EFFECTS OF COAGULATION MEDIUM ON ASYMMETRIC POLYETHERSULFONE MEMBRANE FOR CABON DIOXIDE AND METHANE SEPARATION

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

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DECEMBER 2010

ABSTRACT

This study is concentrated on the ability and the performance of the asymmetric polyethersulfone membrane in gas separation process. Asymmetric flat sheet membranes were prepared by using a simple dry/wet phase inversion method. Experimental investigations were conducted focusing on the effect of the different coagulation medium during the phase inversion toward the permeability and the selectivity of the membrane to the carbon dioxide and methane gases. Three different coagulants medium were used which were water, methanol and water/methanol (50:50). The flats sheet asymmetric membrane then being characterized by using the scanning electron microscopy (SEM) and the Fourier transform infrared spectroscopic (FTIR). Gas permeation tests then run to examine the effect of the different coagulants toward the time of the gases pass through the membrane. From the result of the gas permeability unit calculation, membrane which immersed in water solution has shown the highest permeability. Different coagulant medium will affect the performance of the membrane toward its permeability and selectivity of gases. The water medium solution is the best coagulation medium for the asymmetric polyethersulfone membrane during the phase inversion method with the GPU value of 3.23. As for the conclusion, water is identified as the best coagulation medium for asymmetric polyethersulfone membrane.

ABSTRAK

Kajian ini tertumpu kepada kebolehan dan prestasi membrane poliethersulfone asimetrik dalam proses pengasingan gas. Membrane asimetrik datar lembar disediakan melalui proses pegeringan dan pembasahan. Kajian dijalankan memfokuskan tentang kesan-kesan koagulasi medium yang berbeza-beza terhadap ketelapan dan selektivitas karbon dioksida dan gas metana. Tiga jenis koagulasi medium yang berbeza digunakan iaitu air, metanol, dan campuran air/metanol (50:50). Membrane asimetrik datar lembar kemudiannya ditandakan mengunakan scanning electron microscopy (SEM) dan fourier transform infrared spectroscopic (FTIR). Perngujian ketelapan gas kemudianya dijalankan untuk megetahui kesan koagulasi medium yang berbeza terhadap masa yang melalui membrane. Daripada keputusan pengiraan unit ketelapan gas, membrane yang direndam ke dalam air menunjukkan ketelapan yang tertinggi. Koagulasi medium yang berbeza akan mempengaruhi prestasi ketelapan dan selektivitas membrane tehadap gas-gas yang diuji. Air merupakan koagulasi medium yang terbaik untuk membrane poliethersulfone asimetrik semasa proses fasa inversi dengan nilai GPU ialah 3.23. Konklusinya, air telah dikenalpasti sebagai koagulasi medium terbaik untuk membrane poliethersulfone asimetrik.

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ABBREVATIONS

PES - Polyethersulfone polymer

DMAc - N, N – Dimethylacetamide

CO_2 - Carbon dioxide

CH_4 - Methane

GPU - Gas Permeation Unit

C_2H_6 - Ethane

CO - Carbon monoxide

N_2 - Nitrogen

H_2 - Helium

PARAMETERS/SYMBOL

J - Membrane flux

k - Solubility of gas in Membrane

D - Diffusion Coeffient of Gas Through Membrane

Δp - Partial Pressure Different

l - Membrane thicknes

$Q_{i/j}$ - Volumetric flow rate of gas in standard temperature and Pressure

A - Membrane active surface area

$\alpha_{i/j}$ - Pure gas selectivity

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

A separation process is used to separate a mixture to two or more difference products. The separation processes deal mainly with the transfer and change of energy and the transfer and change of materials, primarily by physical means but also by physical-chemical means (Christie, 2003). Separation process can be classified into process like evaporation, distillation, absorption, adsorption, membrane separation, mechanical-physical separations, and many more.

Uses of membrane have been rapidly growing in the application of gas separation process. This study is concentrated on the ability and the performance of the membrane to separate the carbon dioxide (CO_2) from methane (CH_4). It is because in the gas stream, CO_2 which fall into category of acid gases (as does hydrogen sulfide (H_2S)) will bring harm to the equipment and the pipeline itself because with the combination with water, it is highly corrosive and rapidly destroy pipeline and equipment. Membranes have been widely used in two main CO_2 removal applications which are in natural gas sweetening, and enhanced oil recovery, where CO_2 is removed from an associated natural gas stream and reinjected into the oil well to enhanced oil recovery (David, 1999)

1.2 Problem Statement

In membrane separation the most important part is the permeability and selectivity of the membrane toward the gases that need to be removed to get better separation result. This study is performed to study and review the selectivity and permeability of the membrane which immersed into three different coagulations medium. Beside that the structures of each membrane need to be viewed and characterized by using the Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopic (FTIR).

