Carbon Dioxide Removal from Natural Gas Stream Using Polycarbonate Membrane

by

Nik Ahmad Sabri bin Md Ghazali

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JUNE 2009

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approve by:

…………………………
(AP DR M AZMI BUSTAM)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JUNE 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(NIK AHMAD SABRI MD GHAZALI)

ABSTRACT

This report presents a research study on application of membrane system in removal carbon dioxide from natural gas stream which represented by methane in this project. The morphology of asymmetric membrane is very important factor in order to produce membrane with desirable properties that able to remove carbon dioxide from natural gas stream. The objectives of this research study are to study the effect of various preparation conditions on the morphologies of asymmetric polycarbonate (PC) membrane and its relation to CO_2/CH_4 separation characteristic. Dry/wet phase inversion technique was used to fabricate asymmetric PC membranes. The effect of solvent-non-solvent pair on membrane morphologies and separation characteristic were investigated. The chemical used are dichloromethane (DCM) as more volatile solvent while methanol (MeOH), ethanol (EtOH) and propanol (PrOH) were selected as non-solvents. In addition, methanol (MeOH) and tetrahydrofuran (THF) were used as coagulant and less volatile solvent, respectively. Based on the literatures studied, the propanol and butanol-based membranes showed promising performance. Fourier Transform Infrared (FTIR) Spectroscopy is used for analyzing organic materials in order to obtain specific information about the chemical bonding and also the molecular structures of the membrane. Scanning electron microscopy (SEM) is used to observe the membrane morphologies. Gas permeation unit was used to evaluate the performance of membrane. Experimental results showed that high boiling point of PrOH was responsible in forming highly porous substructure with macrovoid formation in the DCM-based membranes prepared using PrOH as non-solvent. The performance of asymmetric PC membranes was evaluated by measuring CO_2 and CH_4 permeances as well as CO_2/CH_4 ideal selectivity. The results showed that CO_2 and CH_4 were strongly dependent upon membrane morphologies formed during fabrication. A highly porous membrane prepared from DCM-PrOH and was found to give higher CO_2 and CH_4 permeance (CO_2:182 GPU; CH_4:141 GPU) as compared to MeOH (CO_2:149 GPU; CH_4:104 GPU) and EtOH (CO_2:165 GPU; CH_4:129 GPU) membranes. In term of selectivity, the highest CO_2/CH_4 ideal selectivity of the fabricated asymmetric PC membrane is approximately 1.54. In conclusion, asymmetric PC membranes show promising performance and have high potential to be used for CO_2/CH_4 separation.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The removal of carbon dioxide can be accomplished in a number of ways. Varieties of processes and improvement of each have been developed over the years to treat of gas with the aim of optimizing capital cost and operating cost, meet gas specifications and for environmental purpose. The major processes available can be grouped as follows (Maddox, 1982):

- Absorption Processes (Chemical and Physical absorption)
- Adsorption Process (Solid Surface)
- Physical Separation (Membrane, Cryogenic Separation)
- Hybrid Solution (Mixed Physical and Chemical Solvent)

The use of the membrane technology in removing carbon dioxide has promised multiple benefits compared to the conventional process because of a number of advantages such as low capital cost, less space requirement and for its known capability of separating gases of different sizes and shapes, polarity and simplicity in its design.

Membranes are used for natural gas purification mainly with cellulose acetate polymers. However, these materials only have CO_2/CH_4 selectivity from 12 to 15 under typical operating condition (Baker, 2002), well below the low-pressure mixed gas selectivity of 30 for dense membranes with zero permeate pressure (Houde, et al., 1996) Much of the decline in performance is due to plasticization of the membranes with CO_2/CH_4 selectivity of 40 would significantly enhanced the competitive position of membrane relative to alternate technologies such as amine scrubbing (Baker, 2002).

1.2 Problem Statement

Carbon dioxide, which falls into the category of acid gases, is commonly found in natural gas streams at level as high as 80% (Dortmundt and Doshi, 1999). In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and waste pipeline capacity.

1.3 Objectives

Upon completing the project, a few objectives need to be achieved. The objectives of the study are as follows:

i. To fabricate asymmetric polycarbonate (PC) membrane at various preparation parameter using dry/wet phase inversion method
ii. To investigate the effect of preparation parameter on the morphologies of asymmetric PC membrane
iii. To evaluate the performance of asymmetric PC membrane in term of CO_2 and CH_4 permeance as well as CO_2/CH_4 ideal selectivity.

1.4 Scope of Study

The scope of this project is to conduct a literature review on removal of CO_2 from natural gas stream using polycarbonate membrane and the parameters that affect the membrane performance. The next step is to proceed with conducting experiment on fabrication of asymmetric membrane for different parameters that affect the separation process. Through this project student is exposed to explore research problems and build research objectives, applying appropriate methodology, analyzing and interpreting data obtained from the experiment, troubleshooting any predicaments occur ad also reporting the findings.

CHAPTER 2

LITERATURE REVIEW AND THEORY

There were many literatures found about the performance study on polymeric membrane to remove carbon dioxide from natural gas stream and the mechanism of the membrane separation, as well as the durability of the membrane to the plasticization. Therefore, these literatures would be very helpful reference and guideline prior to produce a new or improve membrane properties in removing CO_2 from natural gas stream.

2.1 Membrane Definition and Classification

Membrane is defined as selective barrier between two phases that has ability to transport one component than the other (Mulder, 1996). There is a broad range of membrane applications such as for sea water desalination, waste-water treatment, ultrapure water production for semiconductor industry and nitrogen enrichment from air. Each of these applications requires specific type of membrane morphology to ensure the effective separation (Iqbal, 2007). Figure 1 shows a classification of membrane morphologies.

