

**EFFECT OF COATING ON PERMEABILITY AND SELECTIVITY OF
POLYSULFONE MEMBRANE FOR CO₂/CH₄ SEPARATION**

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ABSTRACT

Polysulfone membrane is one of the potential candidates to be used as membranes for gas separation. Asymmetric polysulfone (PSU) membranes were fabricated through a simple dry/wet phase inversion process. Casting solution developed in this study consisted of polysulfone, N-N dimethylacetamide (DMAc) and ethanol. The dope solution was divided into three polymer composition which is 20 wt%, 25 wt% and 30 wt%. The dope solution was cast using manual casting knife at room temperature. Three membrane samples was produced with different polymer composition; uncoated membrane (A), membrane coated with bromine and treated with methanol (B) and membrane coated with bromine without methanol treatment (C). Permeability of the membrane was examined by using gas permeation test with pure CO₂ and CH₄ as tested gas. The results showed that the selectivity of the PSU membrane increased respectively with the decreasing of polymer concentration and coating treatment have a significant effect on membrane performance. The best membrane selected is membrane B which is polysulfone membrane with 20 wt% polymer composition treated with methanol and coated with bromine. From the data and supported theories by various authors, it can be conclude that coating treatment have a significant effect on membrane performance.

ABSTRAK

Membran polisulfona adalah merupakan salah satu membran yang sesuai digunakan sebagai membran untuk proses pemisahan gas. Membran polisulfona dibuat melalui fasa proses balikan kering/basah. Membran polisulfona dihasilkan dengan proses sebatian dengan partikel polimer polisulfona, N,N dimethylacetamide (DMAc), dan cecair etanol. Terdapat tiga kandungan komposisi polimer polisulfona yang berbeza dihasilkan iaitu 20%, 25% dan 30%. Kepingan membran polisulfona kemudian dibentuk dengan menggunakan pisau khas untuk menghasilkan kepingan membran. Tiga kepingan polisulfona membran yang berbeza diuji iaitu membran A ialah membran yang tidak disalut dengan agen salutan, membran B ialah membran yang disalut dengan agen salutan iaitu bromin dan dirawat dengan metanol dan membran C ialah membran yang disalut dengan bromin tapi tidak dirawat dengan metanol. Ketelapan pada kepingan membran boleh diuji dengan menggunakan set unit ketelapan gas. Kepingan membran diuji dengan gas karbon dioksida dan juga gas metana. Hasil eksperimen yang telah dikumpul menunjukkan kepingan membran yang terbaik adalah membran B yang mengandungi komposisi polimer polisulfona sebanyak 20% yang disalut dengan bromin dan dirawat dengan metanol. Daripada data-data terkumpul dan teori yang disokong oleh penyelidik yang lain, dapat disimpulkan bahawa polimer membran yang dirawat penting bagi memastikan peningkatan prestasi ketelapan dan pemilihan membran.

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LIST OF NOMENCLATURE

%	-	Yield percentage
°C	-	Degree Celsius
T	-	Extraction temperature
V	-	Volume
Q	-	Flow rate of supplied gas (cm ³ /s)
A	-	Area of membrane (cm ²)
α	-	Selectivity
P _{CO2}	-	Permeability of CO ₂
P	-	Constant of permeation
μ	-	Micro
MPa	-	Mega Pascal
KPa	-	kilopascal
T	-	temperature
m	-	Molecular mass
ξ	-	Porosity membrane

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Over the past three decades, membrane processes have been adopted to perform variety of separation operations by different industries. The efficiency as well as the economics of the various industrial processes can be greatly improved if the membrane processes are suitably integrated in the exiting process, particularly, where fractionation of a set of components is more desired than total conversion or separation (Chaturvedi *et al*, 2001).

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 of 1970s. In order to extend its application and compete successfully with traditional gas separation processes such as cryogenics, pressure swing adsorption and absorption, great attention has been made in fabricating high separation performance membranes in both academia and industry. Development of ultrathin-skinned asymmetric hollow fibre membranes from highly selective polymers has been a challenge in gas separation membrane processes (Baker, 1991).

