THE SEPARATION OF CARBON DIOXIDE – METHANE – PROPANE BY USING HOLLOW FIBER MEMBRANE: EFFECT OF FEED PRESSURE AND CO_2 COMPOSITION

By

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12826

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JAN 2013

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CERTIFICATION OF APPROVAL

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Approved by,

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(DR LAU KOK KEONG)

Date: 15th August 2013

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JAN 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I, Ponmani Sivagnanam (I/C No: 900213-06-5021), 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.

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ABSTRACT

Carbon dioxide, CO_2 is known with its corrosive properties when dissolved in water. Therefore, CO_2 is needed to be removed from the natural gas to avoid it from damaging the pipelines and equipment due to its corrosive properties. There are a lot of method to separate CO_2 from natural gas however membrane technology can be considered one of the methods which offers the largest potential in terms of economic feasibility especially in offshore. However there is lack of studies on the effects of multi component feed on the carbon dioxide separation using a membrane. Hence, the main objective of this project is to evaluate the permeance and relative permeance of commercial hollow fiber membrane under different feed pressure and feed CO2 composition using CO_2-CH_4-C_3H_8 as feed. A hollow fiber membrane module is prepared to conduct the lab experiments. Using the prepared module, experiments on the effect of feed pressure and CO2 composition in feed was conducted. The results obtained was analyzed to study the effect. From the analysis, it is learned that the permeance and relative permeance of CO2 increase with pressure in the range of 10 to 18 bar. The permeance and relative permeance of CO2 also increases when CO2 composition is increased from 16 Vol. % CO2 to 67 Vol. % CO2.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The demand for natural gas is increasing rapidly every year. Natural gas mostly consists of methane and several gases such as ethane, propane, butane, higher molecular weight hydrocarbons and other impurities like water vapour, nitrogen, hydrogen sulphide and etc. High CO_2 in natural gas exceeds pipeline specification for carbon dioxide content. Carbon dioxide, which falls into the category of acid, is commonly found in natural gas streams at levels as high as 80%. When combined with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or a more corrosive resistant material is used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO2 must be removed to prevent freezing in the low-temperature chillers. (Dortmundt & Doshi, 1999). Hence a process of CO_2 removal is important process in any natural gas producing or processing plant.

A wide variety of CO_2 removal technologies are available. They include chemical absorption such as the Benfield process and Amine process, physical absorption using the Selexol process, cryogenic processes, adsorption processes and iron sponge. However, they are only appropriate to separate 20% of carbon dioxide content. Thus, membrane system has emerged as important unit operations for CO_2 removal offering specific advantages over more conventional separation procedures especially in remote area such as offshore. The advantages of membrane system are lower capital cost, lower operating costs, deferred capital investment, good weight and space efficiency, adaptability, design efficiency, environmentally friendly and ideal for remote locations. (Schell & Houston, 1983)

Although there are a large number of potential applications for gas separation with polymer membranes, only relatively few of them have become applied in practice. The potential application of a polymer as a separation membrane depends upon the permeability and selectivity of the membrane system. Any modifications which lead to increase in membrane permeability usually cause losses in selectivity and vice versa. Thus there is a lot of researches that had been carried out involving the membrane separation system to enhance its performance through changes in operating and feed conditions. (Xu, Wang, Chen, & Xu, 1999)

1.2 Problem Statement

Despite the significant number of researches that had been carried out, there are lack of researches on the effects multi-component feed on the performance the membrane separation system (Luis, Gerven, & Bruggen, 2012). Hence the performance of a hollow fiber membrane in CO_2 separation from a mixture of CO_2, CH_3 and C_2H_8 is to be studied. The parameters that will be tested are pressure and CO_2 composition in feed.

1.2.1 Significance of project

The aim of the project is to study the relationship between the changes in the in parameters (pressure and CO_2 concentration) and the efficiency of the CO_2 removal using a multi-component hydrocarbon feed; CO_2, CH_3 and $C_2H_{8.}$ The experiment will be conducted using feed of different CO_2 concentration and operating pressure to obtain data for the study. This can be used to evaluate and optimize the membrane system used to remove CO_2.

1.3 Objectives

There are 3 objectives that will be achieved through this project. They are:

- To prepare a hollow fiber membrane module
- To evaluate the permeability and selectivity of commercial hollow fiber membrane under different feed pressure
- To evaluate the permeability and selectivity of commercial hollow fiber membrane under different CO2 composition in feed

1.3.1 Scope of Study

The research will involve the conducting experiments in the lab which includes preparing the module of the hollow fiber membrane. Prior to that, it is necessary to understand the theory of membrane separation. This project can be broken down to identification of appropriate range of parameter (pressure and CO2 composition) to run the experiment and key factors that influence the permeability and selectivity of a membrane. The module is then used to evaluate the performance of the membrane under different feed pressure and also different CO_2 composition in feed. The findings will then be recorded and documented.

1.4. Feasibility of the project within the scope and time frame

The first step in this project will be getting an introduction to the related topics by reading books, journals and research papers. Research will be done in order to better understand the CO_2 removal using the membrane system. Focus will be on the parameters affecting the performance of the membrane. The process of fabricating the model available for experiment flooding will take time, about 1 month. The study of its parameters will take about 2 months and 1 month will be available to incorporate the required parameters and data into a final report and be presented.

