

**PERMEABILITY AND SELECTIVITY STUDY OF POLYETHERSULFONE
MEMBRANE FOR GAS SEPARATION**

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**JUDUL: PERMEABILITY AND SELECTIVITY STUDY OF
POLYETHERSULFONE MEMBRANE FOR GAS SEPARATION.**

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**PERMEABILITY AND SELECTIVITY STUDY OF POLYETHERSULFONE
MEMBRANE FOR GAS SEPARATION**

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

**Faculty of Chemical & Natural Resources Engineering
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APRIL 2010

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

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*Special Dedication to my family members that always love me,
My friends, my fellow colleague
and all faculty members*

For all your Care, Support and Believe in me

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ABSTRACT

The objective of this study is to develop and study the effect of polymer concentration and coating treatment on the membrane performance. The asymmetric polyethersulfone membranes were prepared through a dry/wet phase inversion process. The casting solution developed in this research consisted of polyethersulfone pellet, 1-methyl-2-pyrrolidone (NMP) and methanol. There are three different membrane composition was prepared. The composition is 18 wt%, 23 wt% and 28 wt% of PES was used for permeability test PES membrane was divided into two categories: uncoated and coated with bromine solution. Casting process was done by using manual casting knife. Permeation test was carried out by testing CO₂ and CH₄ permeating through the membrane to check the permeability and selectivity of respective gas to CH₄. Different coating agent gave different rate of permeate while higher polymer concentration enhance the permeation rate. The PES membrane uncoated showed the higher selectivity compare to coat with bromine solution. The selectivity of CO₂/CH₄ was approximately 2.06 at 23% of PES concentration uncoated with bromine. It was believed that different concentration strongly affects the membrane performance.

ABSTRAK

Objektif kajian ini dilakukan adalah untuk membangunkan dan untuk mengkaji kesan kepekatan larutan dan kesan salutan terhadap pencapaian membran. PolyIetersulfona (PES) membran yang tidak simetri telah disediakan menggunakan teknik proses yang ringkas iaitu fasa balikan basah/kering.larutan bahan teracuan yang disediakan untuk kajian ini mengandungi PES, 1-methyl-2-pyrolidone (NMP) dan methanol.Komposisi membrane 18 wt%, 23wt% dan 28wt% digunakan untuk ujian ketelapan. Membrane PES dibahagikan kepada dua kategori , tanpa salutan dan dengan salutan bromin. Proses tebaran dilakukan menggunakan pisau tebaran manual. Ujian ketelapan telah dijalankan dengan menguji gas CO₂ dan CH₄ ke atas membran untuk melihat ketelapan dan pemilihan bagi setiap gas terhadap CH₄. Agen salutan berbeza memberikan nilai ketelapan yang berbeza manakala lebih tinggi kepekatan polimer meningkatkan kadar ketelapan. Membran PES tanpa salutan menunjukkan kadar pemilihan yang tinggi berbanding dengan membran PES dengan salutan larutan bromine. Oleh itu pemilihan bagi CO₂/CH₄ adalah 2.06 pada 23 wt% bagi kepekatan PES tanpa salutan. Maka agen salutan di percayai mempengaruhi prestasi membran dan begitu juga kepekatan polimer

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LIST OF ABBREVIATIONS

CO ₂	-	Carbon Dioxide
CH ₄	-	Methane
PES	-	Polyethersulfone
O ₂	-	Oxygen
N ₂	-	Nitrogen
H ₂	-	Hydrogen
Cl	-	Chlorine
C ₂	-	Carbon
°C	-	Degree celcius
P	-	Permeability
Q	-	Flow rate
A	-	Area
ΔP	-	Pressure difference of penetrant across membrane
α	-	Selectivity
%	-	Percentage
P	-	External gas partial pressure

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CHAPTER 1

1.1 Introduction

1.1.1 Background of Study

Currently gas separation by selective permeation through polymer membrane is one of the fastest growing branches of the separation technology. Gas separation membrane systems have received a lot of attention from both industry and academia. This is because there is a belief that membrane separation processes in some application. In order to accomplish this objective, membrane materials with superior permeability and selectivity and advanced fabrication technologies to yield hollow fibers with an ultra-thin dense selective layer are the primary focuses for most membrane scientists in the last two decades.

Most of the membrane expert have been investigating and synthesizing new polymers that are able to exhibit both higher gas permeability and selectivity since the past 40 years. Presently the structure, pressure-normalized flux and selectivity of the membrane polymer have become the focus of the studies among researchers. In addition they are aiming for defect free ultra thin dense selective layer membrane material. Significant processes have been made in the membrane materials, dope preparation, fabrication technology and fundamental understanding of membrane formation

The selectivity was believed relates to the parameter such as polymer concentration used which strongly affects the membrane performance (Koros et al 2000). Selectivity of membrane can be represented by the ratio of the permeability of any two components through the membrane. This specific characteristic of a membrane were generally varies inversely with gas permeability which means to

achieve a high selectivity, it requires the membrane to operate in low permeability (Scott, 1998).

Based on the previous researchers the limitation of this research was to achieve high gas permeability without a significant decrease in gas selectivity. In order to get the high selectivity membrane without reducing the permeability of membrane, low cost polymer polyethersulfone membrane was sought. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa. That's the trade-off. (Hwang, 1975)

In term of material development, membrane prepared from polyethersulfone (PES) have been received special attention for gas separation due to some of them possessing surprisingly high gas selectivity for gas pair O_2/N_2 and CO_2/CH_4 . Polyethersulfone also have many other desirable properties, such as spin ability, thermal and chemical stability and mechanical strength. These properties are essential to yield a membrane module with stable and predictable long-term performance (Baker, 2008).

1.2 Problem Statement

Today, oil and gas companies were required to remove or substantially reduce CO₂ levels in exhaust streams before they are vented to the atmosphere. Since CO₂ was well known as an acid gas, CO₂ should be removed before natural gas can be distributed to the pipelines. The amount of carbon dioxide should be in small amount because carbon dioxide when react with water will form carbonic acid which may corrode the pipeline. In order to meet the quality standards specified by major pipeline transmission and distribution companies one of the specifications was to ensure the pipeline free of particulate solids and liquid water. Therefore, CO₂ should be removed or the acid gases because they can lead erosion, corrosion and other damage that will not follow the standardization. (Surkov et al, 2000)

A simple process technology was highly desirable which can be applied in remote, unattended or offshore situations. In addition to competitive capital and operating cost, ease operation, quick start-up, and high on stream factors are needed. Currently amine absorption was commonly used for CO₂ separation process. Amine absorption was an effective technique to remove CO₂, however this technique complex and have high capital, operating and installation costs. Therefore new development of separating gas using membrane was developed. However the major problems confronting the use of the membrane based gas separation processes in a wide range of applications was the lack of membranes with high selectivity. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa. In order to get the high selectivity membrane without reducing the permeability of membrane, low cost polymer polyethersulfone membrane was sought.

1.3 Objective of Study

To study the polymer concentration in order to find out the best formulation that gives the best performance of the membrane developed

1.4 Scope of Study

In order to meet the objective, there were some scopes which need to be focused:

- i) To develop polyethersulfone polymer as a membrane for gas separation.
- ii) To fabricate polymer with coating agent.
- iii) To study the permeability and selectivity of different gases (CO₂, CH₄)

CHAPTER 2

LITERATURE REVIEW

2.1 History of Membrane Based Separation

Membrane based separation processes over the last three decades have proved their potential as better alternatives to traditional separation processes. Although reports concerning the permeability of synthetic membranes date back to the mid 19th century, membrane science and technology study started as early in 15th century (Boretos, 1973).

The gas separation early demonstration was using natural rubber membranes date back to the 1830's. Gas separation using polymeric membranes has achieved important commercial success in some industrial processes since the first commercial scale membrane gas separation system was produced in the late 1970's. In order to extend its application and compete successfully with traditional gas separation processes such as cryogenic, pressure swing adsorption and absorption and researches made great attention in fabricating high separation performance in both academia and industry (Wang et al, 2002). Table 2.1 shows the milestone in the development of membrane based separation.

Table 2.1: Milestone in the development of membrane based separation

Name of inventor	Year	Invention
Abbe Nollet	1748	Wine and water separated with animal skin by reverse osmosis
J.K Mitchell	1831	First scientific observation related to gas separation
Thomas Graham	1850	Graham's law of diffusion
J.S. Chiou and D.R. Paul	1987	Prove for the two membranes as a function of CO ₂ conditioning and driving pressure
Stern <i>et al</i>	1989	Development of nine types of polyimide membranes.
Suzuki <i>et al</i>	1998	Fabricated dual-layer hollow fiber membranes composed of a dense polyimide outer layer and a sponge-like inner layer made of another polyimide.
I. Cabasso	1979	Development of polyethyleneimine/polysulfone (PS) hollow fibers for RO.
Nitto Denko	1988	Develop first commercial vapor separation plants.
Li <i>et al</i>	2002	Conducted the first systematic study to investigate the effects of spinning conditions on dual-layer hollow fiber membranes and the causes of interfacial\delimitation between the two layers

A significant advance on polymeric materials for gas separation has also been made in the last 20 years (Koros et al 1988) , many high-permeability and high permselectivity materials have been discovered and synthesized. However, these high performance polymeric materials are often very expensive, while some of them are brittle.