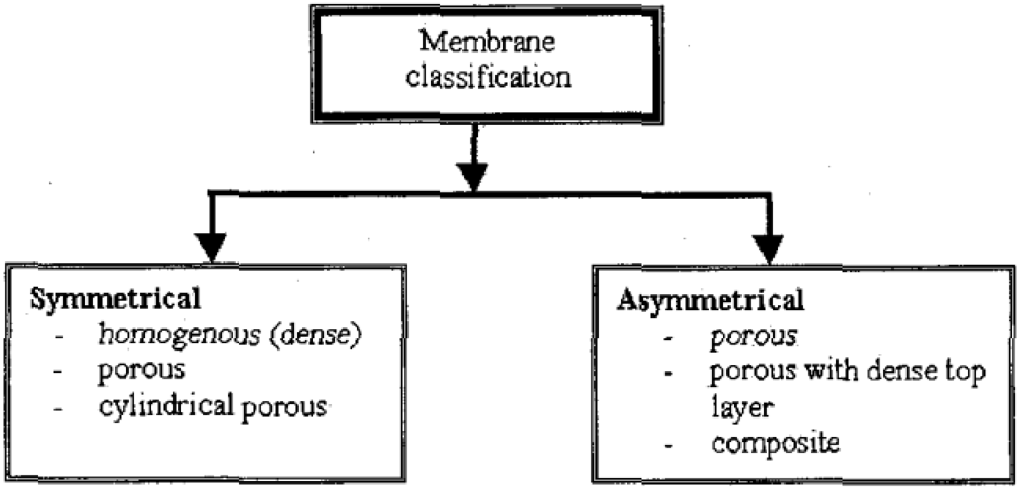


Figure 1: Classification of the typical membrane morphologies

In general, membrane morphologies can be classified into symmetric and asymmetric membrane (Mulder, 1996). Symmetric membrane refers to the membranes that have essentially same structure and transport properties throughout its thickness (Koros, et al., 1996). Symmetric membrane is divided into three categories as shown in the Figure 2.

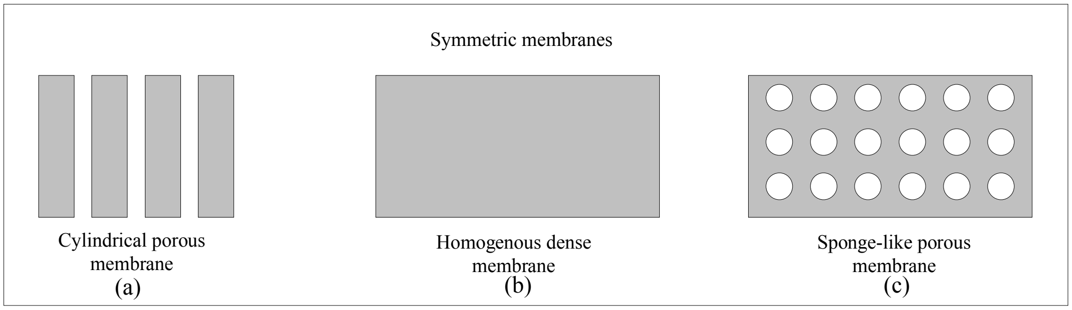


Figure 2: Schematic representation of cross-section of symmetric membranes

a) Cylindrical porous membrane. This membrane consists of finger-like structure that is usually used in small size laboratory experiments such as enzyme and DNA separations from dilute solutions.
b) Homogeneous dense membrane. This membrane consists of a dense film structure through in which permeants are transported by diffusion under the driving force of a pressure, concentration or electrical potential gradient (Baker,

2004). This membrane is often used to study gas separation and pervaporation application (Chen, 2002)

c) Sponge-like porous membranes. This type of membrane has sponge-like closed structure and is usually used for microfiltration. It has normally an average pore size of 0.2 - 5 µm (Chen, 2002).

Asymmetric membrane is a membrane constituted of two or more structural planes of non-identical morphologies (Koros, et al., 1996). It can be classified into groups as illustrated below:

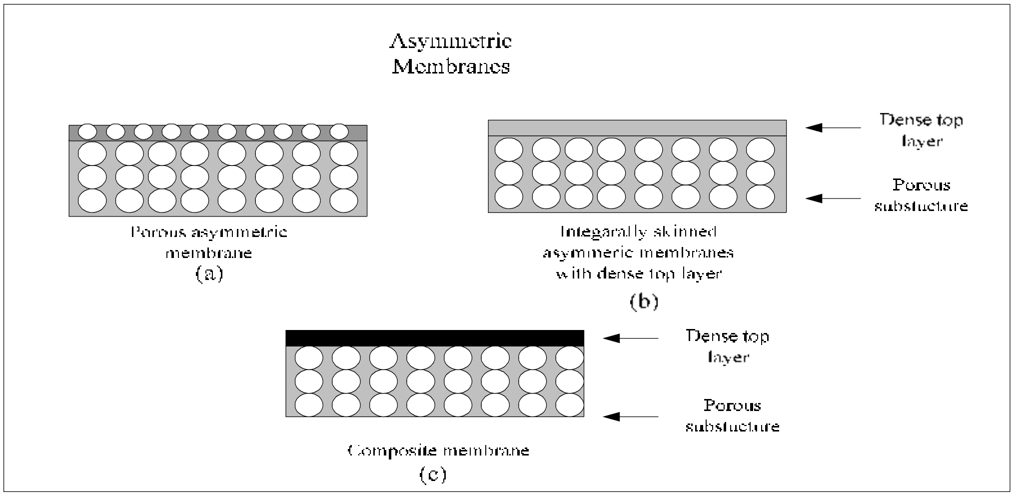


Figure 3: Schematic representation of cross-section of asymmetric membranes

a) Porous top layer membrane. This membrane consists of increasing pore size from top to bottom. Typical applications for these membranes are in microfiltration and ultrafiltration field (Chen, 2002).
b) Integrally skinned and dense top layer membranes which are usually used for gas separation (Chen, 2002). These membranes consist of dense thin layer with a thickness of 0.1 to 0.5 µm supported with the porous substructure with a thickness of about 50 to 150 µm.
c) Composite membrane is a development of asymmetric membrane in which dense layer is placed on top of a support membrane. Both dense layer and support

membrane are made from different materials. This membrane is often used for gas separation and pervaporation (Chen, 2002).

2.2 Polymeric Membrane

Polymeric membranes are the most popular membranes for CO_2 removal from natural gas application because of their high performance, ease of synthesis, long life, thermal stability, mechanical strength and chemical resistance. It can be classified as porous, e.g. micro- or ultra filtration membranes, or as non-porous. One important characteristic of polymers for membrane separation is the state of the polymer, like amorphous, semi crystalline or crystalline. This state is significant for the mechanical, chemical, and thermal stability, and has an influence on the permeation properties (Sarrade, et al., 1998).