CHAPTER 2

LITERATURE REVIEW

This following chapter will describe the theory of membrane separation. Several research papers and journals have been reviewed in order to understand the process. Next, the chapter would also stress on the fundamentals and equations would be incorporated into the project in successfully completing the study on the effect of pressure and CO_2 composition in CO_2 separation using hollow fiber membrane.

2.1 CO_2 removal from Natural Gas

40% of world's known gas reserves are sour. The natural gas from these reserves contain at least 10 % of CO_2 (Lallemand, Rocher, & Aimard, 2006). Besides being a major contributor of the green house effect, the CO_2 from natural gas has to be removed to meet pipeline specification due to its corrosive nature. It also reduces the heating value of natural gas and wastes pipe capacity. It is also important to note that CO_2 is being used for Enhanced Oil Recovery (EOR) through CO_2 flooding (Dinello, Narayan, & Patton, 1989). Hence CO_2 removal is an important process in a natural gas plant. A wide variety of CO2 removal technologies are available. They include chemical absorption such as the Benfield process and Amine process, physical absorption using the Selexol process, cryogenic processes, adsorption processes and membrane process. Currently the most used process is the Amine process (Jahn, Boss, & Broeke, 2012).

2.2 The advantage of using membrane system

Lallemand et al reported that 50% of the world's known gas reserves are small gas fields. Considering Amine process being predominently preferred for CO_2 removal, these gas fields are not economically feasible to start production. The current technology is not selective enough to obtain desired specification. Thus it is too expensive to explore the gas fields. With the rising demand for energy, a more cost efficient process is needed to process these gas fields. The conventional method of CO_2 removal (not including membrane) can only process gas containing less than 20% CO_2 (Schell & Houston, 1983). Thus, Jahn et al. state that a membrane system is preferred as opposed to other methods as it offers more advantage such as operating at remote location, lower operational cost, more open to future scale ups and flexibilty with feed concentration.

2.3 Transport mechanism of membrane system

The mechanism of membrane separation had been described in Langmuir's dual-mode sorption model (Hasan, Scholes, Stevens, & Kentish, 2009). Hasan et al has given the concentration of pure gas A in a membrane as:

$$C_{\mathrm{A}} = K_{\mathrm{DA}} f_{\mathrm{A}} + \frac{C'_{\mathrm{HA}} b_{\mathrm{A}} f_{\mathrm{A}}}{(1 + b_{\mathrm{A}} f_{\mathrm{A}})}$$

When multiple gas species are present for instance a ternary mixture of gases A, B, and C the mobile concentration of gas A becomes:

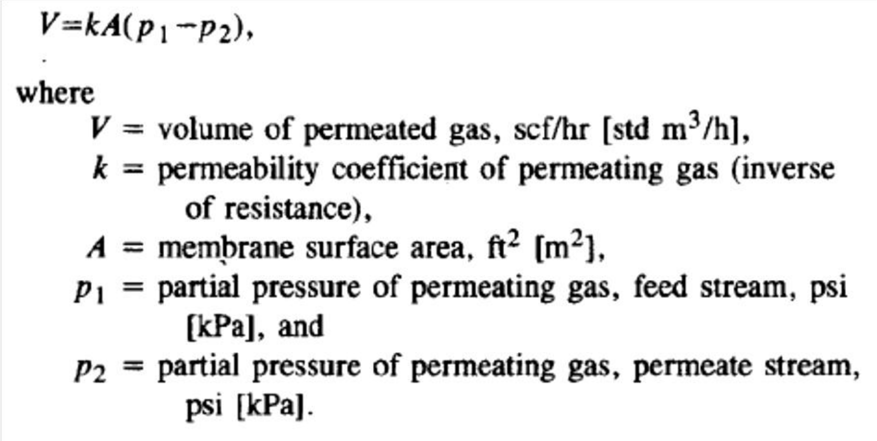
$$C_{\mathrm{MA}} = K_{\mathrm{DA}} f_{\mathrm{A}} \left[1 + \frac{F_{\mathrm{A}} C'_{\mathrm{HA}} b_{\mathrm{A}}}{K_{\mathrm{DA}}(1 + b_{\mathrm{A}} f_{\mathrm{A}} + b_{\mathrm{B}} f_{\mathrm{B}} + b_{\mathrm{C}} f_{\mathrm{C}})} \right]$$

where F_A is defined as the ratio of diffusion coefficients in the Langmuir and Henry's Law region (D_H/D_D). It can be seen that the competition between the gases will further restricts the amount adsorbed in the Langmuir free volume.

Dinello et al. had also done an extensive study on the membrane system through a pilot plant in 1989. They have described the basic principle of membrane separation. For a gas to permeate across a membrane surface, the gas must first dissolve in the high-pressure side of the membrane, diffuse across the membrane wall, and then evaporate from the low-pressure side. Each membrane provides resistance to the gas transport. 2

factors causing the resistance are the size and shape of the gas molecules, and molecular interaction between the membrane and the gas. A gas encountering low resistance to transport is called a fast gas; a gas encountering a high resistance is called a slow gas. CO_2 is a fast gas because of its linear molecular orientation and its high solubility in polymer membranes.