As a result, the fabrication of integrally skinned asymmetric membranes is either no longer feasible or economically attractive because it is too costly to prepare the entire membrane from the same material.

The modern era of gas separation membrane was introduced when polymeric membrane became economically viable. H₂- recovery was the first major application of membrane gas separation technology followed by the CO₂/CH₄ separation and the production of N₂ from air (Pereira,1999).

Then the membrane based gas separation has grown into a US\$150 million per year business and substantial growth in the near future is likely. Several research studies (Pereira, 1999; Di Luccio, 1994; Pinnau, 1994) have focused the membrane formation in order to control the properties of the resulting membrane and optimize the applications, compared to the other developing membrane process such as gas separation and pervaporation (Souza *et al*, 1998).

2.2 Membrane Definition

Membrane is defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid; can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 10 microns to few hundred micrometers (M. Takht Ravanchi *et al* (2009).

Membrane in the original word is known as “membrane” in Latin which mean as skin. Another definition of membrane can be defined as thin barrier that permits selective mass transport or a phase that acts as a barrier to prevent the mass

movement, but allows or regulated passage of one or more species (Bhattacharya *et al.*, 2004).

2.3 Membrane Module

Large membrane areas are normally required in order to apply membranes on a technical scale. A module was defined as the smallest unit into which the membrane area packed. At certain flow rate and composition, a feed enters the module. Both the feed composition and flow rate inside the module change as a function of distance. This was due to the ability of membrane which able to transport one component more readily than other. There are four major types of modules normally used in membrane separation processes which are spiral wound, plate and frame, tubular and hollow fiber.

2.3.1 Spiral Wound Module

Spiral wound module consist of two layers of membrane, placed onto a permeate collector fabric. This membrane envelope is wrapped around a centrally placed permeate drain (see picture below). This causes the packing density of the membranes to be higher. The feed channel is placed at moderate height, to prevent plugging of the membrane unit. Spiral membranes are only used for nanofiltration and reverse osmosis (RO) applications (Lenntech, 2008)

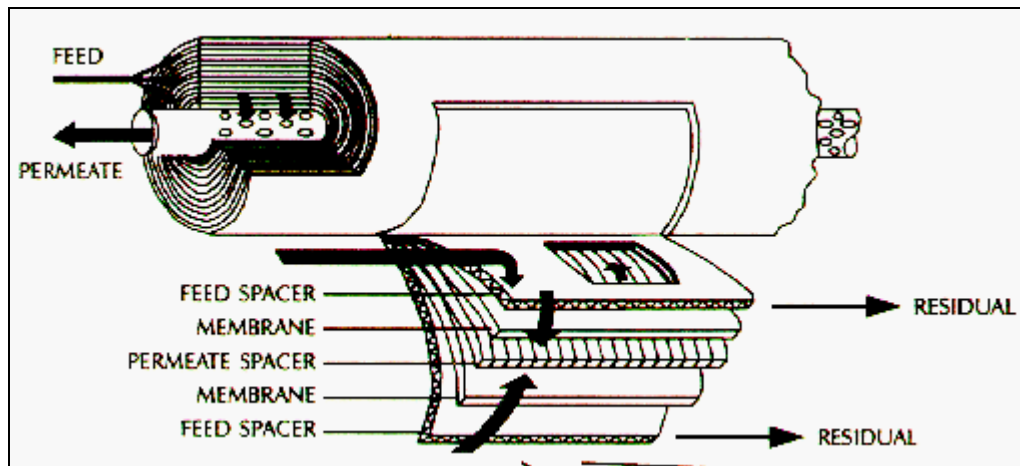


Figure 2.1: Structure of spiral wound membrane module (Lenntech, 2008)

2.3.2 Tubular Module

Tubular membranes are not self-supporting membranes. They are located on the inside of a tube, made of a special kind of material. This material is the supporting layer for the membrane. Because the location of tubular membranes is inside a tube, the flow in a tubular membrane is usually inside out. The main cause for this is that the attachment of the membrane to the supporting layer is very weak. Tubular membranes have a diameter of about 5 to 15 mm. Because of the size of the membrane surface, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low, which results in high prices per module.



Figure 2.2: Structure of tubular module (Lenntech, 2008)

2.3.3 Hollow Fiber Module

Hollow fiber membranes are membranes with a diameter of below $0.1\ \mu\text{m}$. consequentially, the chances of plugging of a hollow fiber membrane are very high. The membranes can only be used for the treatment of water with a low suspended solid content.

The packing density of a hollow fiber membrane is very high. Hollow fiber membranes are nearly always used merely for nano filtration and reverse osmosis (RO).

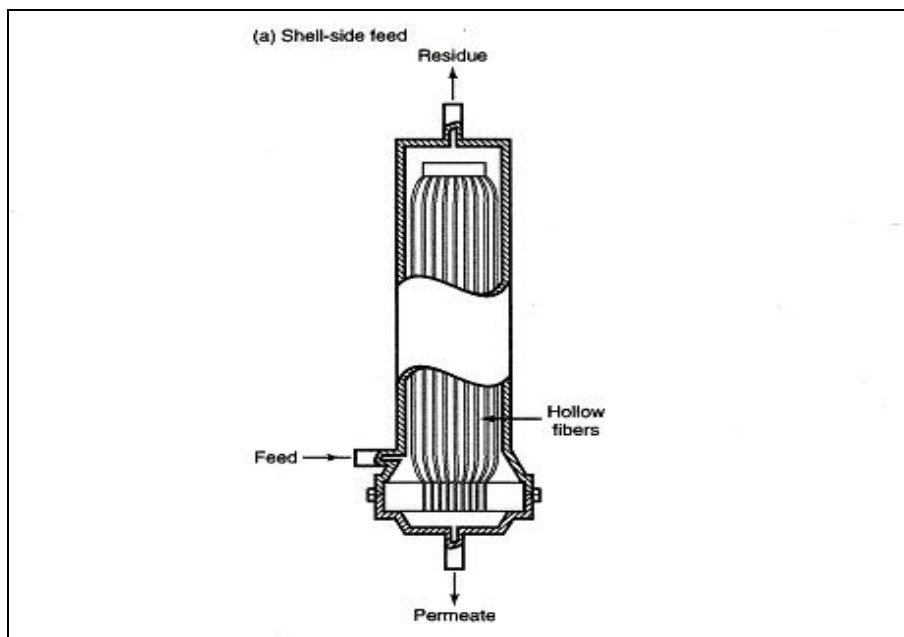


Figure 2.3: Structure of hollow fiber module (Wang *et al.*, 1992)

2.3.4 Plate and Frame Module

Plate-and-frame modules were one of the earliest types of membrane system. A plate-and-frame design (Stern *et.,al*, 1965) for early Union Carbide plants to recovery helium from natural gas is shown in Figure 2.4. Membrane, feed 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.

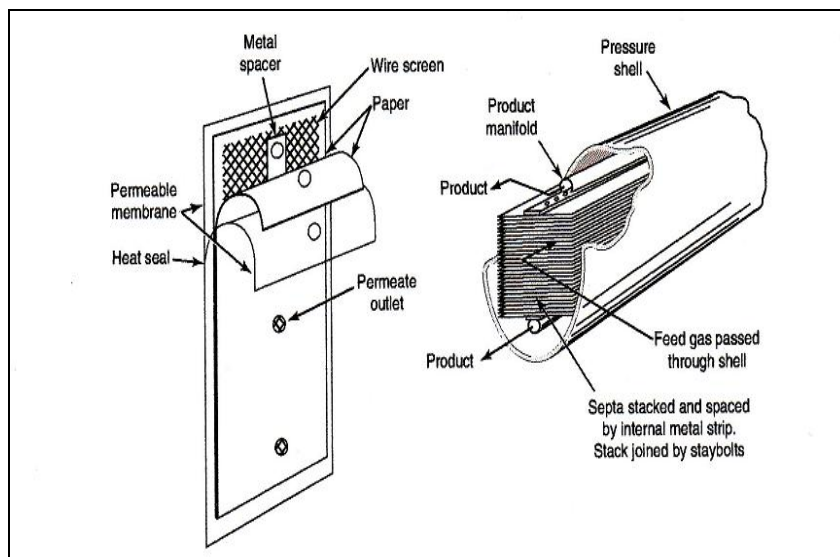


Figure 2.4: Early plate-and-frame designs developed for the separation of helium from natural gas. (Wang *et al.*, 1992)

2.4 Membrane Structure

There are two types of membrane structure namely, symmetric and asymmetric. The difference between these two structures was the physical and chemical properties.

