

DEVELOPMENT OF PVDF MEMBRANE WITH PEG COATING FOR CO₂ AND CH₄ GAS
SEPARATION

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ABSTRACT

Thin film composite membranes were prepared for separation of carbon dioxide from methane using polyvinylidene fluoride (PVDF) as support and polyethylene glycol (PEG) as active layer at various concentrations. Permeance and the ideal selectivity were measured for all membranes under the feed pressure 1 and 2 bar. Influences of affecting parameters on membrane performance (permeances and selectivity) were investigated. For all coated membranes, the carbon dioxide permeance was higher compared to the methane permeances. The SEM study was carried out for investigation of membrane pore sizes. The membranes are coated with 2%, 4% and 6% PEG. For surface image of the membranes were identified by using scanning electron microscopy (SEM). The SEM images exhibited the best surface image with large pores was discovered at concentration 2% PEG. Membranes were also characterized using Fourier Transform Infrared Spectroscopy (FTIR) to detect the presence of PEG functional group in the membrane. The performance of the membrane was proven by conducting the gas permeation test. The selectivity of CO_2/CH_4 at 1 bar was 1.117 (2% PEG) and at 2 bar was 1.155 (6% PEG). Hence, coated membranes were discovered to affect the pore sizes which will consequently affect the permeability and selectivity of PVDF thin film composite membrane. As a conclusion, the increasing value of PEG coating concentration, the greater the feed pressure should be applied due to the resistance of membrane.

ABSTRAK

Membran komposit filem nipis telah disediakan untuk pemisahan karbon dioksida dari metana menggunakan fluorida polyvinylidene (PVDF) sebagai sokongan dan polietilena glikol (PEG) sebagai lapisan aktif pada pelbagai kepekatan. Permeance dan kepilihan yang ideal telah diukur bagi semua membran di bawah tekanan suapan 1 dan 2 bar. Pengaruh mempengaruhi parameter mengenai prestasi membran (permeances dan selektiviti) dengan telah disiasat. Bagi semua membran bersalut, permeance karbon dioksida adalah lebih tinggi berbanding permeances metana. Kajian SEM telah dijalankan untuk siasatan saiz liang membran. Membran disalut dengan 2%, 4% dan 6% PEG. Bagi imej permukaan membran telah dikenal pasti dengan menggunakan mikroskop imbasan elektron (SEM). Imej-imej SEM mempamerkan imej permukaan yang terbaik dengan liang roma yang besar telah ditemui di PEG kepekatan 2%. Membran telah juga dicirikan menggunakan Spektroskopi inframerah transformasi Fourier (FTIR) untuk mengesan kehadiran kumpulan PEG berfungsi dalam membran. Prestasi membran telah terbukti dengan menjalankan ujian penyerapan gas. Kepilihan CO₂/CH₄ pada 1 bar ialah 1,117 (2% PEG) dan pada 2 bar ialah 1,155 (6% PEG). Oleh itu, membran bersalut ditemui untuk menjejaskan saiz liang yang seterusnya akan menjejaskan kebolehtelapan dan selektiviti PVDF membran komposit filem nipis. Kesimpulannya, peningkatan nilai kepekatan salutan PEG, semakin besar tekanan suapan harus digunakan kerana rintangan membran.

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LIST OF ABBREVIATIONS

CO ₂	-	Carbon Dioxide
PEG	-	Polyethylene Glycol
SEM	-	Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
RO	-	Reverse Osmosis
CH ₄	-	Methane
P	-	Permeability
D	-	Diffusion Coefficient in Membrane
PVDF	-	Polyvinylidene Fluoride
P _i	-	Permeability for Gas component
Q	-	Gas Flowrate
A	-	Area
ΔP	-	Pressure in System
P _j	-	Permeability of Another Gas Component
P _j	-	Permeability of Another Gas Component
α	-	Selectivity

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Various technologies exist that have been designed to remove CO₂ from natural gas and recovery CO₂ from landfill gas. Typically, raw natural gas contains 75–90% CH₄ and biogas contains 54–59% CH₄. Due to the high composition of contaminants these gases need to be treated. Separation of CO₂ becoming more important issues due to the most significant sources to pollution. So the upgrading CH₄ for use in the local gas distribution system is possible by applying a membrane system. Membrane processes have been proven to be technically and economically superior to the competing technologies in many industrial applications. This superiority is due to many advantages that membrane technology benefits from, including low capital investment, simplicity and ease of installation and operation, low maintenance requirements, low weight and space requirements, and high process flexibility.