Amorphous polymers are mostly used for membrane separations because the permeability is an order of magnitude higher than that of crystalline polymers. Amorphous polymers appear in a glassy and a rubbery state. In the glassy state the mobility of the polymer chains is very restricted, because the chains cannot rotate freely around their main chain bonds. The chain mobility and the volume between the polymer chains, which is called the “free volume”, are responsible for the solubility and the diffusion of the molecules penetrating through the membrane.

2.3 Asymmetric Membranes

Purpose of developing an asymmetric membrane is to reach higher flux than of symmetric membranes. This type of membrane is a breakthrough to industrial application as it combines high selectivity and high permeation rate in common (Mulder, 1996). These membranes have thin, perm-selective layer supported on a more open porous substrate. Some of the preparation processes of the asymmetric membrane are explained below:

a) Solution-Cast Composite Membranes

A dilute polymer solution in a volatile water-insoluble solvent is spread over surface of a water-filled trough (Ruthven, 1997). Thin polymer produced on the water is then coated onto a microporous support. Membrane thickness produced by this technique can reach 0.5 – 2 μm thick of thin permselective layer (Ruthven, 1997).

b) Phase Inversion (Solution Precipitation)

Casting solution is precipitated into two phase: a solid polymer-rich phase that forms the matrix of the membrane and liquid polymer-poor phase that forms membrane pores. Adjustment of these two phases is necessary to get desired structure of membrane. Polymers precipitation from solution can be achieved through several ways such as cooling, solvent evaporation and precipitation by immersion in water (Gollan, 1987).

From all these fabrication techniques that can be used to prepare asymmetric membrane, phase inversion method is widely applied to fabricate asymmetric membrane as it allows all kind of morphologies to be obtained (Mulder, 1996).

2.3.1 Effect of Polymer Concentration on Asymmetric Membrane Morphologies and Transport Properties

The optimum membrane preparation parameters are very crucial in order to obtain a defect-free and ultra-thin skin layer asymmetric membrane. One way of optimizing the membrane preparation parameters is by varying the polymer concentration of casting solution during fabrication. Varying the polymer concentration may lead to different membrane morphology and performance (Brown et al., 2002). Higher concentration of PS on casting solution increased the O_2/N_2 ideal selectivity but lowered the permeance of O_2. Similar results were also observed by Ismail and Lai (2003). They fabricated asymmetric membrane using PS by varying the concentration of polymer and they found that increasing the PS concentration on casting solution resulted in higher H_2/N_2 ideal selectivity with lower H_2 permeance. Pesek and Koros (1993) had reported that the addition of more polymer into casting solution tend to produce more selective but less productive membrane. In their work, polysulfone (PS) was used as membrane forming material to produce defect-free and ultra-thin asymmetric membrane.

Contradictory results on the effect of polymer concentration were reported by other researchers (Kurdi and Tremblay, 1999; Buonomenna et al.,2004). Buonomenna et al., (2004) also studied the influence of polyetheretherketone (PEEKWC) concentration on membrane performance and morphologies. Kurdi and Tremblay (1999) developed defect-free asymmetric membrane for gas separation using polyetherimide (PEI) as membrane forming material. They fabricated three different membranes prepared from three different concentration of PEI. Each of these membranes was subjected to the permeation test in order to determine the separation performance. From their work, it was found that highest O_2/N_2 ideal selectivity resulted from lower PEI concentration. They applied various test gas such as O_2 and N_2 on the PEEKWC asymmetric membrane. Their results showed that O_2/N_2 ideal selectivity was reduced if high concentration of PEEKWC was present in casting solution

2.3.2 Effect of Solvent Ratio on Membrane Morphologies and Transport Properties

Membrane formation process through dry/wet phase inversion process involves solution processing method that includes solvents and non-solvents additives in controlling the membrane structures and properties. In phase inversion method, casting solution is prepared by dissolving a polymer into solvents that consist of a primary more volatile solvent and a secondary less volatile solvent. The ratio of less volatile solvent and more volatile solvent is one of the important factors in determining the structure and properties of asymmetric membrane (Pesek and Koros, 1993). Controlling the ratio of more volatile solvent to less volatile solvents allows finer adjustment of solvent evaporation and polymer coagulation rates (Pesek and Koros, 1993; Ismail and Lai, 2003). Peinemann (1988) explored the effect of the solvent ratio for asymmetric polyethersulfone (PES) membrane. They showed that increasing the fraction of less volatile solvent enables substantial increases in the gas permeance without loss in selectivity. Better performance due to higher solvent ratio was also studied by Pesek (1993) and Ismail (2003). They prepared asymmetric membrane using polysulfone by varying the solvent ratio and showed that a reduction of solvent ratio caused a decrease in the gas permeance but higher selectivity was obtained.

2.4 Development of Ultra-Thin and Defect-Free Skin Layer of Asymmetric Membrane for Gas Separation

In particular, fabrication of a membrane with high permeability and selectivity is still a problem need to overcome in gas separation application. By fabricating defect-free and very thin skin layer asymmetric membrane, gas separation performance can be increased. In mid 1960s, the collaboration between Sydney Loeb and Srinivasa Sourirajan had successful introduced the first fabrication technique to produce asymmetric membrane for reverse osmosis application. In their method, the casting solution was prepared by dissolving 20 to 25 wt% cellulose acetate into a water-miscible solvent and then was cast as thin film on a glass plate. The cast film was evaporated for 10 to 100 s. After evaporation, a coagulation medium containing water was used to precipitate the film. The membranes were usually post-treated by annealing in a bath of hot water (Baker, 2004).

Loeb-Sourirajan’s technique is the most versatile, economical and reproducible formation process for polymeric asymmetric membrane (Ismail and Lai, 2003). A great deal of work has been devoted to rationalizing the factors affecting the properties of asymmetric membranes prepared by Loeb-Sourirajan’s technique. Various preparation parameters such as polymer concentration, solvent ratio, evaporation time and shear rate have been investigated in order to understand the formation of asymmetric membrane.

2.5 Plasticization

In CO_2/CH_4 membrane separation, it is known that CO_2 acts as a plasticizer. Plasticization occurs when the CO_2 concentration in the polymer is high enough to increase free volume and segmental mobility. Due to the swelling of the polymer matrix, the permeation of CH_4 is accelerated and as a consequence the polymer looses its selectivity (Wessling, et al., 1999). To overcome this methane loss, plasticization should be minimized.