2.4.1 Symmetric Membrane

A symmetric membrane was a membrane that having the same chemical and physical structure throughout the hole. There are two types of symmetric membrane: porous and non-porous.

2.4.1.1 Porous Membrane

A porous membrane is a rigid, highly voided structure with randomly distributed inter-connected pores. The separation of materials by porous membranes is mainly a function of the permeate character and membrane properties like the molecular size of the membrane polymer and pore size distribution.

Porous membrane for gas separation can exhibit very high levels of flux but provide for lseparation and low selectivity (Pandey, 2001).

2.4.1.2 Non-Porous Membrane

The nonporous layer meets the requirements of the ideal membrane, that is, it is highly selective and also thin. The porous layer provides mechanical support and allows the free flow of compounds that permeate through the nonporous layer. Although asymmetric membranes are a vast improvement on homogenous membranes, they do have one drawback. Because they are composed of only one material, they are costly to make out of exotic, highly customized polymers, which often can be produced only in small amounts.

2.4.2 Asymmetric Membrane

A membrane having different chemical and physical structures in direction of thickness was called an asymmetric or anisotropic membrane. This structure was characterized by a non uniform structure an active top layer or skin supported by a porous support or sub-layer. Three types of asymmetric membrane were porous, porous with top layer and composites (Scott, 1998). Figure 2.5 show the asymmetric membrane structure and Figure 2.6 show the typical type of membrane structure.

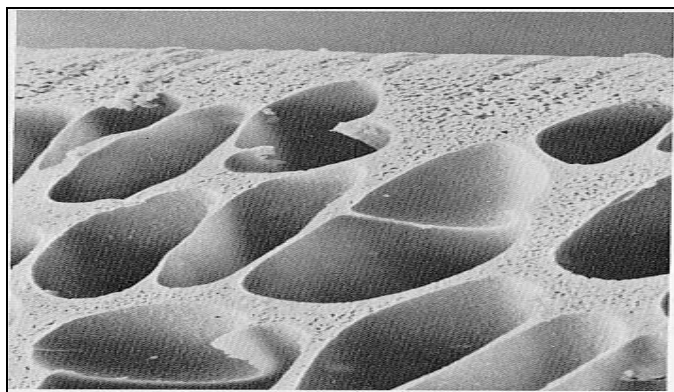


Figure 2.5: Asymmetric membrane structure

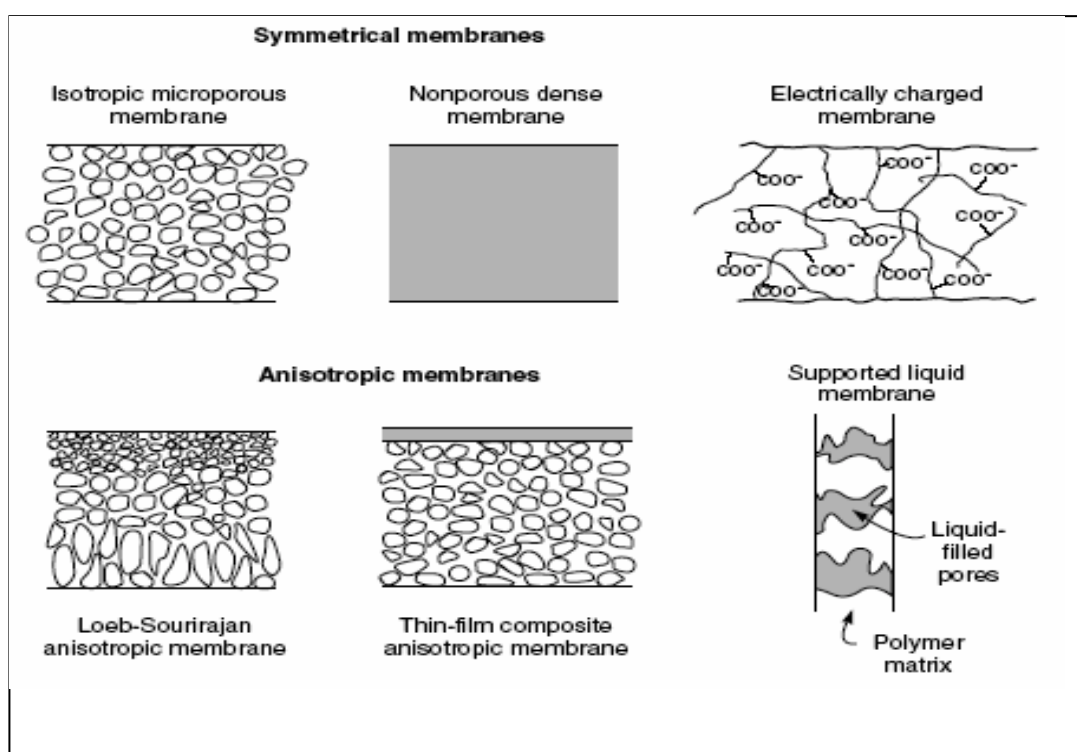


Figure 2.6: Typical types of membrane structure

2.5 Types of Membrane

2.5.1 Polymeric membranes

Generally, gas molecules transport through a polymeric membrane by a solution diffusion mechanism. Other mechanisms include a molecular sieve effect and Knudsen diffusion (Powell and Qiao, 2006).

These transport mechanisms are briefly introduced in inorganic membrane section. The terms permeability and selectivity are used to describe the performance of a gas separation membrane. There appears to be a trade-off between selectivity and permeability. Gas molecules tend to move through free volumes—the gaps between polymeric structures. Because of the movement of the polymer chains, a channel between gaps can be formed allowing gas molecules to move from one gap to another and thus gas molecules can effectively diffuse through the membrane structure. Selective transport of gases can be achieved by use of a polymer which forms channels of a certain size. Large channels will allow faster diffusion of gases through a membrane at the cost of less selectivity.

Membranes are a low cost means of separating gases when high purity is not vital. There are a number of issues associated with the capture of carbon dioxide from flue gas which limit the use of membranes. The concentration of carbon dioxide in flue gases is low, which means that large quantities of gases will need to be processed. The high temperature of flue gases will rapidly destroy a membrane, so the gases need to be cooled to below 100°C prior to membrane separation. The membranes need to be chemically resistant to the harsh chemicals contained within flue gases, or these chemicals need to be removed prior to the membrane separation.

Additionally, creating a pressure difference across the membrane will require significant amounts of power. Polymers studied in various studies include: polyacetylenes (Stern, 1994), polyaniline (Illing *et al.*, 2001), poly (arylene ether)s (Xu *et al.*, 2002), polyarylates (Pixton and Paul, 1995), polycarbonates (Aguilar-Vega and Paul, 1993), polyetherimides (Li and Freeman, 1997), poly (ethylene oxide) (Lin and Freeman, 2004), polyimides (Stern *et al.*, 1989), poly(phenylene ether) (Aguilar-Vega and Paul, 1993), poly(pyrrolone)s (Zimmerman and Koros, 1999) and polysulfones (Aitken *et al.*, 1992). Table 2.2 shows molecular structures of some commonly used polymers. The performances of some polymeric membranes are summarized in figure mainly separating post-combustion flue gas with CO₂/N₂ being the main components (Powell and Qiao, 2006).

Table 2.2 : Performance of polymeric membranes separating CO₂/N₂ (Powell and Qiao, 2006)

Material	Permeance (m³/m².Pa.s)	Selectivity
Polyimide	7.35	43
Polydimethylphenylene oxide	2750	19
Polysulfone	450	31
Polyethersulfone	665	24.7
Poly (4 vinylpyridine /polyetherimide)	52.5	20
Polyacrylonitrile with (ethylene glycol)	91	27.9
Poly (amide-6-b-ethylene oxide)	608	61

Materials for effective separation of gases can follow one of two overall strategies: increasing the rate of diffusion of carbon dioxide through the polymeric structure and increasing the solubility of carbon dioxide in the membrane. The introduction of mixed-matrix membranes may allow superior performance which combines the advantages of polymeric and inorganic membranes materials.(Koros 1998. Figure 2.7 show examples of polymer molecular structures used for CO₂separation (Powell and Qiao, 2006).

