time of the first CO_2 gas or bubble formed for membrane B

The volume difference of membrane C is at the range of 5.0 to 7.1 ml while the time range of the first bubble formation is at the range of 6.04 to 8.35 seconds as showed in Figure 4.3.

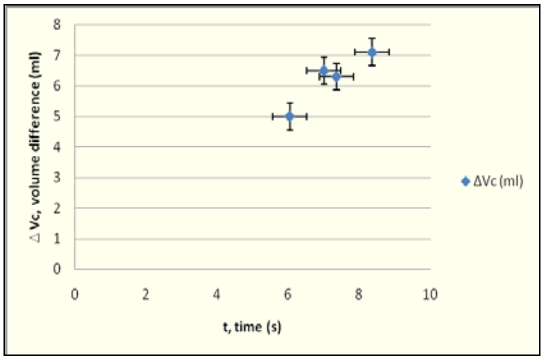


Figure 4.3 Graph of the volume difference versus time of the first CO_2 gas or bubble formed for membrane C

Figure 4.4 shows that the volume difference of the soap water is at the range of 5.50 to 7.50 ml and the time range of the first CO_2 gas or bubble formation is at the range of 1.38 to 2.31 seconds.

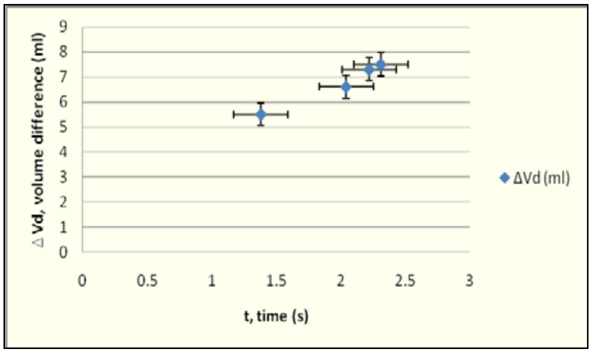


Figure 4.4 Graph of the volume difference versus time of the first CO_2 gas or bubble formed for membrane D

From all the graphs plotted as volume difference of soap water versus time, it is found that the trend of the graph is increase in time resulted increase in volume. In other words, time was proportional with the volume difference. Besides, from all the graphs, the value of time was decreasing from membrane A to membrane D as showed in Figure 4.5. This justifies that membrane D have a better permeability rate.

From all the result data, the permeability value is calculated by using equation (1)

$$\boxed{P_{CO2} = Q/A \cdot P} \qquad (1)$$

which

Q = Flowrate of system (cm^3/s)

A = Area (cm^2)

P = Pressure in system (bar)

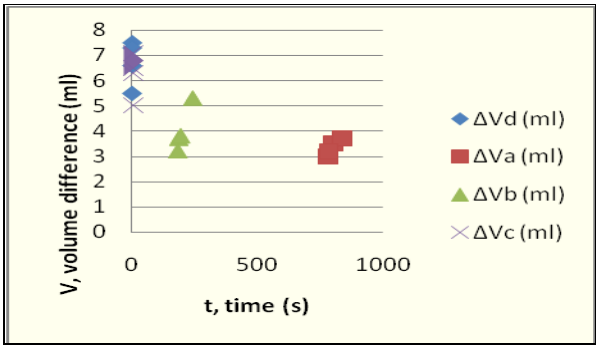


Figure 4.5 Comparison graph of volume difference of four different characteristics of polysulfone membrane

All the calculated data was shown in Table 4.2, 4.3, 4.4, and 4.5. Pressure, area and CO_2 gas flow rate are the parameters.