It is important to know what the best coagulation medium for PES asymmetric membrane is in order to get the best performance of the membrane. Ideal asymmetric membranes for gas separation must meet the following requirements for better performance. First is the skin layer must be defect free to assure that the permeation is exclusively controlled by a solution/diffusion mechanism to achieve maximum selectivity. Secondly is the skin layer should be as thin as possible to maximize the membrane productivity. Thirdly is to the substructure should provide sufficient mechanical strength to support the delicate skin layer during high-pressure operation.

1.3 Objective of Study

The main objective of this study is to investigate the effect of coagulation medium towards the permeability and selectivity of the membrane for the separation of the CO_2 and $CH_{4.}$

1.4 Scope of Research

Based on the objective, this study mainly conducted to develop membrane for gas separation by study the effect of the different coagulation medium toward the membrane. To achieve the objective of the study, few scopes of study are conducted as below:

i. Fabrication of membrane for gas separation base on asymmetric flat sheet membrane.
ii. Various permeability tests conducted for CO_2 and $CH_{4.}$
iii. Membrane characterized by using SEM and FTIR.

1.5 Rationale and Significant

Lots of fact and information in gas separation process using membrane can be studied by doing this project. Furthermore, by doing the analysis of the gas permeation, the selectivity and permeability of the membrane can be further review and studied to get better result of gas separation. Besides that, this opportunity can be used to learn how to fabricate and preparing the asymmetric flat sheet membrane to separate gases.

CHAPTER 2

LITERATURE REVIEW

2.1 History of Membrane

A membrane can be defined as semi-permeable barrier, which separates a fluid and restricts transport of various chemicals in 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 (Srikant, 2008). Transport trough 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 100 microns to several millimeters (mm).

The membrane studies already started in the early eighteenth century when Abbe Nolet used the word ‘osmosis’ to describe permeation of water through a diaphragm in 1748 (Baker, 2004). Through the nineteenth and early twentieth century’s, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical and chemical theories. This can be proved with the measurements of solution osmotic pressure made with membranes by Traube and pfrffer were used by Van’t Hoof in 1887 to develop his limit law, which explains the behavior of ideal dilute solution (Baker, 2004). The concept of a perfectly selective semipermeable membrane was used by Maxwell and others in developing the kinetic theory of gases.

In 1907, Bechold devised a technique to prepare nitrocellulose membranes of graded pore size, which determined by bubble test. Others efforts by Elford, Zsigmondy and Bachmann and Ferry improved on the Bechold’s technique and by the early 1930s microporous collodion membranes were commercially available. Then the next 20 years after that, the early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate. The transformation of membrane separation from a laboratory to an industrial process came first in the 1960 with the development of the asymmetric porous membranes by Loeb and Sourirajan (Nutes, 2001). The membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable microporous support, which provides the mechanical strength (Baker, 2004).

The period from 1960 to 1980 produced a significant change in the status of membrane technology. Building the original Loeb-Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high performance membranes. Using these processes, membranes with selective layers as thin as 0.1 μm or less are now being produced by a number of companies. Method of producing of membranes into large-membrane-area spiral-wound, hollow-fine-fiber, capillary, and plate and frame modules were also developed, and advances were made in improving membrane stability.

By 1980, microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide (Baker, 2004). Today, membranes are used on a large scale to produce portable water from sea and brackish water (desalination), to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and in this project consideration which is to separate gases and vapors in petrochemical processes.

2.2 Membrane Classifications

Membrane can be classified into few types and can be determined by the specific application objective which includes the particulate or dissolve solids removal, hardness reduction or ultra pure water production, removal of specific gases or chemical and many more. The classification of membrane can help to improve the membrane application by knowing to the membrane morphology. Membranes classified according to their morphology are shown in figure 2.1 and the details about the membrane types are discussed in table 2.1.