Currently, the only commercially viable membranes used for carbon dioxide removal are polymer based, for example, cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide. Amine systems are too complex and expensive if compare by using polysulfone membrane. Polysulfone membrane is just a small system which at this flow rate membrane unit very attractive. Besides, the advantages by using polysulfone membrane are low pressure loss filter made of hydrophilic asymmetric polysulfone membrane, uniform pore size structure provides consistent filter ratings, there are no pore size changes and media migration, lower pressure drop elongates filter service life is extended and excellent chemical resistance.

The use of membranes for separation is one of the most important recent developments in process engineering and environmental protection especially in gas separation process to separate gas carbon dioxide. The permeability of solutes at such films depends primarily on size, charge and dielectric effects (Bowen *et al*, 2000). The challenges of this study is to identify selectivity and high permeability for a better in separating in gas separation and to get constant quality upgrade to optimize membrane performance and systems for specific application.

1.2 Problem Statement

Membranes have become an established technology for carbon dioxide (CO₂) removal since their first use in this application in 1981. Gas permeation is already applied industrially to remove carbon dioxide from natural gas (Meyer *et al*, 1991). Carbon dioxide, which falls into the category of acid gases (as does hydrogen sulfide, for example) is commonly found in natural gas streams at level as high as 80%. In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed. Carbon dioxide also reduces the heating

value of a natural gas stream wastes pipeline capacity. In LNG plants, CO₂ must be removed to prevent freezing in the low temperature chillers.

One of the major problems confronting the use of membrane based separation processes in a wide range of applications is the lack of membranes with high flux and high selectivity. During fabrication, membrane formation process plays an important role and certain factors need proper attention in order to produce a good separation membrane. Currently, membrane separation technologies are challenged to maintain their favorable economics while improving the selectivity, flux and durability (Kawakami *et al*, 1996). It was proven that there had been a trade off between selectivity and permeability; high selectivity tends to exhibit less permeability and vice versa. On the other hand, the thinner skin and porous skin layer most probably provide higher flux but poorer rejection due to structural stability problem.

Therefore the membrane performance should be optimized in such a way to enhance other advantages features of membrane. To produce a good membrane quality and performance, the techniques and parameters to control the membrane properties are crucial to be studied and identified. The knowledge in the material selection, solution preparation, preparation environment and technique that contributes to the final morphology of the membrane should be fully understood.

1.3 Objectives of the study

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

1.4 Scope of Study

In order to achieve the objective, the scope of research was to fabricate flat sheet membrane for the usage of permeating gas such as carbon dioxide (CO₂) and methane (CH₄). The permeability and selectivity of polysulfone membrane were tested at different concentration. Furthermore, determination of effect on different coating agent and polymer concentration were investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Membrane

Membrane is clearly the most important part of the separation process. A membrane is a thin, flexible layer of tissue that covers, lines, separates, or connects cells or parts of an organism. A membrane can be described as a thin barrier between two bulk phases that permits transport of some components but retain others. Membrane is also defined as a thin sheet of natural or synthetic material which is permeable to substances in solution (Torrey, 1984).

Membranes that are used in industrial practice can be classified into various manners according to membrane materials, structure, and shape. Membrane material may be organic, inorganic, solid, and liquid. Membrane structure may be dense, porous, composite, or multilayered, or when manufactured from organic and polymeric materials, as hybrid membranes. Biologists who studied osmotic phenomenon used the first membranes of animal and plant origin. The first polymeric materials used as membranes were derived from cellulose nitrate, cellulose acetate or regenerated cellulose, e.g., celluloid, collodian, cellophone and rayon (Traube *et al*, 1867).

A membrane is a permeable or semi-permeable phase, often a thin polymeric solid, which restrict the motion of certain species. This added phase is essentially a barrier between the feed stream for separation and one product stream. This membrane or barrier controls the relative rates of transport of various species through itself and thus, as with all separations, gives one product depleted in certain components and a second product concentrated in these components.

The performance of a membrane is defined in terms of two simple factors, flux and selectivity, which flux defined as permeation rate; volumetric (mass or molar) flowrate of fluid passing through the membrane per unit area of membrane per unit time, while selectivity for mixtures of miscible liquids and gases defined as separation factor is the ratio of the concentration in the permeate divided by that in the feed of two components (Scott, 1996).

2.2 Types of Membrane

There are a variety of membrane are used in gas separation. In essence, a membrane is nothing more than a discrete, thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for example, containing holes or pores of finite dimensions or consisting of some form of layered structure (Scott, 2003).