The driving force for transport of a particular gas through a membrane is the difference in partial pressure of that gas across the membrane. The greater the partial-pressure difference, the greater the driving force. Gas transport across a membrane can be represented as (Dinello, Narayan & Patton, 1989):



$$V=kA(p_1-p_2),$$

where

V = volume of permeated gas, scf/hr [std m^3/h],
k = permeability coefficient of permeating gas (inverse of resistance),
A = membrane surface area, ft^2 [m^2],
p_1 = partial pressure of permeating gas, feed stream, psi [kPa], and
p_2 = partial pressure of permeating gas, permeate stream, psi [kPa].

The permeability coefficient, k, is a function of both the solubility and the diffusivity of the gas in the membrane. The degree of separation achievable between two gases is determined by the ratio of their permeability coefficients, or more commonly known as selectivity. CO2, a fast gas, can be separated from hydrocarbon gases, which are relatively slow gases. As the flux equation above illustrates, as long as a partial-pressure driving force exists, CO_2 will be removed selectively from the gas mixture, along with lesser amounts of the other lower-permeability components.

2.4 Types of membrane

For an efficient gas separation membrane, few aspects need to be considered. They are chemical and mechanical stability (Lin & Freeman, 2005). Chemical stability is important as exposure to acid gas will accelerate the aging and plasticization of the material. Physical stability is important because it needs to be able to withstand pressure as high as possible as the pressure difference is the driving force of the process. Jahn et al. generally divided the membrane into 2 different groups, the selective membrane and the gas-liquid contactors. The key difference between this 2 are, in the gas-liquid contactors the diffusion takes place through a liquid absorbent where as for the selective membrane, the diffusion takes place through the solid membrane (Jahn, Boss, & Broeke, 2012).

As the research is using polyimide hollow fiber membrane, a selective membrane, more focus will be given to it. Cellulose acetate is the most commonly used membrane but Hasan et al. reported that polyimide carry a great potential as it has high thermal and mechanical stability, as well as chemical resistance. His findings were supported by the works of He and Hägg. The shortcomings of polymeric membrane are poor the trade-off of permeability/selectivity, limitation of operation temperature and adverse conditions such as the presence of acid gases SO_2 and NO_x. On the other hand, carbon membranes such as polyimide show promising applications for gas separation especially for CO_2 removal from natural gas (He & Hägg, 2010). More specifically there has been keen interest towards hollow fiber membrane. This is mainly due to better selectivity, thermal and chemical stability, of its high packing density (membrane area per unit volume of vessel) and easier module assembly (Favvas, Kapantaidakis, Nolan, Mitropoulos, & Kanellopoulos, 2007).

2.5 Past Researches Done on CO_2 Separation Using Membrane

The advantage of membrane system in CO_2 separation had been noticed by researchers and a lot of researches had been done of the system. Schrier in 2012 conducted a research on carbon dioxide separation with a two-dimensional polymer. Through his study, he introduced a Langmuir-adsorption model to calculate the effect of surface adsorption of gases on membrane permeance from a mathematical model simulation (Schrier, 2012). This model can be used to predict gas transport through the growing variety of membrane. He managed to prove that tuning the surface adsorption provides an additional means of controlling the transport of molecules through nanoporous materials. The hydrocarbon polymer, PG-ES1 used in the simulation is capable of unprecedented permeance and selectivity for CO2 separation from N_2 and CH_4. The CO_2 permeance is 3×10^5 gas permeation units (GPU). The CO_2/N_2 selectivity is 60, and the CO_2/CH_4 selectivity exceeds 500.

In research conducted in 2009, the performance of a glassy polymeric membrane of changes significantly upon exposure to a mixed gas stream of toluene and hexane (Hasan, Scholes, Stevens, & Kentish, 2009). Hasan et al. stated in his paper that in a stream of CH_4/CO_2, carbon dioxide permeability falls due to competitive sorption relative to the pure gas value. Addition of impurity levels of hexane or toluene causes the permeability of both gases to fall further, again through competitive sorption. The result was modeled using a dual sorption model. The rate of permeability decline upon hydrocarbon exposure was modeled using simple first-order kinetics. The recovery of membrane performance once the hydrocarbon is no longer present is much slower, indicating that Langmuir desorption may have become the rate controlling step.

Jahn et al. in 2013 made a comparison of CO_2 flux obtained from different membrane processes through experiments. The experiment was however conducted using gas-liquid membrane contactor which is said to be carrying a huge potential in CO_2 separation (Jahn, Boss, & Broeke, 2012). The study uses pure gas and also binary gas of CO_2-H_2 and CO_2-CH_4. Jahn et al. concluded that CO_2 flux across selective membrane is higher for inorganic membrane and membrane contactors compared to polymer membrane. In the case of liquid-gas membrane contactor, the carbon dioxide flux is decreasing with increasing permeate side pressure whereas the CO_2 flux increases with increase in feed pressure.