Various phenomenological models have been postulated to describe plasticization behavior. (Stern and Saxena, 1980) modified the dual mode transport model with a diffusion coefficient that is an exponential function of concentration to describe this plasticization behavior. Later, (Mauze and Stern, 1982) modified the model to replace the total concentration by the so-called “dissolved” concentration, neglecting the concentration associated with Langmuir sorption mechanism, while maintaining the exponential diffusion expression.

According to (Wind, J. D., 2002) in a plasticized membrane, the sorption, diffusion, and swelling processes are all interdependent. The key to controlling plasticization is to control the membrane swelling, since this is related to the increase in polymer chain segmental mobility facilitated by the CO_2 sorption.

CHAPTER 3

METHODOLOGY

3.1 Synthesis

Phase Inversion method works on principle of a polymer solution loses solvent by evaporation or exchange with non-solvent, followed by precipitation of the polymer in a mixture of solvent and non-solvent.

There are a few methods of preparing an asymmetric membrane (Pinnau and Koros, 1991):

- Dry
- Wet
- Dry/wet

However, the common method used is the dry/wet phase inversion technique. Chemicals details are provided in APPENDIX A.

3.2 Membrane Preparation

The preparation for the membrane as follows:

a) The polycarbonate is dried for 16 hours prior to use.
b) The casting solution is prepared by dissolving 12.5 gm of polycarbonate in 55 gm of dichloromethane (DCM), 27.5 gm of tetrahydrofuran (THF) and requisite quantity of a non-solvent (5%).
c) TEC is added to solution to control the rate of evaporation.
d) The mixture is stirred for 4 hours to prepare a clear solution followed by degassing for 4 hours.
e) The solution is cast onto a glass plate using a casting knife with a gap setting of 250 μm.

f) The DCM is allowed to evaporate in a stream of nitrogen released through a ¼ inch diameter tube moving back and forth above the cast solution before immersion into methanol bath.
g) The membrane is peeled out of the glass plate and air-dried for 16 hours.

3.3 Analysis and Characterization

For membranes to perform satisfactorily, they must produce desired surface morphology which has high porosity but low in macrovoid formation. In order to achieve the objectives of this project, the following testing will be conducted:

1. Scanning Electron Microscope (SEM)
2. Fourier Transform Infrared (FTIR) Spectroscopy
3. Gas Permeability Test

3.3.1 Scanning Electron Microscopy (SEM)

SEM pictures are taken to study the membrane morphology as SEM is capable to observe the materials in micro and submicron ranges. Sample must be prepared before it can be analyzed under SEM. Surface and cross-section of the membranes is chosen randomly and then cut using blade. Samples are then gold-coated using a sputter coater.

After coating, membrane samples are imaged and photographed by employing an electron microscope. The SEM is a microscope that uses electron rather than light which provide the images of resolution up to 1 000,000 magnification.

The preparation of the sample for this testing is easy because most of SEM only required the sample to be electrically conductive. The process is when SEM generates the high energy electrons and focused on the specimen.

3.3.2 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy provides specific information about chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials.

Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces a spectrum that can be used to identify functional groups and compounds.

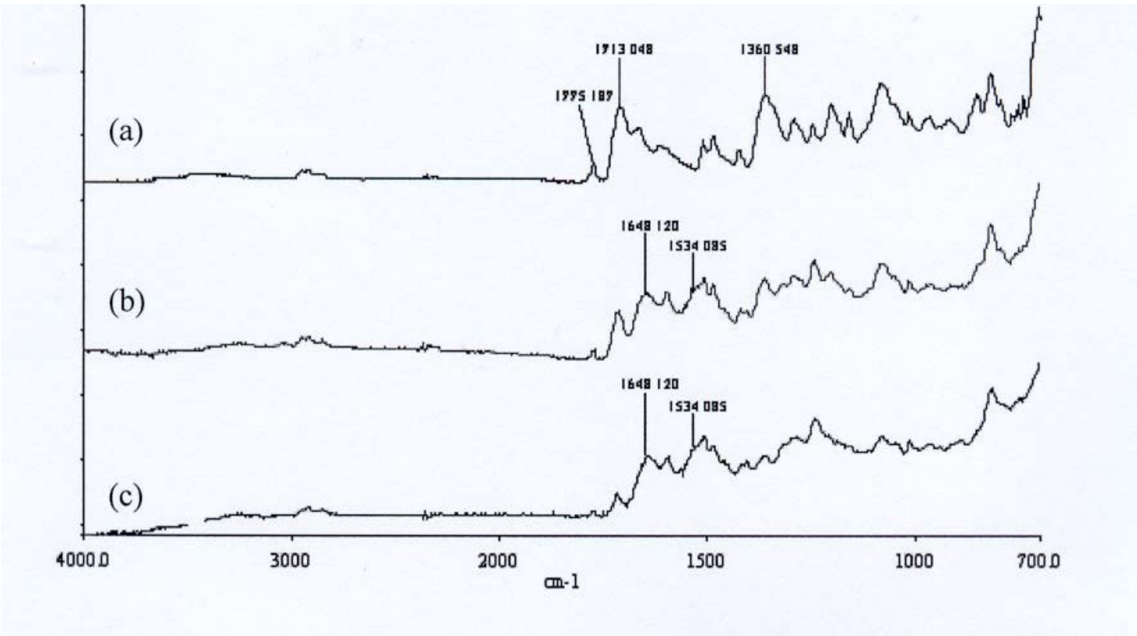


Figure 4: Sample FTIR spectra

FTIR spectroscopy is based on the idea of the interference of radiation between two yields and interferogram. The latter is a signal produced as a function of the change of path length between the two beams. The two domains of distance and frequency are inter-convertible by the mathematical method of Fourier transformation.

The basic components of an FTIR spectrometer are shown schematically in figure below. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier transformation.