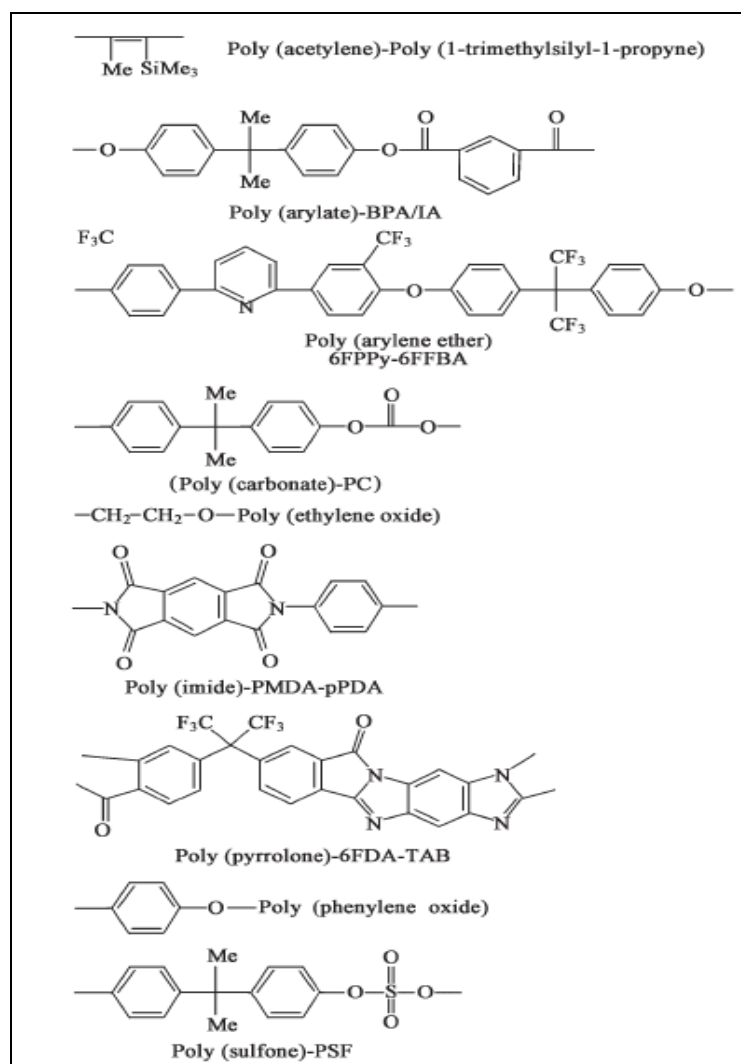


Figure 2.7: Examples of polymer molecular structures used for CO₂ separation (Powell and Qiao, 2006).

2.5.2 Inorganic Membrane

Inorganic membranes can be classified into two categories based on structure: porous and dense. In porous inorganic membranes, a porous thin top layer is casted on a porous metal or ceramic support, which provides mechanical strength but offers minimum mass-transfer resistance. Alumina, carbon, glass, silicon carbide, titania, zeolite, and zirconia membranes are mainly used as porous inorganic membranes supported on different substrates, such as α -alumina, γ -alumina, zirconia, zeolite, or porous stainless steel.

Surface modification by covalently bonding a layer of selected compounds with appropriate functional groups is one of the more convenient ways to alter membrane performance. Such modification can increase the performances by changing the mean pore size and promoting an eventual specific interaction between the surface of the membrane and the permeating molecules to enhance permeation.

The dense inorganic membranes consist of a thin layer of metal, such as palladium and its alloys, or solid electrolytes, such as zirconia. These membranes are highly selective for hydrogen or oxygen separation. Gas transport occurs via solution-diffusion mechanism or charged particles in dense membranes. The low permeability across the dense inorganic membranes limits its wide applications as compared to porous inorganic membranes.

There are four main transport mechanisms by which gas separation using porous inorganic membranes can be described, described by Figure 2.8.

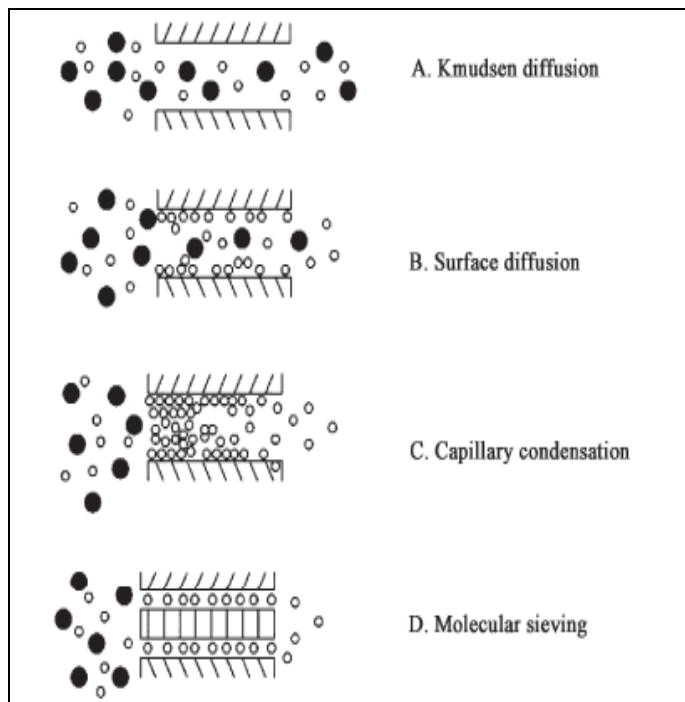


Figure 2.8: Transport mechanism through micro porous membranes (Shekhawat *et al.*, 2003).

2.5.3 Carbon Membrane

Carbon membranes for gas separations are typically produced by the pyrolysis of thermosetting polymers. The pyrolysis temperature, typically in the range of 500 to 1,000°C, depends upon the type of precursor material and dictates the separation performance of the carbon membranes (Shekhawat *et al.*, 2003). Pyrolysis of polymeric compounds leads to carbon material with a narrow pore size distribution below molecular dimensions (< 1 nm), which makes it possible to separate gases with very similar molecular sizes. The predominant transport mechanism of most carbon membranes is molecular sieving. The selection of precursor polymer, the membrane preparation method, and the carbonization process determine the performance of carbon molecular sieve membranes.

The mechanical stability can be improved by supporting a thin carbon membrane on a porous support material, such as α - alumina. The high thermal and chemical stability of these membranes provide hope in gas separation applications, such as separation of CO₂ in flue gas emissions from power plants.

2.5.4 Alumina Membrane

The generally mesoporous structure of alumina dictates that transport within such membranes by a Knudsen diffusion mechanism (Shekhawat *et al.*, 2003). With mixtures such as CO₂/N₂, where the gases have similar mass, and CO₂/H₂, where selectivity toward the heavier component is required, alumina is undesirable as a material for membrane separation layer. Alumina finds its use in the separation of gases mainly as support, where its sound structural properties, and chemical and hydrothermal stabilities beyond 1,000°C make it very desirable. A few attempts have been made to modify alumina membranes to facilitate CO₂ surface diffusion with limited success. In order to achieve high separation factors in systems like CO₂/N₂, an interaction between one of the gases in the mixture and the membrane surface can be introduced by chemical modification of separation layers.

2.5.5 Silica Membrane

Silica is a viable starting material for the fabrication of CO₂ selective membranes, primarily because of its innate stability and easy modification of its structures. Unlike alumina, which tends to undergo phase transition at relatively low temperature, or carbon, which can exhibit substantial changes in pore size in oxidizing environments, silica shows exceptional thermal, chemical, and structural stability in both oxidizing and reducing environment. Sol-gel method and chemical vapor deposition (CVD) technique are used to prepare silica membranes.

2.5.6 Zeolite Membrane

Zeolites are crystalline aluminosilicates with a uniform pore structure and a minimum channel diameter range of 0.3 to 1.0 nm. The presence of molecular-sized cavities and pores make the zeolites effective as shape-selective materials for a wide range of separation applications. This ability to selectively adsorb molecules by size and polarity is the key to the unusual efficiency of synthetic zeolites as the basis for gas separation. Separation occurs in zeolite membranes by both molecular sieving and surface diffusion mechanisms. Zeolite membranes are usually prepared by *in-situ* hydrothermal synthesis on porous stainless steel, α -alumina, or γ -alumina support tubes or disks for the gas permeation studies.

Membranes of various zeolites, such as ZSM-5 (Kusakabe *et al.*, 1996), Y type (Kusakabe *et al.*, 1997), silicalite (Lin *et al.*, 2000), A type (Aoki *et al.*, 2000), P type (Dong and Lin, 1998), modernite (Bernal *et al.*, 2000), and silicoaluminophosphate (Poshusta *et al.*, 2000) have been synthesized on porous supports. Typically the heat of adsorption of gases on most zeolites increase in this order: H₂ < CH₄ < N₂ < CO₂ (Poshusta *et al.*, 2000). This order is consistent with the electrostatic properties of each molecule. Carbon dioxide preferentially permeates in CO₂/N₂, CO₂/CH₄, and CO₂/H₂ mixtures at low temperatures, because CO₂ adsorbs more strongly on zeolites than the other gases. For the CO₂/N₂ and CO₂/CH₄ mixtures,

CO₂ is smaller in size and thus permeates faster at elevated temperature. However, the selectivities are the same for the CO₂/N₂ or CO₂/CH₄ systems at elevated temperatures due to the absence of competitive adsorption.