Pressure of system, P = 2 bar

Area, A = 19.635 cm^2

CO_2 gas flow rate, F = 0.5 L/min

Table 4.2 Result of membrane A

No	t(s)	ΔVa (ml)	Q (cm^3/s) x 10^3	P_{CO2} (cm/s.bar) x 10^3
1	803.4	3.5	4.356	0.111
2	841.2	3.7	4.398	0.112
3	782.4	3.0	3.834	0.098
4	787.2	3.2	4.065	0.104

Table 4.3 Result for membrane B

No	t(s)	ΔVb (ml)	Q (cm^3/s) x 10^3	P_{CO2} (cm/s.bar) x 10^3
1	184.8	3.7	20.022	0.510
2	241.2	5.3	21.973	0.560
3	192.6	3.8	19.730	0.500
4	181.2	3.2	17.660	0.450

Table 4.4 Result of membrane C

No	t(s)	ΔVc (ml)	Q (cm^3/s) x 10^3	P_{CO2} (cm/s.bar) x 10^3
1	7	6.5	928.571	23.65
2	8.35	7.1	850.299	21.65
3	7.35	6.3	857.143	21.83
4	6.04	5	827.815	21.08

Table 4.5 Result of membrane D

No	t(s)	ΔVd (ml)	Q (cm^3/s) x 10^3	P_{CO2} (cm/s.bar) x 10^3
1	2.31	7.5	3246.753	82.680
2	2.04	6.6	3235.294	82.390
3	1.38	5.5	3985.507	101.490
4	2.22	7.3	3288.288	83.740

Summary of gas permeability which was reported in the cited literature was shown in Tables 4.2, 4.3, 4.4, and 4.5. The tables also include the results obtained in this study for CO_2 gas separation by using polysulfone membrane. CO_2 gas flow rate is found to be increasing from membrane A to D. The comparison graph of the CO_2 gas flow rate is shown in Fig. 4.6. It was found that membrane D resulted the highest CO_2 gas flowrate which are 3.2468, 3.2353, 3.9855, and 3.2883 cm^3/s.

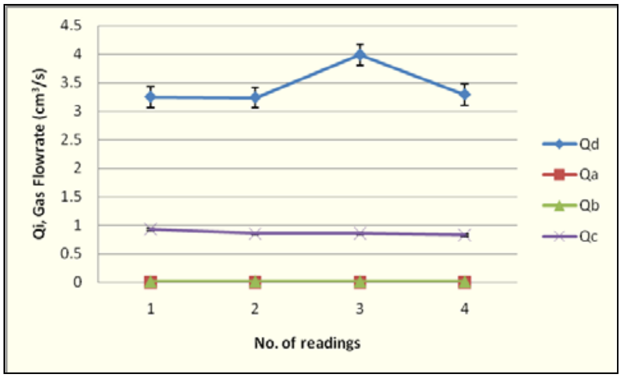


Figure 4.6 Comparison graph of CO_2 gas flowrate versus no. of readings taken for membrane A, B, C, and D

The most efficient and effective CO_2 separation was determined. It was found that Figure 7 has the same trend with the permeability result which is shown in Figure 4.7.

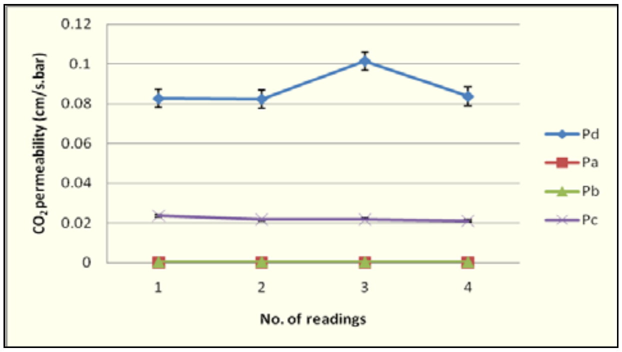


Figure 4.7 Comparison graph of the permeability of CO_2 separation versus no. of readings taken for membrane A, B, C, and D

From Figure 4.7, it is found that the permeability value for membrane A is the lowest and the membrane D resulted the highest permeability value. It showed that the membrane performance of membrane D was the best membrane compared to the other 3 membranes that resulted the highest permeability which was 0.1015 cm/s.bar. Membrane A gave the lowest permeability value which was 0.0824 cm/s.bar.