For a hollow fiber carbon membrane, the permeability for different gases, CO_2, O_2 and N_2, were in accordance with the order of kinetic diameters for gas molecules (<4 A˚), which indicated that the molecular sieving mechanism was dominated for the transport process across the membrane (He & Hägg, 2010). He et al. stated in his paper that the gas permeability will decrease with the presence of water vapor which may be caused by the pore blocking. The feed pressure and retentate flow rate showed the more significant influences on the carbon membrane separation performance. In investigating the effect of feed pressure, He et al. found that the increase in feed pressure is accompanied by increase in CO_2 recovery but decrease in CO_2 purity. Which means there would be a heavy loss of hydrocarbon if a membrane system is used at a elevated pressure despite increasing the CO_2 flux

When comparing pure gas and mixed gas, there will be a decrement in concentration of penetrant in the polymer mixed gas due to the competitiveness effect between the gases for available of a fixed number of Langmuir's sites (Jusoh, Lau, & Shariff, 2012). According to Jusoh et al. reduction of penetrant concentration in the membrane for CO_2 is higher than CH_4 because CO_2 sorption in these microvoids is favorable and CO_2 has a higher affinity towards free volume defect sites than CH_4. However increase in pressure is said to have reduced the selectivity due to decrease in diffusivity caused by combination effect effects of two gases; CO2 and CH4 and polymer matrix loosening phenomena.

Besides the study on effects of mixed gas on the selectivity and permeability, there was a study done on the effect cross flow model and co-current flow model (Yang, Wang, Wang, & Wang, 2009). Yang et al. proved that that the difference between the cross-flow model and the other co-current model is minor. By increasing feed side pressure and decreasing permeate side pressure, the membrane area required decreases and the CH4 recovery increases. For the two stage system, the recycle flow rate decreases as the selectivity increases. Therefore, as the CH_4 permeability increases, the membrane area of the first stage decreases. They have achieved CH_4 recovery of more than 98% and product purity of more than 98% by the single-stage system. The separation target was achieved by using the two-stage system with a membrane selectivity of 20.

Kurako et al. developed a multi-layer microporous silica xerogel membrane by sol-gel method. The ratio of the permeances, CO_2/N_2 for this membrane attained more than 60 at 298 K (Kurako, Kubo, & Yazawa, 2010). The gas permeances of this membrane (AL-

1 membrane) were about 5–10 times higher than PG membrane. Application of the membrane to an enrichment of CO_2 from the air was also investigated. CO_2 in the air (about 300 ppm) was concentrated to more than 1000 ppm by using the membrane at 298 K. However, this membrane can only be applied to the recovery of CO_2 from the gases with low CO2 concentration.

There are also researches that are being done on improvisation of existing membrane using thermal and chemical method (Cho, Beltran, Africa, & Nisola, 2011). Modification of commercially available membrane was proven as convenient technique to tailor PI membrane properties for specific applications. Both thermal and chemical modifications remarkably improved the hollow fiber polyimide membrane membrane performance in terms of CO_2 permeance and CO_2/CH_4 selectivity. However, since pure gas systems were tested in this study, further investigations using actual gas mixtures are necessary to determine the behaviour of the modified membranes under realistic conditions and to observe CO_2 plasticization in more detail as it often causes a decline in membrane performance.

2.6 Summary

Table shows the literature review on past researches done on membrane CO_2 separation system.

Table 1 Summary of Literature Review

Author(s)	Findings
Schrier, 2012	• Developed a Langmuir-adsorption model to calculate the effect of surface adsorption of gases on membrane permeance • Simulated the CO2 separation from N2 and CH4 using hydrocarbon polymer, PG-ES • The CO2 permeance is 3 × 105 gas permeation units (GPU) • The CO2/N2 selectivity is 60, and the CO2/CH4 selectivity exceeds 500
Hasan et al., 2009	• Simulated the effect of exposure to mixed gas in CO2 separation using a dual sorption model • CO2 permeability falls significantly due to competitive sorption relative to the pure gas value • The recovery of membrane performance once the hydrocarbon is no longer present is much slower
Jahn et al., 2013	• Made a comparison of CO_2 flux obtained from different membrane processes through experiments using pure gas and also binary gas of CO_2-H_2 and CO_2-CH_4 • CO_2 flux across selective membrane is higher for inorganic membrane and membrane contactors compared to polymer membrane • CO_2 flux is decreasing with increasing permeate side pressure whereas the CO_2 flux increases with increase in feed pressure
He et al., 2010	• Permeability will decrease with the presence of water vapor which may be caused by the pore blocking • Increase in feed pressure is accompanied by increase in CO_2 recovery but decrease in CO_2 purity