1.2 PROBLEM STATEMENT

One of the most fundamental problems facing the earth today is global warming. The emissions of CO₂, the most important greenhouse gas must be reduced. The burning of fossil fuels and biomass is the most significant source and also drilling from wellhead which come out with methane, CH₄. In these cases, the similarities there are containing CO₂ and CH₄.

Natural gas is the one that contributes major fuel for transportation after diesel. The composition of natural gas varies from one location to another and its quality highly depends on the concentration of the contaminants. After drilling from wellhead, the natural gas, CH₄ containing other contaminants which is the high acid gas CO₂. CO₂ is corrosive and would normally require stainless steel equipment. Otherwise, the concentration of CO₂ must be minimizing to make sure the natural gas can be selling. To meet market requirements, this contaminant must comply with such concentration specifications as less than 2% CO₂.

Available techniques for natural gas separation include membrane, absorption, adsorption, and cryogenic distillation. Among these separation technologies, research is directed towards high performance, efficient materials and processes to achieve cost effective CO₂ capture for the lowest energy penalty. Therefore it is important to develop a membrane can separate CO₂ and CH₄ efficiently.

1.3 OBJECTIVES

The aim of this study is to develop PVDF membrane with PEG coating for CO₂ and CH₄ gas separation. Hence, the objective is

- To produce Thin Film Composite (TFC) PEG-PVDF membrane.
- To investigate the effect of concentration of additives through permeability of PVDF membrane for CO₂ /CH₄ gas separation.

1.4 SCOPE OF RESEARCH

Based on the objective, the scopes of study are highlighted as follows:

- Study the preparation of PVDF-PEG membrane using dip coating method.
- Study the significant permeability of CO₂ and CH₄ through PVDF-PEG membrane.

1.5 RATIONALE AND SIGNIFICANCE

The purpose of this study is to develop a coated membrane that will result separating CO₂ and CH₄ efficiently. The coating technique, on the other hand, increased the separation factor by plugging the large pores and defects of the selective layer using materials such as silicone rubber. Besides that the most important thing is the developed membrane must be high pressure resistance and high permeable to CO₂. Then the cost of separation of CO₂ and CH₄ will be decreased by using this separation technology.

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE GAS SEPARATION

Membranes for natural gas processing were first commercialized in the 1980s for CO₂ removal (Schell, 1989) and have been the dominant membrane gas separation process since then. There are also other processing stages in natural gas treatment that can utilize membranes, and these are also now being commercially deployed. In particular, the removal and recovery of heavier hydrocarbons from the raw gas, dehydration, as well as separation of nitrogen and other inert gases is possible (Zolandz, 2001). These processes are undertaken to produce natural gas at the necessary composition for consumption, as well as to recover valuable components. A good example of this is the recovery of heavier hydrocarbons, such as butane.

In all of these situations, polymeric membranes are the focus of commercialization because of their ease of manufacture (Zolandz, 2001). Other materials, such as inorganic

membranes, demonstrate high performance under research conditions but module fabrication is still too expensive to compete against current polymeric modules. However, it is worthwhile noting that only a small number of polymers of the many hundreds developed in the research laboratory have themselves reached their commercial potential. In 2002, only nine polymeric materials made up 90% of the total gas separation membrane market (Baker, 2002).

Polymeric membranes are generally non-porous and gas permeation is described by the solution diffusion mechanism. 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 dependent upon molecular size but also relies on the chemical interaction between the gases and the polymer. Polymeric membranes are further classified as rubbery or glassy dependent on the value of their glass transition temperature relative to ambient. Rubbery membranes selectivity is generally solubility based while glassy membrane selectivity is generally diffusion based.

Here, the application of polymeric membranes to natural gas processing is on membranes applied to carbon dioxide gas separation. The review covers available membrane materials, additives properties, their performance and limitations and processing strategies.

2.1.1 Historical

The gas separation properties of membranes have been realized for more than a century. The early documented reports root back to the works of Mitchell, Fick, and Graham of the mid-nineteenth century. In 1831, Mitchell measured the rates of escape of ten gases through natural rubber balloons (Mears, 1986). At approximately the same time, Fick developed his famous laws of diffusion by studying gas transport across a nitrocellulose membrane (Paul, 1994).

A few decades later in 1866, Thomas Graham observed the separation of gases using natural rubber via Knudsen diffusion (Stanly, 1986). In 1920, H. A. Daynes recognized the relation between time lag and diffusion coefficient by studying the non-steady state transport behavior of gases through a membrane (Paul, 1994).