Figure 5: Basic components of an FTIR spectrometer

3.3.3 Gas Permeability Test

The pressure-normalized fluxes of the membranes are determined using pure carbon dioxide (CO_2) and methane (CH_4) gases with purity of 99.99%. Membranes are cut into a circular disc of 13.5 cm^2 in area. All the experiments is carried out at ambient temperature (30±2 ^{o}C) at pressure drop of 2 until 5 bar. Rate of gas permeation are measured by using a soap bubble flow meter. The pressure-normalized fluxes, $(P/l)_i$ of pure gases such as CO_2 and CH_4 is calculated by (Ismail, et al., 2004);

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta p_i A}$$

Where P/*l* is defined as pressure-normalized flux for gas *I* (permeability coefficient divided by effective skin thickness)(cm^3(STP)/cm^2.s.cmHg), Q_i is the volumetric flow rate of gas *I* (cm^3/s) at STP, Δp_i is the membrane pressure drop (cmHg), and A is the membranes surfaces area (cm^2). The common unit of pressure-normalized flux is GPU.

$$GPU = 1X10^{-6} \frac{cm^3 (STP)}{cm^2 - \sec - cmHg}$$

Membrane selectivity, α_{ij} with respect to any gases, *i* and *j*, is the ratio of pressure-normalized fluxes,

$$\alpha_j^i = \frac{(P/l)_i}{(P/l)_j}$$

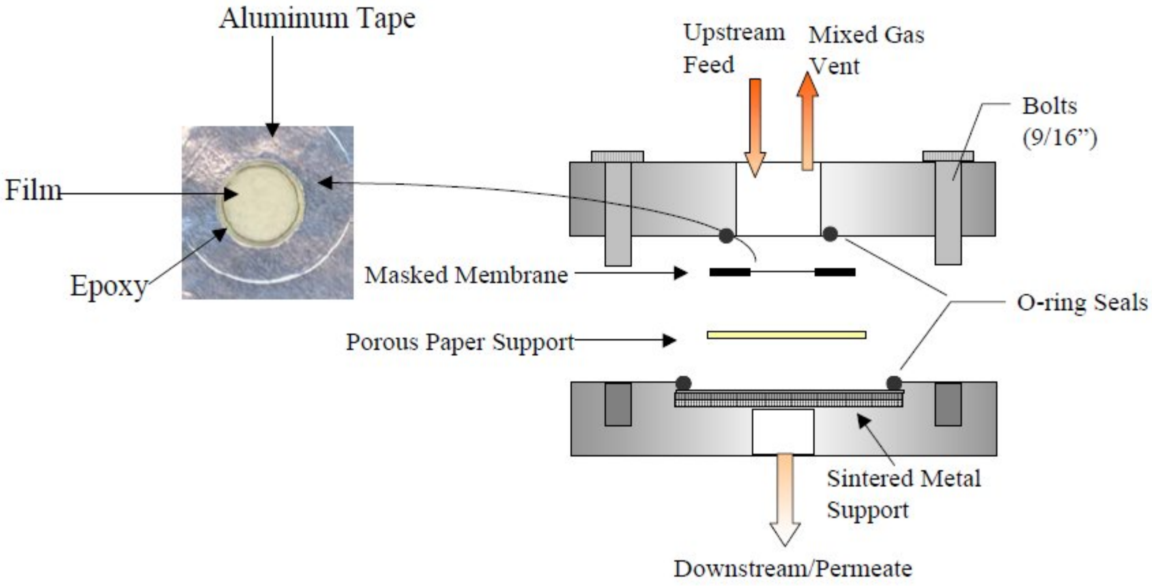


Figure 6: Permeation Cell Schematic

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Formation and Morphology of Asymmetric PC Membrane

Asymmetric polycarbonate (PC) membranes were fabricated at various preparation parameters using phase inversion technique. Results of parameters such as formation of macrovoid in the substructure and overall porosity of the membrane are discussed below:

4.1.1 FTIR Analysis

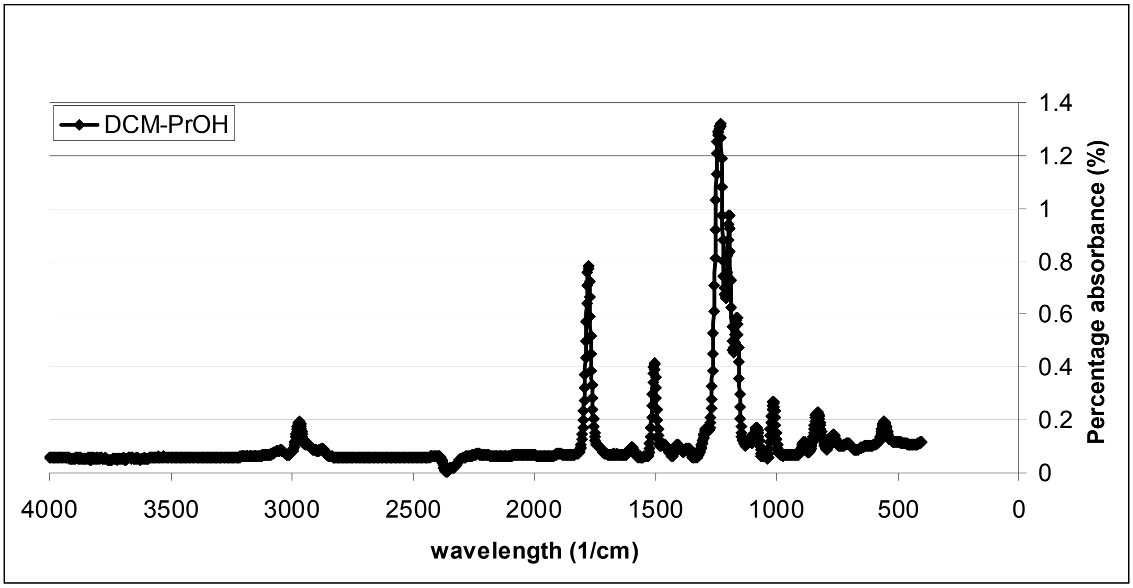
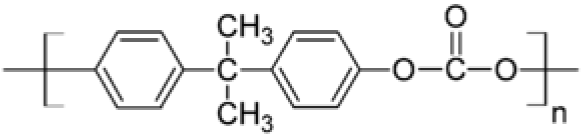


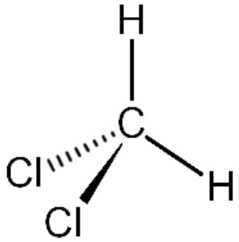
Figure 7: FTIR Result for Polycarbonate Membrane (DCM-PrOH)