Mixed-matrix and hybrid membranes

These molecular sieves possess superior gas transport properties, but have significant problems with their processibility. Incorporation of molecular sieves within a polymer membrane possibly provides both the processibility of polymers and selectivity of molecular sieves (Nomura *et al.*, 1997). Many research direct at mixed-matrix membranes; the polymer-zeolite pairs include polydimethylsiloxane-silicalite (Tantekin-Ersolmaz *et al.*, 2000), polyimide-carbon molecular sieve (Vu *et al.*, 2003), polyimide-silica (Kusakabe *et al.*, 1996), Nafion-zirconium oxide (Apichatachutapan *et al.*, 1996), HSSZ-13-polyetherimide (Husain and Koros, 2007), acrylonitrile butadiene styrene-activated carbon (Anson *et al.*, 2004). It is known that the permeability of a gas through a zeolite-filled polymeric membrane depends on the intrinsic properties of the zeolite and the polymer (Tantekin- Ersolmaz *et al.*, 2000).

However, their performance suffers from defects caused by poor contact at the molecular sieves/polymer interface. This can allow the gases to flow non-selectively around the solid particles. Sonication and decantation techniques have been suggested to overcome this issue (Vu *et al.*, 2003). The successful implementation of this membrane development depends on both, the selection of polymeric matrix and inorganic zeolite, and the elimination of interfacial defects (Anson *et al.*, 2004). A similar concept is hybrid membrane where a porous inorganic support material is surface-modified with chemicals which have good affinity with CO₂. Strictly speaking, the hybrid membrane might better be named surface-modified inorganic membrane so that not to be confused with mixed-matrix membrane.

This helps CO₂ separation in two ways porous inorganic materials allows large flux while the chemical provides selectivity (Luebke *et al.*, 2006; Shekhawat *et al.*, 2003).

The studied chemical-inorganic pairs include polyether-silica (Kim *et al.*, 2005), trichlorosilane- γ -alumina (Luebke *et al.*, 2006), organosilane-Vycor glass (Singh *et al.*, 2004), tetrapropylammonium-silica (Yang *et al.*, 2002), titania-trimethoxysilane (Abidi *et al.*, 2006), γ -aluminatrimethoxysilane (Abidi *et al.*, 2006), hexagonal mesoporous silica-aminopropylhydroxysilyl (Knowles *et al.*, 2005; Chaffee, 2005).

2.6 Advantage of Membrane Technologies

The technologies of membrane separation have been developing to be the top of process separation. The advantage of membranes separation has been found in certain processes such as producing, separation, recovering, and drying (Koros et al 1998). The advantages are:

1. The membranes are highly selective and so it has high effectiveness in separation process.
2. The membrane based separation processes are costly effective and environmentally friendly.
3. These polymers not only exhibit better thermal and mechanical properties than natural polymer, but also presented a wide range of gas transport and separation properties.
4. Membrane processes are characterized by low energy consumption, possibility of different module design and easy scale up. These advantages make processes superior to many other established separation processes.
5. Membrane process is able to recover minor but valuable components from a main stream without substantial costs.
6. The separation process of membrane do not used large or complex machine that have to more from a part of plant to another plant. It only consist some instrument that is easy to operate. This process can be continuously.

2.7 Membrane Separation Processes

Transport through the membrane takes place when a driving force is applied to the components in the feed. In most of the membrane processes, the driving force is a pressure difference or a concentration (or activity) difference across the membrane. Parameters such as pressure, concentration (or activity) and even temperature may be included in one parameter, the chemical potential μ . Another driving force in membrane separations is the electrical potential difference.

2.8 Gas Separation Using Membrane

Gas separation membrane, currently, only eight or nine polymer materials have been used to make at least 90% of the total installed gas separation membrane base. Several hundred new polymer materials have been reported in the past few years, and many have substantially higher permeabilities and selectivities. Thus, it is surprising that so few are actually used to make industrial membranes. However, permeability and selectivity are only two of the criteria that must be met to produce a useful membrane; others include the ability to form stable, thin, low-cost membranes that can be packaged into high-surface-area modules. To obtain high permeation rates, the selective layer of gas separation membranes must be extremely thin (Pinnau *et al.*, 1999).

To date, two-thirds of the total gas separation market has involved the separation of nitrogen or water from air and of hydrogen from ammonia purge gas or syngas. These are clean gas streams, free of components that might foul or plasticize the membrane, so hollow-fiber modules function well. However, growing application areas for membranes are in natural gas treatment, refineries, and petrochemical plants, where the gas streams contain high levels of plasticizing, condensable vapors that degrade membrane performance.

The gas might also contain suspended particulates or oil mist, which are easily trapped in stagnant areas of the module and lead to irreversible membrane fouling. The gas streams also vary in composition and flow. To address these issues, robust membrane systems able to handle changes and upsets are required. Significantly more careful and expensive pretreatment to avoid these problems is required in hollow-fiber membrane systems than in spiral-wound units. The balance between the benefits of low-cost hollow-fiber and more reliable spiral wound modules is more even in these applications. (Pinnau *et al.*, 1999). Gas separation using membrane was shown in Figure 2.9.

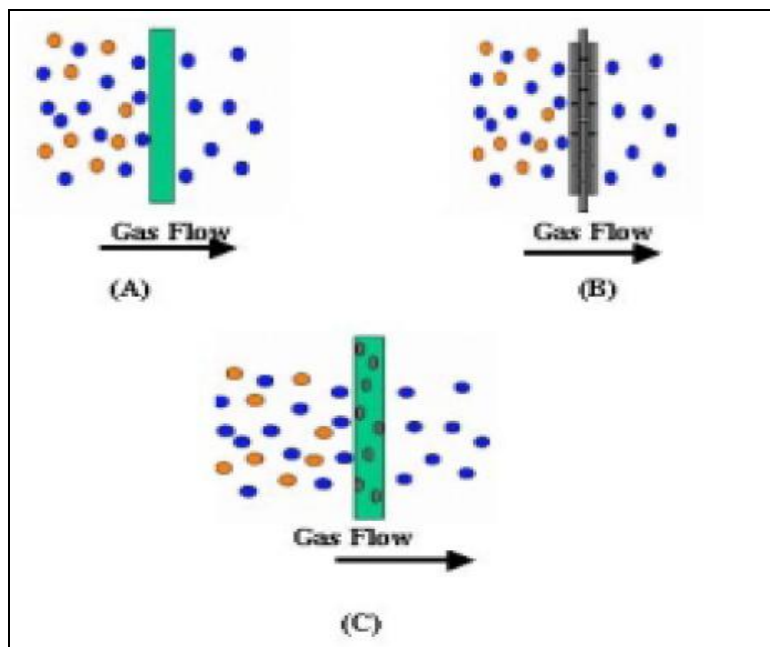


Figure 2.9: Gas separation using membrane

2.9 Membrane Formation

Membrane can be formed by using phase inversion techniques: thermal precipitation, air casting of dope solution, precipitation from the vapor phase and immersion precipitation (Wilson,2000).Figure 2.10 show the phase inversion technique

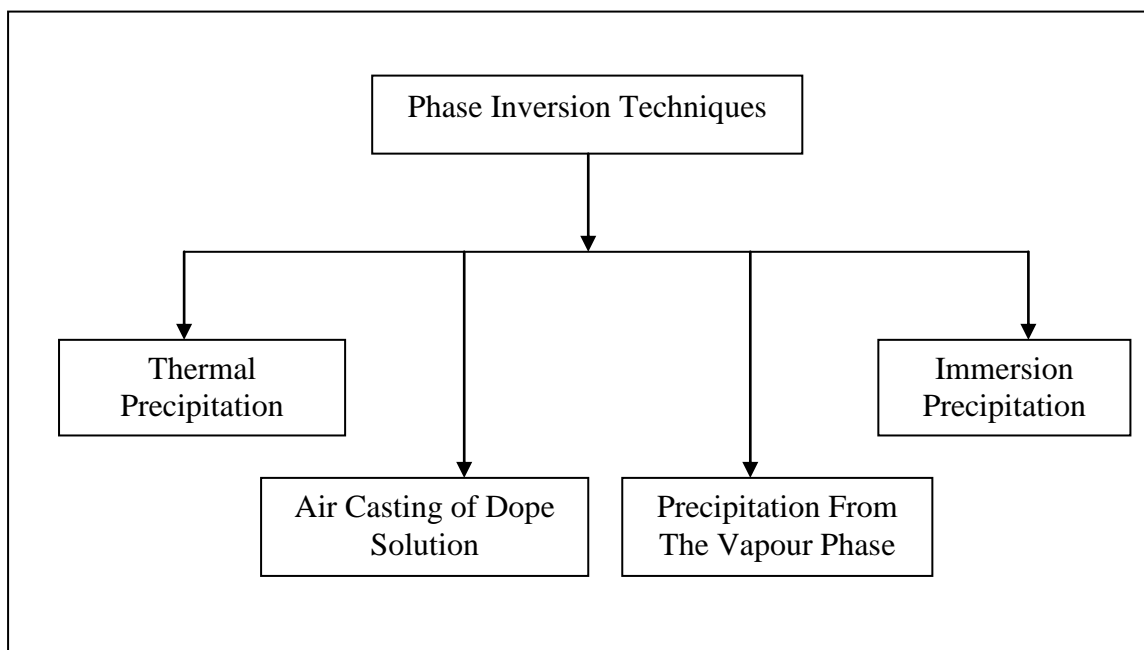


Figure 2.10: Phase inversion techniques

2.10 The mechanism of Membrane Formation by Phase Inversion Separation

Membrane gas separation by polymer membrane is a proven technology and has been found in a wide range of industrial applications. Membranes can be prepared by phase inversion techniques and can be categorized into four different techniques.