Jusoh et al., 2012	• There will be a decrement in concentration of penetrant in the polymer mixed gas due to the competitiveness effect between the gases for available of a fixed number of Langmuir's sites • Reduction of penetrant concentration in the membrane for CO_2 is higher than CH_4 because CO_2 sorption in these microvoids is favorable and CO_2 has a higher affinity towards free volume defect sites than CH_4. • Increase in pressure is reduces the selectivity due to decrease in diffusivity
Yang et al., 2009	• Difference between the cross-flow model and the other co-current model is insignificant • Increasing feed side pressure and decreasing permeate side pressure, decreases the membrane area required and increases CH4 recovery • Achieved CH_4 recovery of more than 98% and product purity of more than 98% by the single-stage system using membrane selectivity of 20%
Kuroku et al. 2010	• Developed a multi-layer microporous silica xerogel membrane by sol-gel method • Ratio of the permeances, CO_2/N_2 for this membrane attained more than 60 at 298 K • Can only be applied to the recovery of CO_2 from the gases with low CO2 concentration
Cho et al., 2011	• Modified commercially available membrane using thermal and chemical methods to improve membrane properties for specific applications • Both thermal and chemical modifications remarkably improved the hollow fiber polyimide membrane membrane performance in terms of CO_2 permeance and CO_2/CH_4 selectivity

2.7 Research Gap

It can be summarized from this literature review that CO_2 removal using the membrane system is a promising venture mainly due to its advantages compared other technology in terms of operational cost and space requirement. There are a lot of studies on membrane separation technology. From the literature review, it can be observed that the researches are generally divided into simulation of membrane performance, development of mathemathical model, development of new membrane and optimization of existing membrane.

Despite the wide range of researches that are being done on CO_2 separation using membrane system, most of the researches are focused on binary component separation and pure gas separation. Hence there is still a large gap between the lab-scale and the real application in the industry (Luis, Gerven, & Bruggen, 2012). There is a uncertainty over the effectiveness of these membranes under industrial conditions where the feed gas is made up of multi component. It can be clearly seen that there is a gap in understanding the effect of multi component feed on the membrane performances.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology and Project Activities

The methodology for conducting this research project is exploration and discovery. As this project is mainly an empirical research, the results obtained from this research can be used to compare with other literature results. The project activities in this research are mainly experimental work. After thorough literature review is done, experimental works can be conducted to investigate the effect of feed temperature and composition of propane toward the separation of CO_2 - Methane – Propane.

3.2 Experimental Procedures/Approach

Figure 1 shows the general project flowchart that will be implemented in this research project.

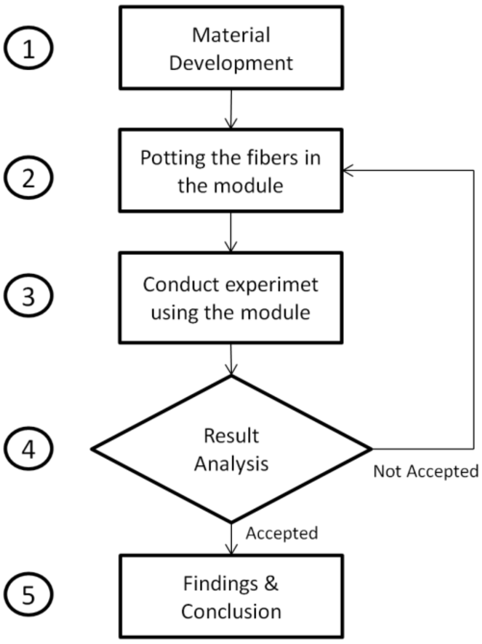


Figure 1 The schematic diagram depicting the general approach in this project

3.3 Module Preparation

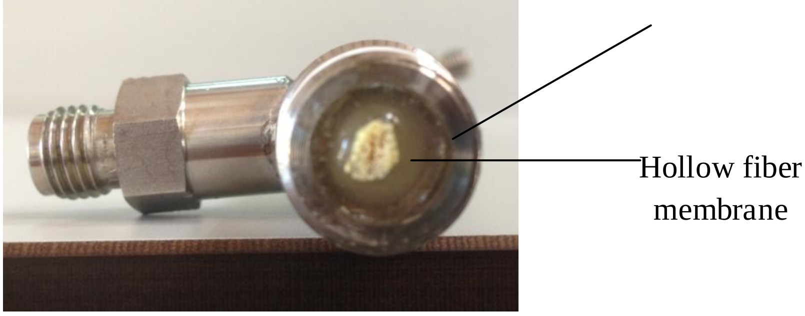


Figure 2 Cross- Section of Module

The module does not need to be developed as it is already available subject to prior research conducted by previous students. However, it needs to be prepared before potting the fibers. As seen in Figure 2, the epoxy holding the membrane needed to be removed by means of drilling. This was done by drilling using a hand drill.