Despite many experimental works, the progress of membrane separation techniques was very slow in the early stages. The major problem with the early membranes was their insufficient selectivity and low fluxes. The first breakthrough came about with the introduction of asymmetric membranes by Loeb and Sourirajan (Loeb and Sourirajan, 1960). They successfully produced a membrane with a very thin dense layer and a relatively thick porous sub layer. The dense layer was responsible for the separation, while the porous sub layer provided mechanical strength to the selective layer with minimum resistance to the permeation of components.

2.1.2 Asymmetric membranes

Among various types of membranes suitable for gas separation, the asymmetric membranes have revealed themselves to be exceptionally effective (Wang Onley, 1991). An asymmetric membrane may be defined as an entity composed of an ultrathin dense skin over a thick porous structure of the same or different material. Asymmetric membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure. Figure 2.1 shows asymmetric membrane structure.

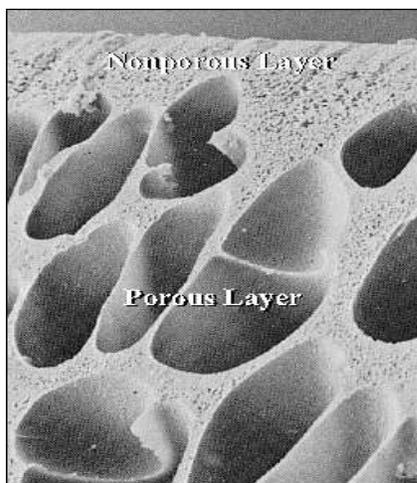


Figure 2.1: Asymmetric membrane structure

The surface layer and its substructure may be formed in a single operation or separately. The surface layer performs the separation and is the principal barrier to flow through the membrane. The open support layer provides mechanical strength.

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; therefore, the membrane should be as thin as possible. Conventional film fabrication technology limits manufacture of mechanically strong, defect-free films to about 20 μm thickness. In composite membranes, the layers are usually made from different polymers. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by asymmetric membranes are so great that almost all commercial processes use such membranes.

2.1.3 Module of membrane

2.1.3.1 Flat-Sheet membrane

Flat-Sheet membrane form can be made in very thin selective membrane layers. This means the permeances of flat sheet membranes is high. Also, flat sheet membranes did not require more pretreatment of the feed to remove particulates, oil mist and other fouling components. For practical application in gas separation membranes, the selective layer is usually made as thin as possible to have as high a flux as possible.

Figure 2.2 shows the flat sheet membranes, porous membrane support plates, and spacers forming the feed flow channel are clamped together and stacked between two endplates and placed in housing. Its design has its origin in the conventional filter press-concept. Membrane, feed spacers, and product spacers are layered together between two end plates.

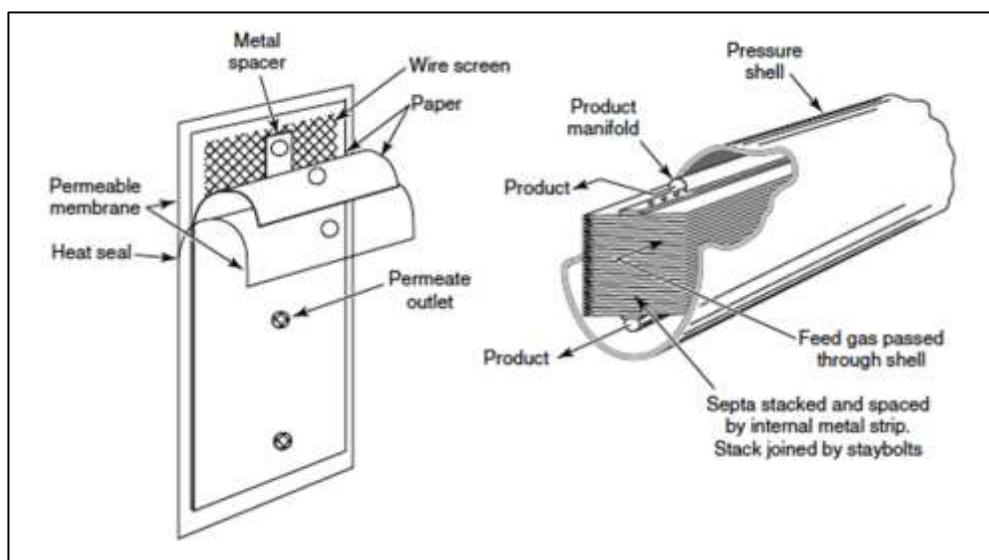


Figure 2.2: Early plate-and-frame design developed by Stern et al. for the separation of helium from natural gas.

The feed mixture is forced across the surface of the membrane. A portion passes through the membrane, enters the permeate channel, and makes its way to a central permeate collection manifold. Plate-and-frame units have been developed for some small-scale applications 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 electro dialysis and pervaporation systems and in a limited number of reverse osmosis and ultrafiltration.