In the air casting technique process, the polymer is dissolved in a mixture of a volatile solvent and less volatile nonsolvent. During the evaporation of the solvent, the solubility of the polymer decreases and then phase separation take place (Van, 1996).

In the precipitation from the vapor phase process, phase separation of the polymer solution is induced by penetration of nonsolvent vapor in the solution. Thermal induced phase separation (TIPS) technique is based on the phenomenon that the solvent quality usually decreases when the temperature is decreased. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying. In the immersionprecipitation case, a polymer is cast as a thin film on a support or extruded through a die, and is subsequently immersed in a nonsolvent bath. Precipitation can occur because of the good solvent in the polymer solution is exchanged with nonsolvent in the coagulation bath. The differences between the four techniques originate from differences in the desolvation mechanisms (Van *et al.*,1996).

Among these techniques, immersion precipitationis widely used to produce commercial gas separation membranes and other membrane based separation (Van *et al.*, 1996). Immersion precipitation technique can be further divided into three categories namely wet, dry and dry/wet phase inversion technique as shown in Figure 2.11.

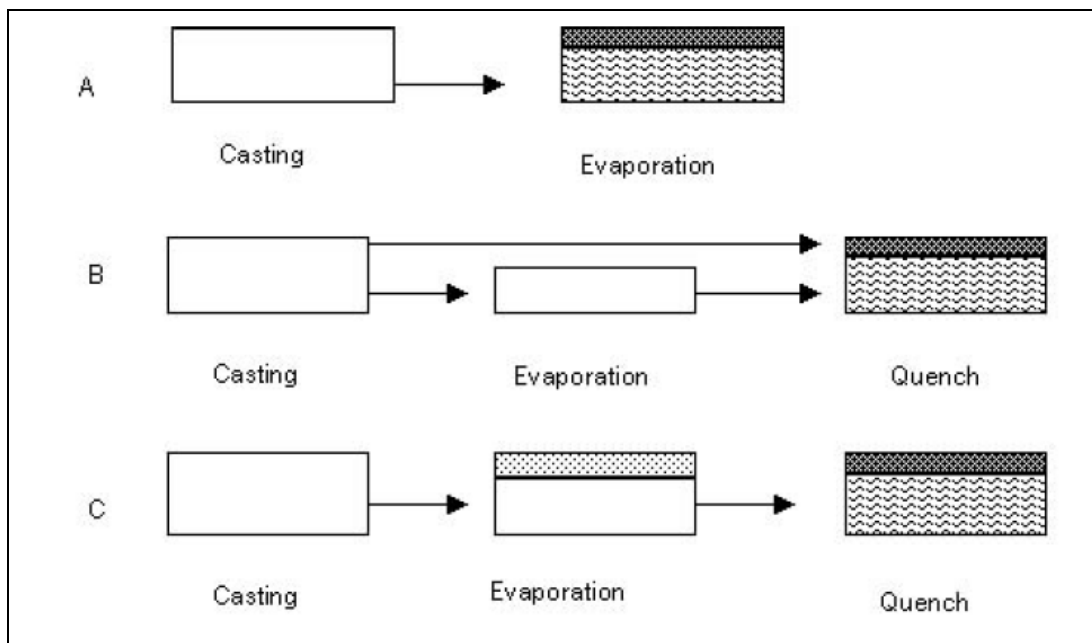


Figure 2.11: Schematic representations of immersion precipitation phase inversion processes: (A) dry, (B) wet, (C) dry/wet.

2.10 Research Done by Other Researcher

The current research done by other researcher was the gas separation performance of a mixed matrix membrane flat sheet based on polyethersulfone/polyimide miscible blend incorporated with zeolite particles. The ideal separation factors of O₂/N₂ were higher compared to the value reported for the PES/PI blend has significant effects on the membrane structure and properties. At low shear rates, the permeability of oxygen and permeability of nitrogen decreased, while the their selectivity of oxygen and nitrogen increased (Ismail *et al*, 2008).

Another research has proved that the selectivity of the coated polyethersulfone membrane was relatively higher than uncoated membrane. The selectivity was found to be 7.95 at 32.67% of polyethersulfone concentration. (Ismail *et al*, 2008)

Table 2.3: Summary of research done by other researcher

Researcher	Membrane Material	Findings
Serkov and Kanchih, 1977	Polymeric membrane	Found that preorientation was developed during precipitation, which significantly determined the subsequent stretch ability, structure and physical properties of the spun fibers.
Brandrup, 1989	Polymeric membranes, such as polysulfone and cellulose acetate	Have low CO ₂ /CH ₄ and CO ₂ /H ₂ selectivities and, more importantly, high H ₂ permeabilities and are therefore inadequate.
Tantekin-Ersolmaz <i>et al</i> , 2000	Polymeric membrane	Zeolites may be useful in enhancing the permeability and selectivity of polymeric materials when the correct zeolite-polymer pair is selected
Tai et al., 2004	Polyethersulfone	α_{PO_2} =10.8 GPU and α_{CO_2/N_2} =6.0 (25C) - Heat treatment 75 c improves the gas permeance and ideal selectivity, - Heat treatment 150 c reduce permeance and selectivity
Ying Kong et al, 2008	Polyethylene glycol and polyethersulfone	- α_{S_2} =3.63, α_{CO_2} =3.37 kg/m ² h

CHAPTER 3

RESEARCH AND METHODOLOGY

3.1 Material Selection

3.1.1 Polyethersulfone (PES)

Polyethersulfone is a heat resistant, transparent, amber, non-crystalline engineering plastic. Polyethersulfone was tough and rigid resin similar to conventional engineering plastic such as, polycarbonate, at room temperature. Produces membranes with higher porosity, well-interconnected pores and surface properties that are different from the properties of the pure membrane forming polymer.

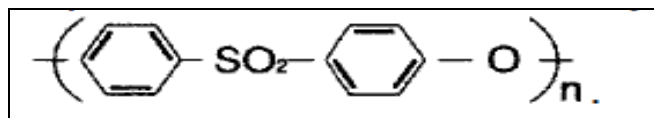


Figure 3.1: Polyethersulfone (PES) molecular structure (Salamone, 1998)

The greatest characteristic of PES is that it has by far better high-temperature properties than conventional engineering plastics. Specifically, PES remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200°C. The physical properties of polyethersulfone was shown in Table 3.1.

Table 3.1 : Physical properties of polyethersulfone

Physical Properties	Unit
Density	1.37 g cm ⁻³
Flammability	V-0 @ .4mm
Radiation resistance	Good fair
Lower working temperature	-110°C
Initial tear strength	7.5- 16.9 g μm ¹
Water absorption - equilibrium	2.2%
Water absorption- over 24 hours	0.4-1%

3.1.2 N-Methyl-2-pyrrolidone (NMP)

N-Methyl-2-pyrrolidone (NMP) is a water miscible organic solvent with formula C₅H₉NO. It has hygroscopic colorless liquid to slightly yellow liquid with a mild amine odor. It miscible with water and conventional organic solvent. NMP belongs to dipolar aprotic solvent which also includes the di methylformamide and dimethyl sulfoxide.

3.1.3 Methanol

Methanol is light, volatile colorless, flammable, poisonous liquid with a distinctive odor that was somewhat milder and sweeter than ethanol. At room temperature it was a polar liquid and was used as an antifreeze, solvent, fuel and as a denaturant for ethyl alcohol. It was also used for biodiesel via transesterification reaction (Cheng *et al.*, 1994). The physical properties of methanol was shown in Table 3.2.

Table 3.2: Physical properties of methanol

Physical properties	Unit
Molar mass	32.04 g/mol
Appearance	Colorless liquid
Density	0.7918g/cm ³
Melting point	097 °C (176K)
Boiling point	64.7° C (337.8)
Solubility in water	Fully miscible

3.1.4 Bromine

Bromine is the only liquid nonmetallic element at room temperature. The Melting point bromine was 7.2 degree celcius.and has the boiling point 58.8 degree celcius. It was a dense, mobile, reddish-brown liquid, that evaporates easily at standard temperature and pressures to give a red vapor that has strong disagreeable odor resembling that of chlorine. It bonds easily with many elements and has a strong bleaching action (West,2007)

3.2 Research Design

The flowchart of the research design for this study was shown in Figure 3.2.