FTIR is able to trace the structural changes of the polycarbonate membrane sheet that may occur during its fabrication process. Based on figure above, the transmittance represents the existing of OH group, chloride group, benzene group, aldehyde or ketone group, and also ether group. All functional groups represent the polycarbonate, DCM, THF, and ethanol. The result shows no structural changes due to chemical reaction during the formation of membrane sheet and thus can be confirmed that sheet formed is polycarbonate membrane sheet. Chemical structures which are expected in the membrane sheet shown below:

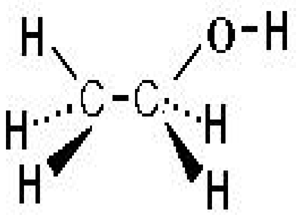
i) Polycarbonate (PC)



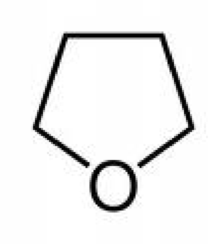
ii) DCM (Dichloromethane)



iii) Ethanol

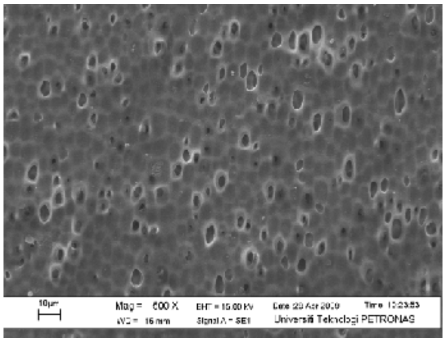
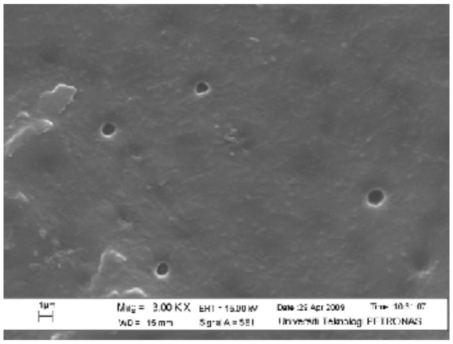


iv) THF (Tetrahydrofuran)



4.1.1.1 Effect of Solvents – Non-solvents Pair

Figure 8 shows the SEM images of surface layer of asymmetric PC membrane prepared from various DCM - non-solvents pair. Solvent and non-solvent selection plays an important role in controlling the membrane morphologies and properties. Result of SEM images shows various non-solvents used produced different membrane morphologies in terms of porosity and macrovoid formation. Referring to the images, the asymmetric PC membranes were successfully produced using DCM at different non-solvents used. The morphology of DCM-PrOH membrane was characterized by higher porosity and macrovoid substructure while DCM-MeOH and DCM-EtOH membranes have lower porosity and macrovoid-free substructure.

Surface side	
	DCM-MeOH membrane (a)
	DCM-EtOH membrane (b)

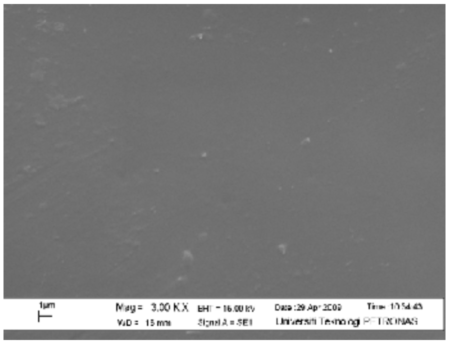
	DCM-PrOH membrane (c)

Figure 8: SEM images of top layer of membrane at various DCM – non-solvent pair a) PC/DCM/MeOH. b) PC/DCM/EtOH. c) PC/DCM/PrOH.

4.2 CO_2/CH_4 Separation Characteristic

The feed pressure was varied within 2 bar – 5 bars while temperature is assumed constant at 27^oC during experiment. All membranes prepared at the various experimental conditions were subjected to the same operating conditions in order to determine their gas separation characteristic.

For a reliable result, three membranes which were prepared under same preparation condition were tested twice in a single gas permeation set-up. Experimental results showed that asymmetric PC membranes prepared from various preparation parameters were reproducible as the deviation is small and not affect the gas separation characteristic of the membranes.

4.2.1 Effect of DCM – Non-solvents Pair

The gas separation characteristic is determined by plotting the permeance of CO_2, CH_4 and CO_2/CH_4 ideal selectivity of each membrane with respect to feed pressure. The permeance of CO_2 and CH_4 of various DCM – non-solvent membrane are presented in Figure 9 and 10, respectively.

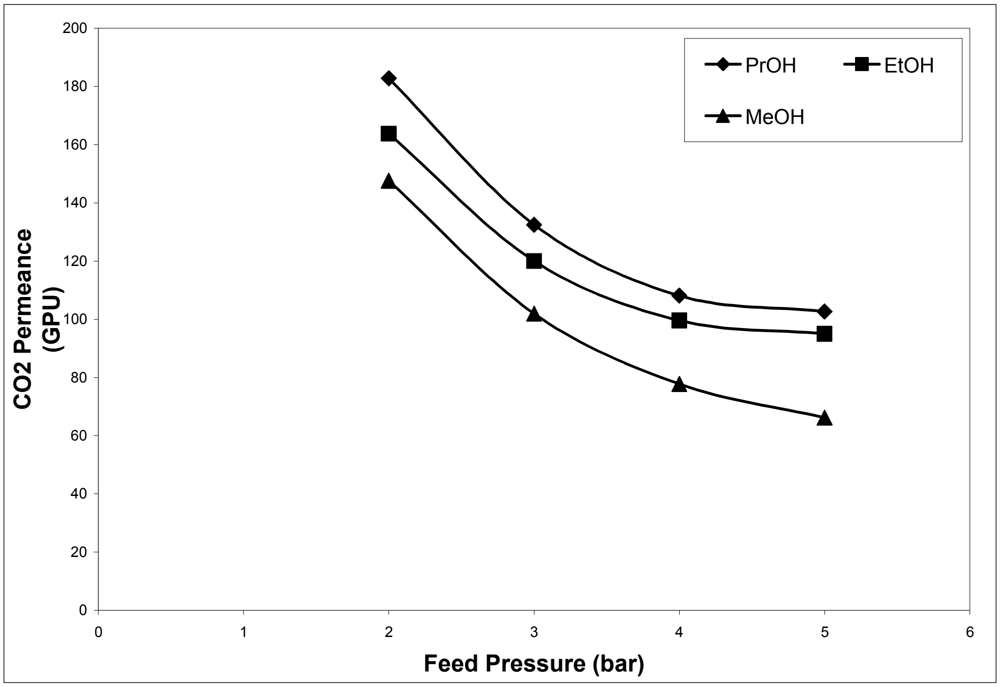


Figure 9: CO_2 permeance of membranes prepared from various DCM – non- solvent pair at various feed pressures