The result of permeability value is supported by Ettouney and Majeed (1997) which reported the permeability value is 1.1×10^{-6} to 3.3×10^{-7} cm/s.bar.

Higher permeability was produced by the polysulfone membrane when a higher pressure was used (C. Y. Ching, 2005). When operating high pressure to the system the time taken for the permeate to pass through the membrane decreased. In other words, lower for time taken lead higher permeability rate. But the situation might be different when low temperature of water in water bath was used (Masduki, 2005).

In addition, the theory of the parameters such as operating pressure, temperature and membrane model is as reported in the work of Wang and Kamiya (1995). The temperature dependence can be well expressed by the Fick's Law and the volume of CO_2 is smaller than in rubbery polymers and the appreciable temperature dependence is in the range of 15-75 ^{0}C.

The membrane let in air before immersed in water for at least a day produced a better permeability compared to membrane which did not be let in air and immersed only a few minutes in water. The theory of Baker (1994) supported the experimental data on the phase inversion method. CO_2 permeability test on polysulfone membrane was successfully done.

Most gas separation processes require that the selective membrane layer be extremely thin to achieve economical fluxes. Typical membrane thicknesses were less than 0.5 µm and often less than 0.1 µm. The sensitivity of gas separation membranes to defects posed a serious problem to early developers. Generation of a few defects was very difficult to avoid during membrane preparation and module formation (Scott, 1998).

The advantages when using small scale permeability test unit method were; the pleated membrane cartridges, which were fabricated with high speed equipment, were cheap, disposable, reliable, and hard to beat when the solution to be filtered had a relatively low particle level.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion and Recommendation

The phase inversion method was an inexpensive, simple and reliable way to fabricate polysulfone membrane. Polysulfone membranes with the thickness of 2 µm and four different characteristics resulted by different immersion time were produced. The performance determination of CO_2 separation study was successfully completed.

From the Tables 2, 3, 4, and 5 the graph of the CO_2 gas flow rate shown in Figure 7 is produced. It has the same trend with the permeability result which was shown in Figure 8.

Measured permeability data in polysulfone (glassy polymer) are consistent with literature studies. In this regard, immersion time of membrane impacts in membrane performance. This behavior was found from CO_2 where the permeability value for membrane A is the lowest and the membrane D gives the highest permeability value. It showed that the membrane performance of membrane D was the best compared to the other 3 membranes with the permeability of 0.1015 cm/s.bar. It can also be noted that membrane A gave the lowest permeability value which was 0.0824 cm/s.bar.

From the result data and supported theories by various authors such as Ettouney and Majeed (1997), Wang and Kamiya (1995) and Ching C. Y. (2005) it can be concluded that different immersion time gave impacts to the performance of polysulfone polymer membrane for CO_2 separation.

It was also found that increasing CO_2 gas flowrate resulted to increasing permeability. In other words, the CO_2 gas flowrate was proportional with CO_2 gas permeation. It was supported by Da Costa *et al.* (1999) that quoted the permeability of CO_2 increases as the temperature or flow increases when the transport of CO_2 through the membrane was activated. This study has promising characteristics that it was useful for the petrochemical plants.

It was recommended that glove and mask have to be worn during the dope membrane preparation, to ensure an individual safety. Besides that, the CO_2 tank had to be handled by only a competent person and all the experiment tools were prepared to ensure that the experiment was smoothly running.

Further studies were needed in order to expand the knowledge in chemical or related industries. Research on differentiations of permeability and other parameters of polysulfone membrane at different immersion times has to be increased and was supported by better resources. The study on this related topic also has to be emphasized in improving the emerging technology such as CO_2 membrane separation of the produced or sales gas.

The contribution of major capital expansion to the plant need to be reduced in order to achieve a higher profit and enhance the economic status of our beloved country. And in the future, may this study make membranes as large scale gas separation process a reality.

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