Figure 2.3 shows a plate and frame modules which provides good flow control on both permeate and feed side of the membrane, but the large number of spacer plates and seals lead to high module costs. The feed solution is directed across each plate in series. Permeate enters the membrane envelope and is collected through the central permeate collection channel.

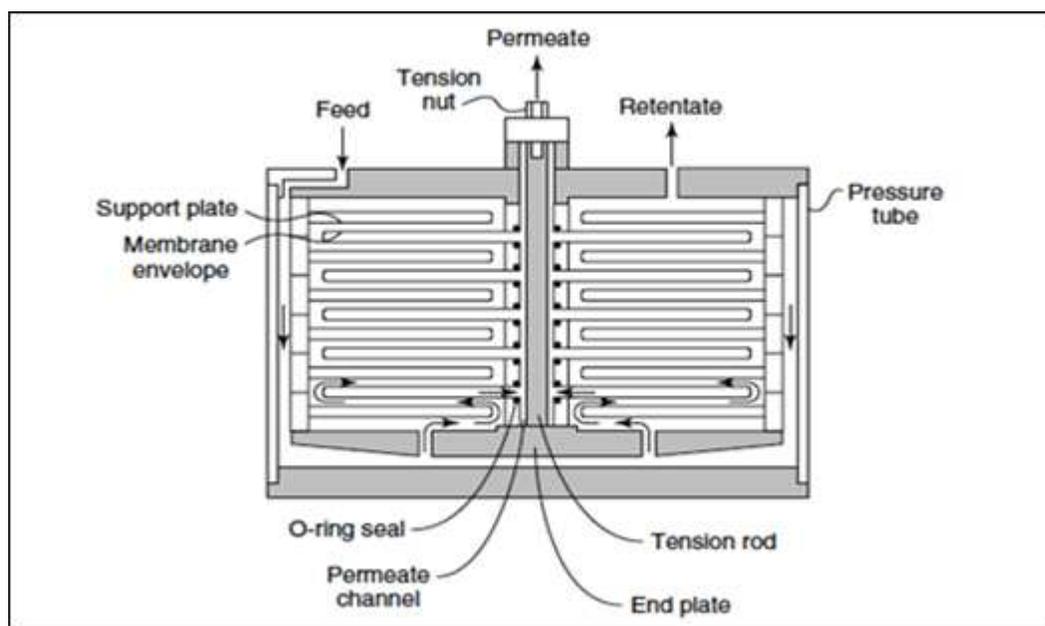


Figure 2.3: Schematic of a plate and frame module

2.1.3.2 Hollow Fiber membrane

The same basic spinning process is used for the preparation of hollow fiber membranes, which have an outer diameter of 50 to 100 μm . In hollow fiber membranes, the selective layer is on the outside of the fibers, which are installed as a bundle of several thousand fibers in a half loop with the free ends potted with an epoxy resin in a pressure tube as indicated in Figure 2.4. The filtrate passes through the fiber walls and flows up the bore to the open end of the fibers at the epoxy head.