3.4 Potting of fibers

Before potting of fibers into the module prepared, the packing density needs to be decided. The packing density can be calculated based on this formula.

$$\text{packing density } (\phi) = \text{no. of fibers } (n) \times \frac{\text{cross} - \text{section area of a fiber } (A_{\text{fiber}})}{\text{cross} - \text{section area of module } (A_{\text{module}})}$$

Equation 1: Membrane Packing Density

For the purpose of this experiment, a constant number of 10 fibers had been set as the packing density is not one of the parameter tested. The figure of 10 is chosen due to the constraint set by the module's diameter. The outer diameter of the membrane is 0.04 cm where as the inner diameter of the module is1.74 cm. Using Equation 1, the packing density is calculated to be 9.82×10^{-3} or 0.99 %. The fiber potting can be divided into several categories. They are:

- Module bundle preparation
- Module assembly
- Epoxy resin casting

3.4.1 Module bundle preparation

1. The required fiber numbers and fiber length are calculated based on the diameter of hollow fibers and the length of module.
2. The fibers are cut to a desired length, visibly defective fibers are removed, and placed in parallel order and put together as a fiber bundle
3. A piece of paraffin film is cut to a dimension of about 40 mm long and 10 mm wide. Holding the film at each end, it is stretched slowly without snapping to four or five times of its original length, wrapped on one end of the fiber bundle before it relaxes to a natural status. The wrapped end is cut with a razor blade to yield a smooth cross-section
4. This end is encircled with a thin string and made sure its diameter is smaller than the inner diameter of the shell

3.4.2 Module assembly

1. Place the shell vertically on a holder and leave enough space under the module shell so that it can accommodate the fiber bundle.
2. Lay a long string through the shell lumen and tie with the thin string that is roped upon the fiber bundle .
3. Pull the long string gently upwards so that the fiber bundle is housed in the shell at a designated position. The untied portion of the fiber bundle should be suspended freely and hung loosely; thus the fibers become ordered and packed naturally when being pulled into the shell.
4. Repeat the step (3) in Module bundle preparation and wrap the other end of fiber bundle with a piece of paraffin film. Each end should emerge out of the module shell with a length of 10 mm.

3.4.3 Epoxy resin casting

1. Apply a layer of Araldite® 5 min curing adhesive on the cross-sections of the bundle ends to seal each hollow fiber and prevent the creeping of epoxy through the fiber lumens by the capillary flow.
2. Suitable proportion of epoxy and hardener are mixed.
3. Fill a 50 ml syringe with the epoxy resin mixture slowly so that no air bubbles are generated. Put in the piston and manually push it forward to discharge any air trapped in the syringe. Then continuously push the piston till the liquid-like epoxy mixture completely covers the space.
4. Leave the module in a dry room overnight so that the epoxy can completely dry.

3.5 Gas separation testing unit

Hollow fiber membrane module is installed in the experimental set up as shown in diagram below.

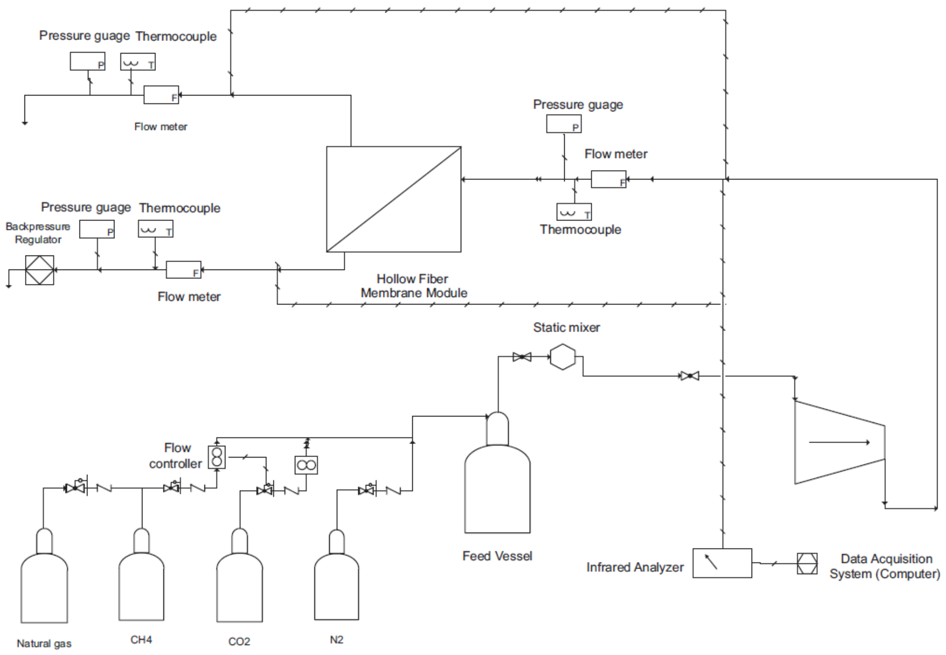


Figure 3 Flow sheet of gas separation testing unit for experimental validation

The testing unit mainly consists of gas cylinders, mass flow controllers, compressor, and infrared analyser. There are 2 experiments that will be conducted in this study. They are:

- The effect of feed pressure on relative permeance and permeance of gases
- The effect of CO2 composition on relative permeance and permeance of gases

3.5.1 Starting the System

1. Main power supply inside the control panel is turned on
2. Main power supply to computer is switched on
3. NI lab view is activated and the software is allowed load completely
4. Analyzer switch on the control panel is switched on

5. The operating temperature is set according to the experiment

Figure 4 Gas Separation Unit’s Control Panel

3.5.2 Heating up the Hot Water System

1. The main power in the hot water system’s control panel is powered up
2. The heater temperature is set up to 80 ℃
3. The hot water is circulated inside the heat exchanger using the pump.
4. The valve at the top of Methane, Carbon Dioxide and Propane are opened respectively