For this research, non porous membrane will be considered. That is because, nonporous, dense membranes consist of a dense film through which permeates are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various component 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, non porous, dense membrane can separate permeates of similar size if their concentration in the membrane material (solubility) differs significantly. Most gas separation, use dense membranes to perform the gas separation (Geankoplis, 2003).

Even though non porous membrane are suitable and had choose for gas separation process , by the way at below will be describe the other type of membrane just for basic knowledge and to differ between non porous membrane and to the others.

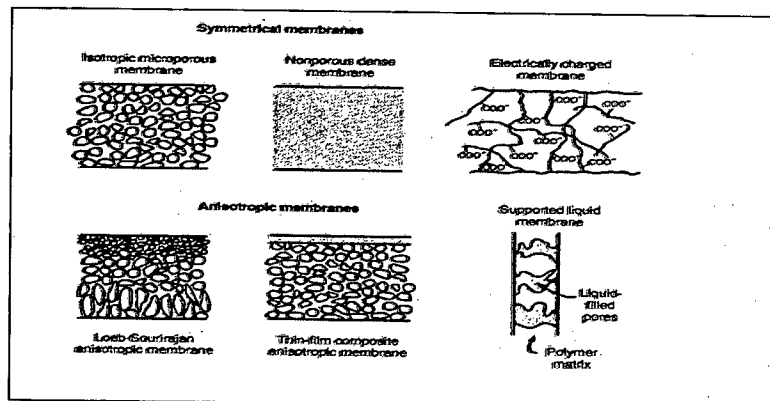


Figure 2.1: Schematic diagrams of the principle type of membranes
(Baker, 2004)

2.2.1 Microporous Membranes

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.

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

Thus, 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, in ultrafiltration and microfiltration (Geankoplis, 2003).

2.2.2 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 advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial process use such membranes (Scott, 1998). Asymmetric membranes consists of two structurally distinct layer, one of which is a thin, dense selective skin or barrier layer and the other a thick, porous matrix substructure layer whose main function is to provide a physical support for the skin (Pandey, 2001).

2.2.3 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 (Geankoplis, 2003).

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. Usually these membranes have an anisotropic structure to improve the flux (Geankoplis, 2003).

2.2.4 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 low separation and low selectivity (Pandey, 2001).

2.3. The Mechanism of Membrane Separation

There are five possible mechanisms for membrane separation (Paul *et al*, 1982). Knudson diffusion, molecular sieving, solution-diffusion separation, surface diffusion and capillary condensation, of which the first three are schematically (Fritzsche *et al*, 1990). Figure 2.2 shows mechanisms for membrane gas separation.

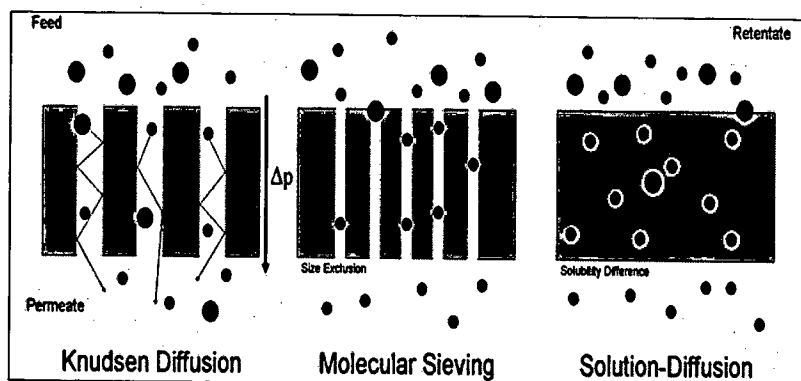


Figure 2.2: Schematic representation of three of the different possible mechanisms for membrane gas separation, Knudsen diffusion, molecular sieving and solution-diffusion (Yompulskii, 2008).

2.3.1 Molecular Sieving

Molecular sieving are the main mechanisms for nearly all gas separating membranes. Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules (Fritzsche *et al*, 1990).

2.3.2. Knudson Diffusion

Knudson separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls, which is related to the molecular weight. Specifically, the selectivity for any gas pair is determined by the inverse ratio of the square root of their molecular weight. For selectivity carbon dioxide over nitrogen (CO_2/N_2) and carbon dioxide over hydrogen (CO_2/H_2) separation, Knudsen diffusion predicts a selectivity of less than unity (Hughes, 1996).