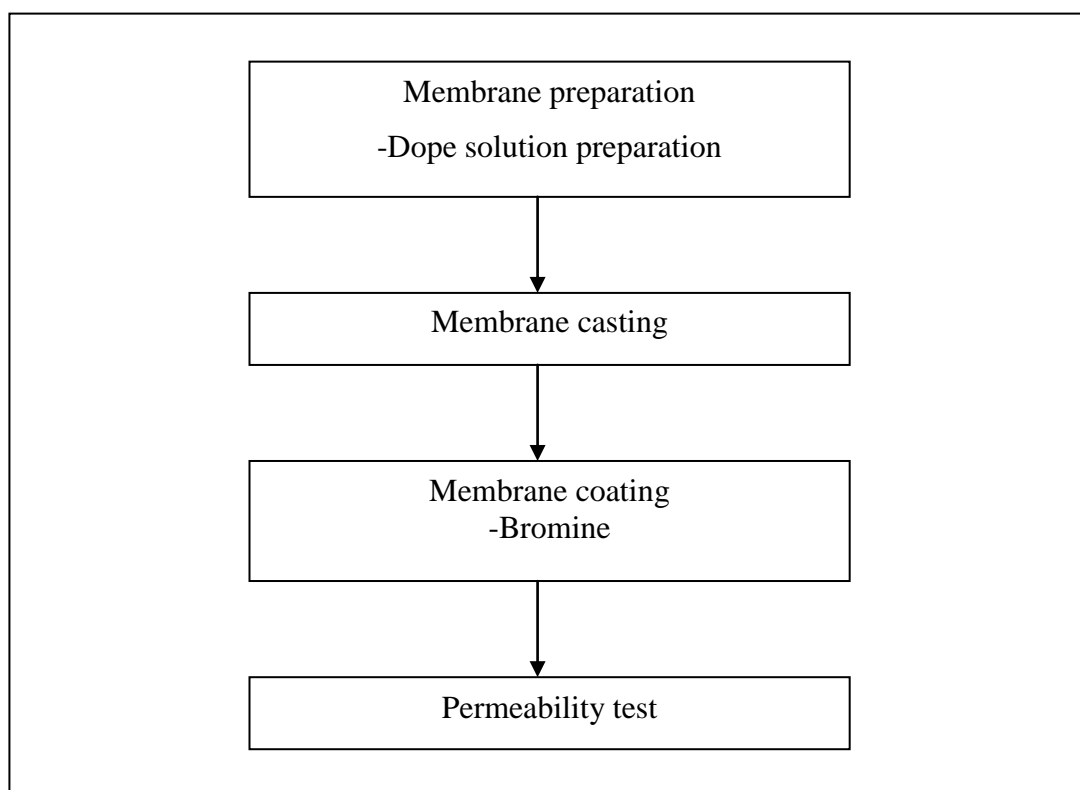


Figure 3.2: Flowchart of membrane preparation, characterization and permeation test.

3.3 Membrane Preparation

In this study, membrane preparation involved a stage which is preparation of dope solution. After dope solution was prepared so that the solution can be cast and immersed to get the flat sheet membrane before coating process done to seal any defects on the membrane produced.

3.3.1 Dope Solution Preparation

The polymer was dried for 1 day in a vacuum oven in order to remove all absorbed water.vapor. Then it was dissolved in NMP and methanol. Methanol was used to prevent complete removal of the glycol during routine washing such that the membrane as produced is hydrophobic. The nonsolvent additive can be any low molecular weight aliphatic glycol which not sufficiently attracted to the polyethersulfone. The solution stirred with heating temperature of 40-60 degree celcius to achieve homogeneity. The solution was kept in a storage bottle and degassed by using ultrasonic bath to remove any traces air bubble.

3.3.2 Membrane Casting

Using manually casting knife, polyethersulfone membranes was prepared according to dry/wet phase separation process followed by immersion in a nonsolvent bath and membrane drying. Casting process was conducted at room temperature. A small amount of casting solution was poured onto a glass plate. Before immersed into the coagulation medium, evaporation was done on membrane during the casting process. Then, glass plate and the membrane were immersed into the coagulation with water as the coagulant medium. The membrane was transferred to a water bath for 1 day after the coagulation process complete. Finally the membrane were washed with methanol for 1 day. The membrane was dried for at least 2 days at room temperature.

3.3.3 Membrane Coating

3 wt% of coating solution was prepared by dissolving bromine in distilled water and measure their PH until 2. The membrane was dipped in the beaker for two days, then they were dried at room temperature for one day. The membrane was cut into a circular disc.

3.3.4 Gas Permeation Test

The experiment was carried out at room temperature with the set of pressure drop 2 bar. The membrane was cut into circular disc and tested using industrial carbon dioxide and methane with 95% purity. The permeation rate was measured by using soap bubble flow meter. The permeation rate can be calculated by using:

$$P_i = Q/A \cdot \Delta P \quad (3.1)$$

where

Q= Flowrate of gas (cm³/s)

A= Area (cm²)

ΔP = pressure in system (bar)

P_i= permeability for gas component

The selectivity can be calculated by using

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

where

P_i = permeability of one gas component

P_j = permeability of another gas component

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of Polymer Concentration on Permeability and Selectivity

Permeability and selectivity of PES membranes with respect to CO₂ and CH₄ were studied at different polymer concentration. It was expected that different permeation properties and selectivity are obtained from membranes with different concentration. Increasing polymer concentration in casting solution formed a dense and thicker skin layer, resulting in more selective but less productive asymmetric membrane for gas separation. The polymer concentration were obtained from other researcher as stated in table 4.1. Figure 4.1 shows the effect of polymer concentration on selectivity for uncoated and coated membrane with bromine.

Table 4.1: Composition of casting solution with different polymer concentration

Component	Solution Composition (wt %)		
Polyethersulfone (PES)	18%	23%	28%

4.2 Effect of Coating Agent on Membrane Performance

An average value of permeability and selectivity for uncoated membrane and coated membrane with bromine for 18%wt, 23%wt and 28% wt was tabulated in Table 4.2. This average value was taken from the average value of three times measurement for each sample and test gases.

Table 4.2 Summary of average value of separation properties of uncoated and coated membrane at different polymer concentration.

Uncoated			
Solution	Permeability CO ₂	Permeability CH ₄	Selectivity CO ₂ /CH ₄
18%	8.63x10 ⁻⁴	9.95x10 ⁻⁴	0.87
23%	7.65x10 ⁻⁴	4.97x10 ⁻⁴	1.54
28%	5.86x10 ⁻⁴	2.84x10 ⁻⁴	2.06
Coated			
Solution	Permeability CO ₂	Permeability CH ₄	Selectivity CO ₂ /CH ₄
18%	4.18x10 ⁻⁵	2.58x10 ⁻⁴	0.16
23%	6.84x10 ⁻⁵	1.81x10 ⁻⁴	0.37
28%	3.82x10 ⁻⁵	1.15x10 ⁻⁴	0.33

All of uncoated membrane showed better performance in selectivity meanwhile the coated membrane with bromine are vice versa. This probably due to the defects and enhancement of free volume in the ultra thin skin layers. Tiny defect in the skin can cause a dramatic decreased in selectivity. In order to separate a mixture of gas with a porous membrane the pore size of the membrane must be much smaller than the mean free path of the gases (Tanabe, 1999)

All of coated membrane with bromine exhibited a poor selectivity for each gas that pass through the membrane. This was due to existent of defects at the surface layer. For the uncoated membrane the CH₄ gas is permeate higher than CO₂.

This was probably due to the molecular weight of methane which is 16g/mol, much lighter than carbon dioxide 44g/mol. The smaller molecular weight the faster of the gas pass through the membrane. The higher the polymer concentrations give the less permeability (Tanabe, 1999). Therefore, to obtain high performance polyethersulfone membrane, surface layer should be free from defect.

Result of uncoated membrane exhibit better performance compared with coated membrane with bromine. From the result it was shown that the uncoated membrane selectivity produce was membrane higher than coated with bromine. A hypothesized of bromine molecules would alter the free volume distribution in such way as to hinder the transport of large gas molecules without a significant reduction in the flux of the more permeable gas (Barbari et al, 1995).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this research, the study of permeability and selectivity of polyethersulfone membrane has been completed. The analysis was to determine the permeability and selectivity of different gases that can pass through the polyethersulfone membrane. Polymer concentration has been identified as one of the factor that influences the performance of the membrane as well as coating agent. All of the coated membrane exhibited a poor selectivity but higher in permeability, probably due to the pores or defects and the enhancement of free volume in the ultrathin skin layer. It was proven that bromine is not the best coating agent for enhance the performance of membrane.

The uncoated membrane with treated with methanol showed increasing trend of membrane selectivity. It showed that coated with bromine does not given any signs as good coating agent because bromine are not polar enough to make an aromatic bonding with the polyethersulfone. The polyethersulfone membrane with the best combination of pressure-normalized flux and selectivity of CO₂/CH₄ was prepared from solution containing polymer concentration of 28% and exhibited average CO₂ pressure normalized of 586 GPU and selectivity 2.06.