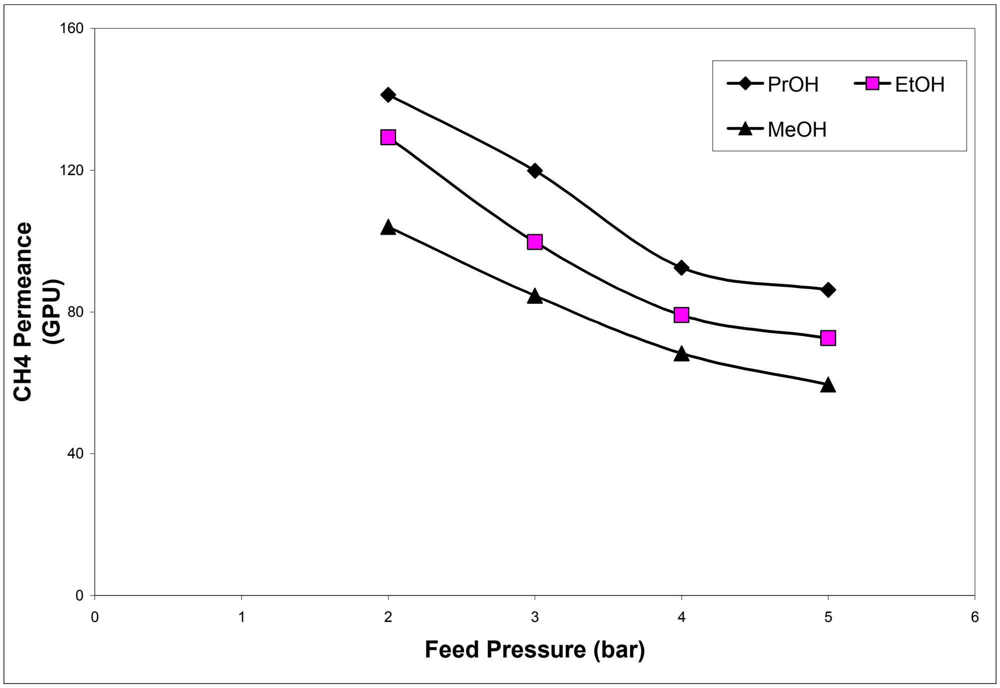


Figure 10: CH_4 permeance of membranes prepared from various DCM –nonsolvents pair at various feed pressure

According to Figure 9 and 10, CO_2 and CH_4 permeances increase in the order of DCM-MeOH <DCM-EtOH < DCM-PrOH solvent system. The significant differences of gas permeances among membranes prepared from various solvent - non-solvent pairs could be explained by referring to their morphologies as shown by SEM images, Figure 8. The porosity of substructure played an important role in determining the performance of membrane especially in terms of gas permeance. CO_2 and CH_4. Permeances of DCM-PrOH membrane were higher than that of DCM-EtOH and DCM-MeOH membrane. This is because DCM-PrOH membranes have more porous substructure with the presence of macrovoid as compared to other membrane. High porosity substructure makes the membrane become less restricted, thus allowing for the sorbed gas to diffuse more easily across the bulk structure of the membrane. While, denser and less porous substructure causes more hindrance for the sorbed gas to diffuse over the entire structure of membrane thus producing lower CO_2 permeance. In the case of DCM-PrOH membranes, the high CO_2 and CH_4 permeances were probably due to the formation of pores on the skin layer of the membranes and solution diffusion mechanism which occur in dense surface of the membrane that lead to lower CO_2/CH_4 ideal selectivity as shown in Figure 11.

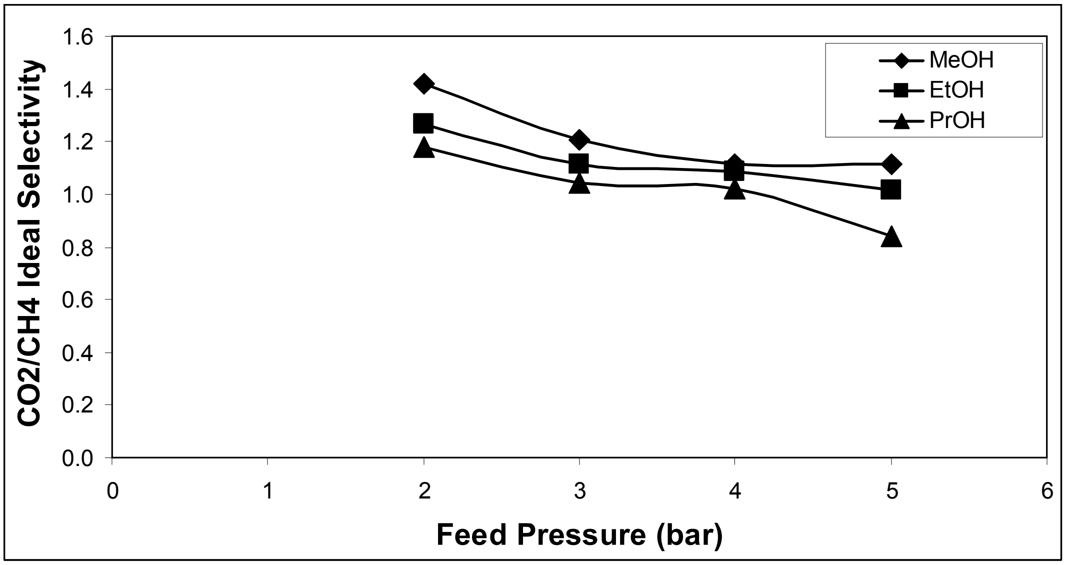


Figure 11: CO_2/CH_4 ideal selectivity of membranes prepared from various DCM – non-solvent pair at various feed pressures