Figure 5 Hot Water System's Control Panel

3.5.3 Setting up Feed Gas

1. The inlet and outlet valve for CO_2 and CH_4 are opened
2. The propane flow is regulated using the flow meter at 30 SLPM
3. The feed pressure regulator is set according to the experiment
4. The flow rate for CO_2 and CH_4 are set according to the experiment mass flow controller

Figure 6 Feed Gas Controller

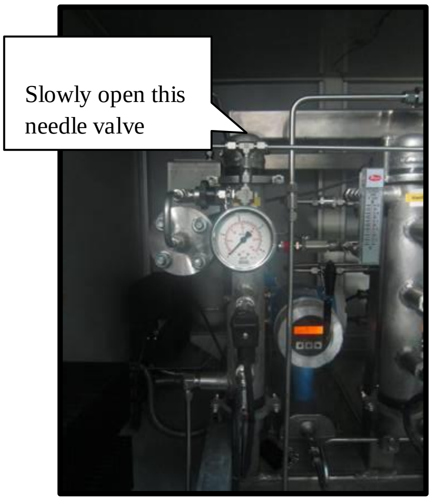
3.5.4 Setting up Manual Back Pressure Regulator

1. Use the high pressure regulator to regulate the retentate side pressure
2. Turn the knob clockwise up to set the pressure to 1 bar less than the feed pressure

Figure 7 The Back Pressure Regulator

3.5.5 Taking the reading

1. Slowly open the needle valve at the top of manifold 1, 2, 3 or 4 respectively.
2. Open the inlet valve to the gas analyzer
3. Wait till the reading of gas analyzer stabilizes
4. Take the reading of the gas analyzer
5. The process is repeated using different feed conditions.



Slowly open this needle valve

Figure 8 Manifold 2 (Feed)

3.6 Analysis of Results

The result obtained through the experiments are analysed mainly in terms of permeability and selectivity. The permeability for individual gases can be calculated using:

$$\boldsymbol{P_A = \frac{\dot{m}_A \times MW_A \times 22400}{A_m \times \Delta P}}$$

Where $\dot{m}_A$ = Mass flow rate of A, g/s

MW_A = Molecular weight of A, g/mol A

A_m = Surface area of membrane, cm^2

ΔP = Pressure difference between feed and permeate side, cmHg

The selectivity of CO_2 over the other gases can be calculated using:

$$\boldsymbol{\alpha_{AB} = \frac{P_A}{P_B}}$$

Where P_A = Permeability of A, GPU

P_B = Permeability of B, GPU

Then a graph of Permeance versus Pressure and Selectivity versus Pressure is plotted for experiment 1. Meanwhile for experiment 2, Permeance versus CO_2 composition and Selectivity versus CO_2 Composition is plotted.

3.7 Key Milestone

Table 2 Key Milestone

No	Key Milestones	Timeline
1	Extended proposal submission	FYP 1 Week 7
2	Proposal defense	FYP 1 Week 8
	Preparation of module	FYP 1 Week 10-12
5	Chemical Requisition: Propane	FYP 1 Week 11-14
6	Submission of Interim Draft Report	FYP 1 Week 13
7	Submission of Interim Report	FYP 1 Week 14
8	Experiment 1: Effect of Feed Pressure	FYP 2 Week 2-3
9	Experiment 2: Effect of CO_2 Composition	FYP 2 Week 4-5
10	Analysis of Results	FYP 2 Week 4-6
11	Submission of Progress Report	FYP 2 Week 8
12	Pre-SEDEX	FYP 2 Week 11
13	Submission of Draft Report	FYP 2 Week 12
14	Submission of Dissertation (soft bound)	FYP 2 Week 13
15	Submission of Technical Paper	FYP 2 Week 13
16	Oral Presentation	FYP 2 Week 14
17	Submission of Project Dissertation (Hard Bound)	FYP 2 Week 14

3.8 Gantt Chart for FYP 1 and 2

Table 3 Gantt Chart for FYP 1

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	First meeting with coordinator and supervisors	🟥	🟥						Mid-semester break							
2	Preliminary Research Work		🟥	🟥	🟥	🟥	🟥									
3	Submission of Extended proposal							🟥								
4	Proposal Defense									🟥	🟥					
5	Preparation of Module											🟥	🟥	🟥		
6	Chemical Requisition: Propane												🟥	🟥	🟥	🟥
7	Submission of Interim Draft Report														🟥	
8	Submission of Interim Report															🟥

Table 4 Gantt Chart for FYP 2

No.	**Detail/ Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Conduct experiment: Effect of Pressure	🟥	🟥	🟥	🟥	🟥			Mid-Semester Break							
2	Conduct Experiment:Effect of CO2 Composition				🟥	🟥										
3	Analysis of Result				🟥	🟥	🟥									
4	Documentation of Project							🟥								
2	Submission of Progress Report									🟥						
4	Pre-SEDEX preparation										🟥	🟥	🟥			
5	Submission of Draft Report													🟥		
6	Submission of Dissertation (soft bound)														🟥	
7	Submission of Technical Paper														🟥	
8	Oral Presentation															🟥
9	Submission of Project Dissertation (Hard Bound)															🟥

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experiment 1: Effect of Feed Pressure on CO_2 Permeance and Relative Permeance

Several experiments were conducted at different pressure to study the effect of feed pressure on the separation of CH_3-CO_2-C_3H_8. A graph of The results obtained are shown in tables below.