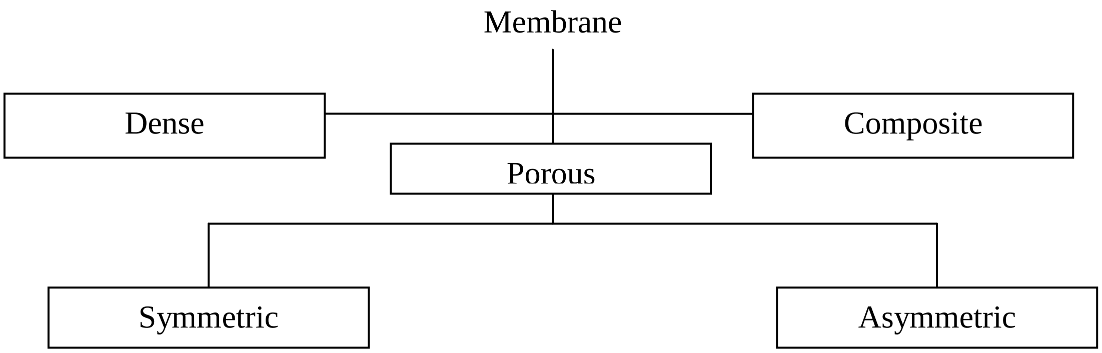

Figure 2.1 Membrane classification

Table 2.1: Membrane type and characteristics.

Membrane type	Characteristics	References
Microporous membranes	The membrane behaves almost like a fibre filter and separates by a sieving mechanism determined by the pore diameter and particle size. Materials such as ceramics, graphite, metal oxides, and polymers are used in making this type of membrane. The pores in the membrane may vary between 1 nm to 20 microns.	Srikant, 2004
Homogeneous Membranes	This is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be separated efficiently when their concentrations differ significantly.	Srikant, 2004
Asymmetric membranes	An asymmetric comprises a very thin (0.1 to 1.0 micron) skin layer on a highly porous (100 – 200 microns) thick substructure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of membrane material or pores size, and the mass transport rate is determined mainly by the skin thickness. Porous sub-layer acts as a support for the thin, fragile skin and has little effect on the separation characteristics.	Srikant, 2004
Nonporous, dense	Nonporous, dense membranes consist of a dense film through which permeants are transported by	Baker, 2004

membranes	diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of mixture relate to the relative transport rate within membrane materials which is determined by the diffusivity and solubility in the membrane material. Most gas separation, pervaporation, and reverse osmosis membranes use dense membranes to perform the separation.	
Electrically charged Membranes	Electrically charged membranes can be dense or microporous, but are most 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 anions in the surrounding fluid. Similarly, a membrane containing fixed negatively charged ions is called a cation-exchange membrane. Separation 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.	Srikant, and Baker, 2004

2.3 Membrane Modules

Nowadays with the advance technology in membranes separation, the materials to form a membrane have been formulated to get the best separation result. For that reason, different types of membrane module are designed and available in the market. The configurations of membrane module have been discussed in table 2.2. According to Srikant, 2004, the following membrane modules are largely used for industrial applications:

I. Plate and frame module
II. Spiral wound module
III. Tubular membrane module
IV. Capillary membrane module
V. Hollow fiber membrane module

Table 2.2: Configuration of Membrane module (Philip, 1988)

Membrane modules	Details
Hollow Fiber - Capillary	• Very small in diameter membrane (< 1mm) • Consist large number of membranes in a module and self supporting • Density is about 600 to 1200 m^2/m^3 (for capillary membrane). Up to 30000 m^2/m^3 (hollow fiber). • Size is smaller than other module for given performance capacity. • Process is inside-out. Permeate is collected outside of membrane.
Plate and Frame	• Structure is simple and the membrane replacement is easy.

	• Similar to filter press • Density is about 100 to 400 m^2/m^3. • Membrane is placed with feed sides’ facing each other. • Feed flows from its sides and permeate comes out from the top and the bottom of the frame. • Membranes are held apart by a corrugated spacer.
Spiral Wound	• Formed from a plate and frame sheet wrapped around a center collection pipe. • Density is about 300 to m^2/m^3. • Its diameter can up to 40cm. • Feed flow axial on cylindrical module and permeate flow into the central pipe.
Tubular	• Not self supporting and normally are inserted in other materials tube with diameter more than 10mm. • Density is not more than 300 m^2/m^3. • Membranes replacement is easy.

2.4 Membrane Applications

Membranes are becoming popular in separation process industries in recent day. There are various types of membrane separation have been developed the specific industrial applications. The following are the some of the widely used processes that use membrane.