Low selectivity of DCM-PrOH indicated that both CO_2 and CH_4 can pass through the membrane easily. Consequently, CO_2 and CH_4 permeances of DCM-PrOH membrane would be higher as compared to highly selective DCM-MeOH and DCM-EtOH membranes. High selectivity of DCM-MeOH and DCM-EtOH membranes indicate that the sub-layer of these membranes were denser and less macrovoid formation compared to DCM-PrOH. Transport mechanism in these membranes was affected by solution-diffusion mechanism in which polar gas of CO_2 was absorbed more than CH_4. The sorbed CO_2 would then diffuse through the bulk structure of the membrane to the permeate side. Therefore, CO_2 permeance of asymmetric DCM-MeOH and DCM-EtOH membranes was always higher compared to CH_4 permeance.

CO_2 permeance of all the membranes was also found to decrease as feed pressure increase. This is typical behavior of CO_2 transport mechanism through dense membrane due to solution diffusion mechanism (Koros et al., 1977; Sanders, 1988; Ismail and Lorna, 2002). CH_4 permeance of these membranes also slightly increases as feed pressure increase due to increasing of diffusion coefficient of CH_4 (Lin and Chung, 2001).

CO_2/CH_4 ideal selectivity of DCM MeOH was higher than that of DCM-EtOH membrane. This is because CH_4 permeance of DCM-EtOH membrane was higher than that of DCM-MeOH membrane thus contributed to the decreasing selectivity. CO_2/CH_4 ideal selectivity of membranes was decreased as feed pressure increase. The same trend of CO_2/CH_4 ideal selectivity against feed pressure was also reported by Jordan and Koros (1990).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Fabrication of asymmetric polycarbonate (PC) membrane at various preparation parameters such as morphology and CO_2/CH_4 separation characteristic is investigated. These membranes were prepared using dry/wet phase inversion method. Chemicals used in this project were dichloromethane (DCM) as more volatile solvents, Tetrahydrofuran (THF) as less volatile solvent, methanol (MeOH), Ethanol (EtOH) and propanol (PrOH) as non-solvents and methanol (MeOH) as coagulant. Preparing asymmetric PC membrane by adding MeOH as non-solvent would result less porous with no formation of macrovoid on membrane substructure. Overall porosity of membrane decrease in the order of non-solvent used, PrOH>EtOH>MeOH. According to permeation studies, different morphologies of asymmetric PC membrane resulted from various non-solvents pair used during preparation significantly changed the performance of membrane. It showed that CO_2 and CH_4 permeances of DCM-PrOH membrane were higher as compared to DCM-MeOH and DCM-EtOH membranes. However, the CO_2/CH_4 ideal selectivity of DCM-PrOH membrane was very low implying that high CO_2 and CH_4 permeances were could be due to the more porous and macrovoid skin layer of membrane ($\alpha_{CO_2/CH_4} = 1.19$ for DCM-PrOH membrane). High ideal selectivity of CO_2/CH_4 was obtained for DCM-MeOH and DCM-EtOH membranes ($\alpha_{CO_2/CH_4} = 1.42$ for DCM-MeOH membrane, $\alpha_{CO_2/CH_4} = 1.29$ for DCM-EtOH membrane). In these membranes, porosity of substructure and transport mechanism of solution diffusion played important role in which CO_2 permeance of DCM-PrOH membrane would be higher as compared to other membranes due to high porosity of membrane substructure and dense skin layer supported.

5.2 Recommendation

Based on this work, some recommendations as future works may provide further improvement into the mechanism of asymmetric PC membranes formation are listed below:

Study on the crystallization behaviour of PC membrane is necessary to produce dense skin asymmetric PC membrane thus can improve the membrane reliability. Other preparation parameters such as effect of casting rate, humidity condition during preparation and less volatile solvent composition may be considered as they can affect the performance of asymmetric PC membrane.

The effect of prolong CO_2 exposure and higher feed gas pressure on asymmetric PC membrane stability is also necessary. So, further study on the effect of multicomponent feed gas on the performance of asymmetric PC membrane may be done by having mixed gas permeability tests conducted for some membrane films that have shown high CO_2/CH_4 ideal selectivity.

Incorporation of in-organic material such as zeolite and carbon molecular sieve during preparation phase of PC membranes can be good option in enhancing the performance of membrane in removing CO_2 from natural gas. As polymeric membranes have thermal and temperature stability issues, blending in-organic material may overcome these prolems.

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APPENDIX

APPENDIX A

Properties

A.1 Polymer

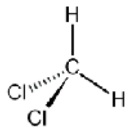
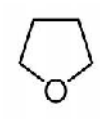
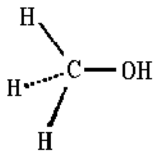
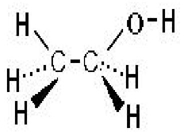
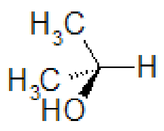
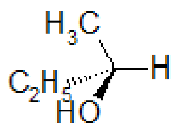
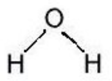
Table A.1 Properties of polycarbonate used in this study

	Polycarbonate
Manufacturer	LG-DOW
Type	Amorphous
Characteristic	Good dimensional stability, shiny surface, high termal stability, sensitivity to stress cracking
Density (gr/cm^3)	1.2
Mr	254 g/mole

A.2 Chemicals

The chemicals used in this study are dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), propanol (PrOH), tetrahydrofuran (THF) and water. Chemical properties are presented in Table A.2

Table A.2 List of properties of pure components

	DCM	THF	MeOH	EtOH	PrOH	BuOH	Water
Supplier	Merck	Merck	Merck	Merck	Merck	Merck	Tap Water
Purity (Mole %)	99.5	99	99.9	99.5	99.5	99	100
Molecular weight (g/mol)	85	72.11	32	46	60	74	18
Molecular structure							
Melting point (^{o}C)	-95	-108.4	-98	-114	-88	-108	0
Boiling point (^{o}C)	40	66	64	78	82	108	100
Liquid density (g/cm^3)	1.33	0.8892	0.79	0.789	0.78	0.808	0.998