2.3.3 Solution Diffusion

Surface diffusion is the migration of adsorbed gases along the pore walls of porous membranes (Hwang *et al.*, 1975). The rate of surface diffusion is determined by the level of interaction between the adsorbed gases and pore surface (Hill *et al.*, 1956).

This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Hence, separation is not just diffusion dependent but also reliant on the physical-chemical interaction between the various gas species and the polymer, which determines the amount of gas that can accumulate in the membrane polymeric matrix. The relationship between permeability, diffusivity and solubility can be described by:

$$P = Q/A\Delta P \quad (2.1)$$

where P is the permeability coefficient, a measure of the flux of the membrane ($\text{cm}^3(\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$). The common unit of permeability is the barrer ($10^{-10} \text{cm}^3(\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$). D is the diffusivity coefficient ($\text{cm}^2 \text{s}^{-1}$), the mobility of molecules within the membrane and S the solubility coefficient ($\text{cm}^3(\text{STP}) \text{cmHg}^{-1}$), which measures the solubility of gas molecules within the membrane. For ideal gases, the permeability is related to the gas permeation rate through the membrane (Q), the surface area of the membrane (A), and the driving force for separation, the pressure difference across the membrane. The ideal selectivity (α) of one gas, A, over another gas, B, is defined as:

Selectivity

$$\alpha = \frac{P_A}{P_B} \quad (2.2)$$

Where, P_A = Permeability of desired gas (CO_2)

P_B = Permeability of other component gas (CH_4)

2.4 Membrane Modules

Industrial membrane plants often require hundreds to thousands of square meters of membrane to perform the separation required on a useful scale. Before a membrane separation can be performed industrially, therefore, methods of economically and efficiently packaging large areas of membrane are required. These packages are called membrane modules. The development of the technology to produce low-cost membrane modules was one of the breakthroughs that led to commercial membrane processes in the 1960s and 1970s.

The earliest designs were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press: these are called plate and frame modules. Membranes in the form of 1 to 3 cm diameter tubes were developed at about the same time. Both designs are still used, but because of their relatively high cost they have been largely displaced in most applications by two other design the spiral-wound module and the hollow fiber module.

Despite the importance of membrane module technology, many researchers are astonishingly uninformed about module design issues. In part this is because module technology has been developed within companies, and developments are only found in patents, which are ignored by many academics. The following sections give an overview of the principal module types, followed by a section summarizing the factors governing selection of particular types for different membrane processes.

Cost is always important, but perhaps the most important issues are membrane fouling and concentration polarization. This is particularly true for reverse osmosis and ultrafiltration systems, but concentration polarization issues also affect the design of gas separation and pervaporation modules.

2.4.1 Plate and Frame Modules

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 2.3. 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.

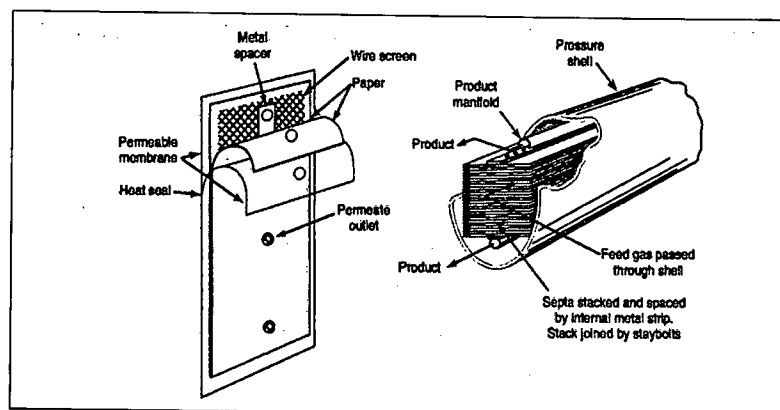


Figure 2.3: Early plate-and-frame designs developed for the separation of helium from natural gas (Baker, 2004).

Plate-and-frame units have been developed for some small-scale applications, but these units are expensive compared to the alternatives, and leaks through the gaskets required for each plate are a serious problem. Plate-and-frame modules are now only used in electrodialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration applications with highly fouling feeds (Gunther, 1965).

2.4.2 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 tubes. 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 (Baker, 2004).