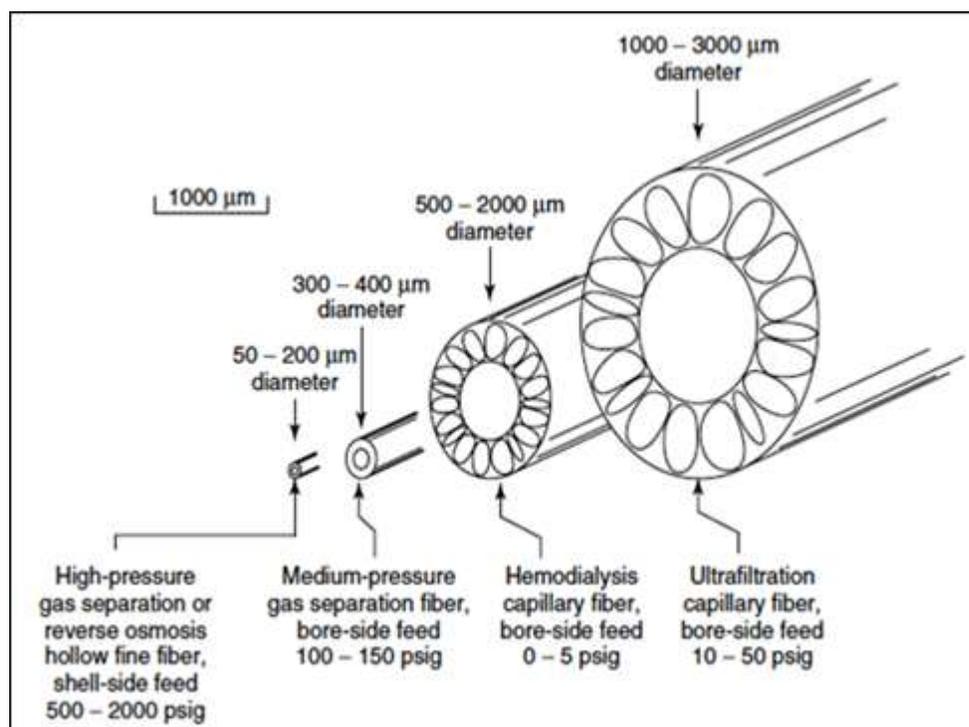


Figure 2.4: Schematic drawing of a hollow fiber module

The hollow fiber membrane module has the highest packing density of all module types available on the market today. Its production is very cost effective and hollow fiber membrane modules can be operated at pressures in excess of 100 bars. The main disadvantage of the hollow fiber membrane module is the difficult control of concentration polarization and membrane fouling. When operated with liquid solutions the modules do not tolerate any particulates, macromolecules or other materials that may easily precipitate at the membrane surface. Therefore, an extensive pretreatment is required when hollow fiber membranes are used for the treatment of liquid mixtures. The main application of the hollow fiber module is today in reverse osmosis desalination of sea water and in gas separation. Both applications require high operating pressures and low cost membranes which have a long useful life. In reverse osmosis, of sea water an extensive pretreatment of the sea water is required.

Hollow fiber membrane modules are formed in two basic geometries. The first is the shell-side feed design illustrated in Figure 2.4 and used, for example, by Monsanto in their hydrogen separation systems and by Du Pont in their reverse osmosis systems. In such a module, a loop or a closed bundle of fibers is contained in a pressure vessel. The system is pressurized from the shell side; permeate passes through the fiber wall and exits through the open fiber ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fiber wall must support considerable hydrostatic pressure, the fibers usually have small diameters and thick walls, typically 50 μm internal diameter and 100 to 200 μm outer diameter.

2.1.3.3 Spiral Wound membrane

In spiral-wound modules, two flat-sheet membranes are sealed together to form an envelope enclosing a separator in between. The separator prevents the two membranes from collapsing and provides mechanical strength, while exhibiting minimum resistance toward the flow of permeates. One or more of these envelopes are wound around a cylindrical collector.

The spiral-wound module is widely used today in reverse osmosis, ultrafiltration, and gas separation. Figure 2.5 shows a spiral-wound module installed in a multimodule pressure vessel. Typically four to six modules are installed in a single pressure vessel.

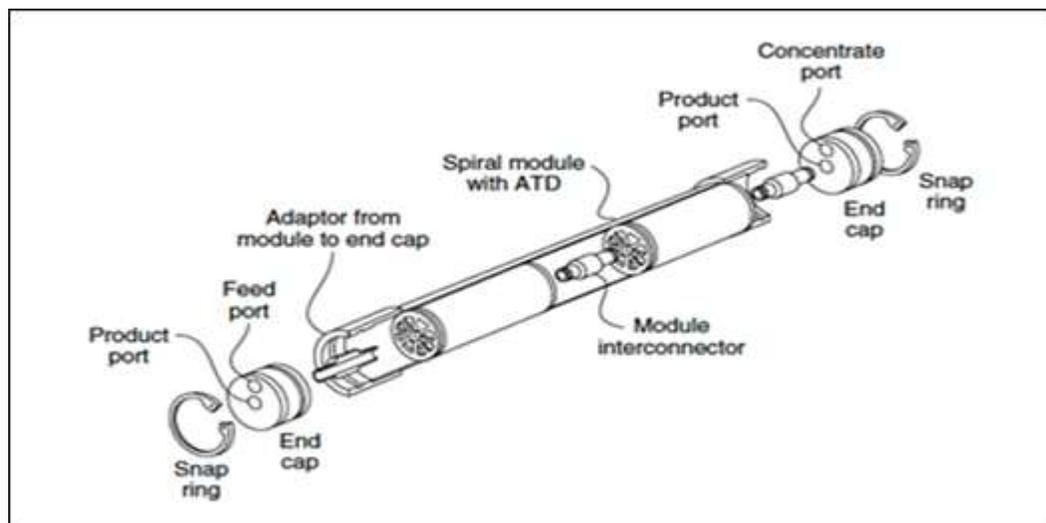


Figure 2.5: Schematic of a spiral-wound module installed in a multimodule pressure vessel.