Higher polymer concentration showed higher selectivity but less in permeability value. These effects were found to influence the structure of the active

layer thickness. The results clearly suggested that when polymer concentration increases, the active layer thickness will also increase.

5.2 Recommendation

It was strongly recommended that further study should be done in order to figure out the effectiveness of polyethersulfone membrane coated with other bromine. Besides that other coating agent should be used as coating agent for instance polydimethylsiloxane (PDMS) in order to enhance the performance of membrane selectivity. PDMS is a type of silicone rubber that can seal any defects occurred. On the other hand, it is also recommended to use automatic casting knife to change the manual casting knife. Automatic casting knife will definitely give more variable parameter to study such as rate of evaporation and determination of shear rate.

Formation of defect-free and ultrathinskin layer asymmetric membrane for gas separation seems to be the most challenging aspect in the production polymeric asymmetric membrane for gas separation due to its high permeability and selectivity. It is foreseen that in the future, this aspect will be concentrated in the development of defect free skin layer from various type of polymer especially polyimide, polysulfone, cellulose acetate, polyethersulfone and polyaramide.

REFERENCES

- Aguilar-Vega M, Paul D R, (1993). Gas transport properties of polyphenylene ethers. *Journal of Polymer Science Part B: Polymer Physics*. 31(11): 1577–1589.
- Aitken C L, Koros W J, Paul D R,(1992). Effect of structural symmetry on gas transport properties of polysulfones. *Macromolecules*, 25(13): 3424–3434.
- Al-Juaied M, Rochelle G T, (2006). Absorption of CO₂ in aqueous diglycolamine. *Industrial and Engineering Chemistry Research*, 45(8): 2473–2482.
- Baker, R.W. 2000. Membrane Technology and Application. Membrane Technology and Research, Inc. McGraw-Hill, New York.
- C.C. Pereira, R. Nobrega, K.V. Peinemann, C.P. Borges, (2003) Hollow fiber membranes obtained by simultaneous spinning of two polymer solutions: a morphological study, *Journal of Membrane Science*. 226 35.
- Chung, T.S., Lin, W.H and Vora., R.H. (2000). The effect of shear rates on gas separation performance of 6FDA durene polyimide hollow fibers. *J. Membr. Sci.*, 167: 55-66. D.L. Wang, K. Li, W.K. Teo, Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol systems, , *Journal of Membrane Science* 115 (1996) 85.
- D.F.Li, T.S. Chung, R. Wang, Y. Liu, (2002) Fabrication of fluoropolyimide /polyethersulfone (PES) dual-layer asymmetric hollow fiber membranes for gas separation, , *Journal of Membrane Science*. 198 (2002) 211.

- Fattah, K. A., Hamam, S. M., Al-Enez, G., Ettoueny, H. M., & Hughes, R. (1992). A nonideal model for analysis of gas separation permeators. *Journal of Membrane Science*, 65(3), 247–257.
- Feng, X., & Huang, R. Y. M. (1997). Liquid separation by membrane pervaporation: A review. *Industrial and Engineering Chemistry Research*, 36, 1048–1066.
- Gani, R., Hytoft, G., Jaksland, C., & Jensen, A. K. (1997). An integrated computer aided system for integrated design of chemical processes. *Computers and Chemical Engineering*, 21(10), 1135–1146.
- Gür, T.M. (1994). Permselectivity of zeolite filled polysulfone gas separation membranes. , *Journal of Membrane Science*, 93: 283.
- G. and Gür, T. (1989). A new composite membrane for selective transport of gases, in: Proceedings of the 6th International Symposium on Synthetic Membranes in Science and Industry. Tübingen, Germany.
- Hachisuka, H., Ohara, T. and Ikeda, K. (1996). New type asymmetric membranes having almost defect free hyper-thin skin layer and sponge-like porous matrix. *Journal of Membrane Science.*, 116: 265-272.
- H. Suzuki, K. Tanaka, H. Kita, K. Okamoto, H. Hoshino, T. Yoshinaga, Y. Kusuki, (1998) Preparation of composite hollow fiber membranes of poly (ethylene oxide)-containing polyimide and their CO₂/N₂ separation properties, . *Journal of Membrane Science.*, 146- 31.
- Ismail, A.F., Shilton, S.J., Dunkin, I.R. and Gallivan, S.L. (1997). Direct measurement of rheologically induced molecular orientation in gas separation hollow fibre membranes and effects on selectivity. . *Journal of Membrane Science.*,, 126: 133-137.
- Ismail, A.F. and Shilton, S.J. (1998). Polysulfone gas separation hollow fiber membranes with enhanced selectivity. . *Journal of Membrane Science.*, 139: 285-286.
- Ismail, A.F. and David, L.I.B. (2001). A review on the latest development of carbon membranes for gas separation. , *Journal of Membrane Science.*, 193:1-18.
- J.S. Chiou and D.R. Paul(1987), Effects of CO₂ exposure on gas transport properties of glass polymers, , *Journal of Membrane Science.*, 32 (1987) 195.

- L.M. Robeson, W.F. Burgoyne, M. Langsam, A.C. Savoca, C.F. Tien, (1994) High performance polymers for membrane separation, *Polymer* 35 4970.
- Pinnau, I.; Freeman, B. D.(2001) Formation and Modification of Polymeric Membranes: Overview in Membrane Formation and Modification; Pinnau, I., Freeman, B. D., Eds.; *ACS Symposium*
- Powell C E, Qiao G G, (2006). Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases. *Journal of Membrane Science*, 279: 1-49.aq
- R.W. Baker, (2002) *Future directions of membrane gas separation technology*, *Ind. Eng. Chem. Res.*, 41(6) 1393-1411
- R.W. Baker and K. Lokhandwala,(2008) Natural Gas Processing with Membranes: An Overview, *Ind. Eng. Chem. Res.*, 47(7) (2008) 2109–2121. 768
- S.A. Stern,(1994) Polymers for gas separations: the next decade, , *Journal of Membrane Science*. 94 -1.
- Tanaka, K.; Tabuchi, A.; Hao, J.; Kita, H.; Okamoto, K.(1996) Permeation and Separation Properties of Polyimide Membranes to Olefins and Paraffins. *J. Membr. Sci.* **1996**, 121, 197.
- Wijmans, J. G., & Baker, R.W. (1995). The solution–diffusion model—a review. *Journal of Membrane Science*, 107, 1–21.
- Wijmans, J. G. (2004). The role of permeant molar volume in the solution–diffusion model transport equations. *Journal of Membrane Science*, 237, 3950.

APPENDIX A

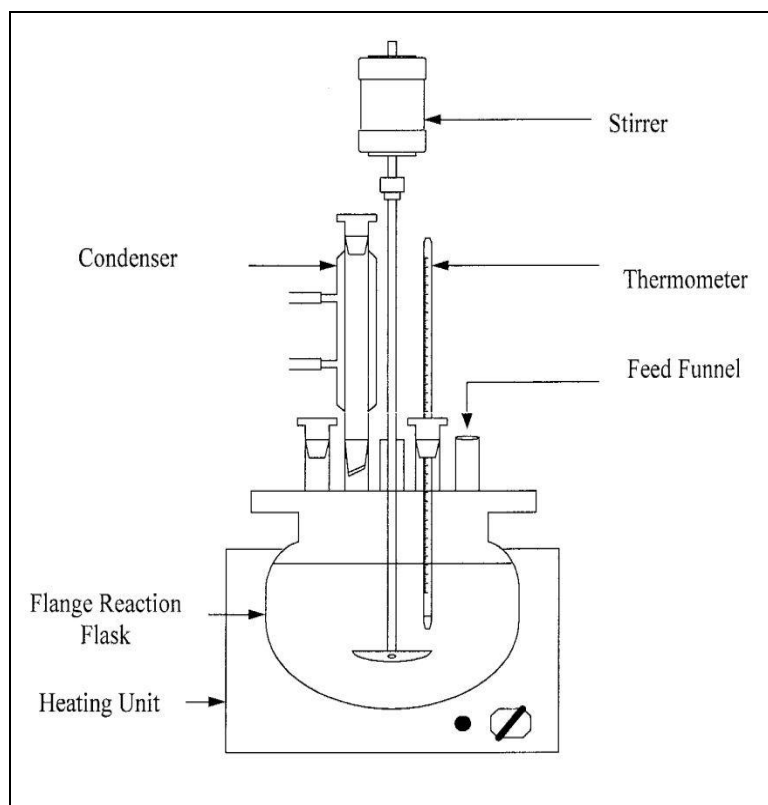


Figure A: Preparation of casting solution system (Dope preparation system)

APPENDIX B**Figure B:** Sample of dope solution

APPENDIX C**Figure C: Manual casting knife**

APPENDIX D

Figure D: Sample of membrane uncoated and coated with bromine

APPENDIX E**Figure E:** Gas permeation unit