Based on the results obtained, the permeability of individual gas can be plotted in a graph of Permeability vs. Pressure. The permeability for individual gases are shown in Figure 9,10, and 11 respectively.

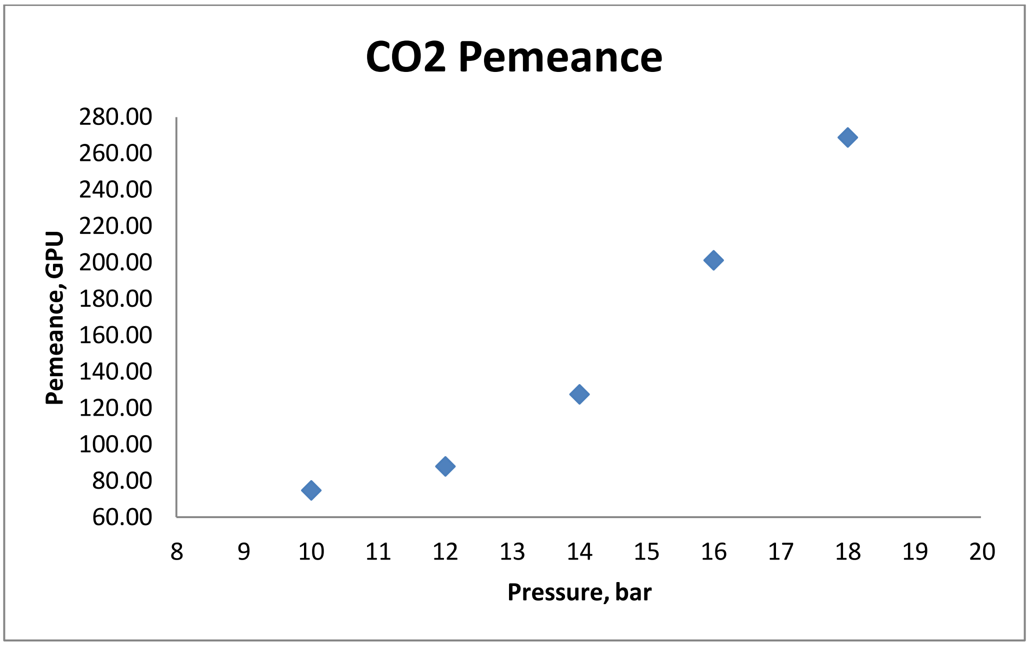


Figure 9 Graph of CO2 Permeance vs. Pressure

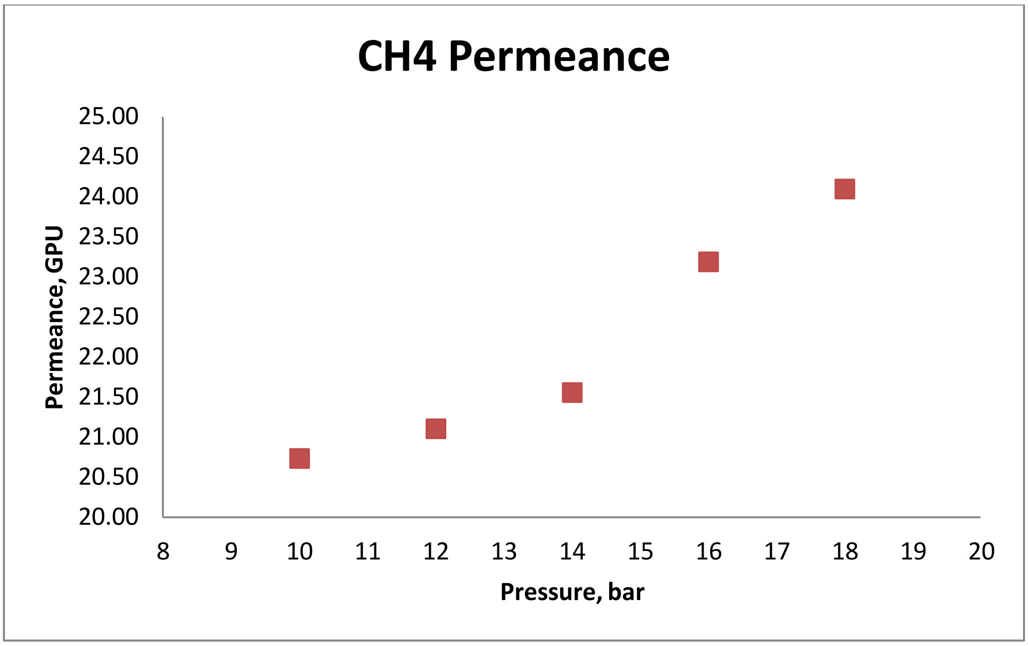


Figure 10 Graph of CH4 Permeance vs. Pressure

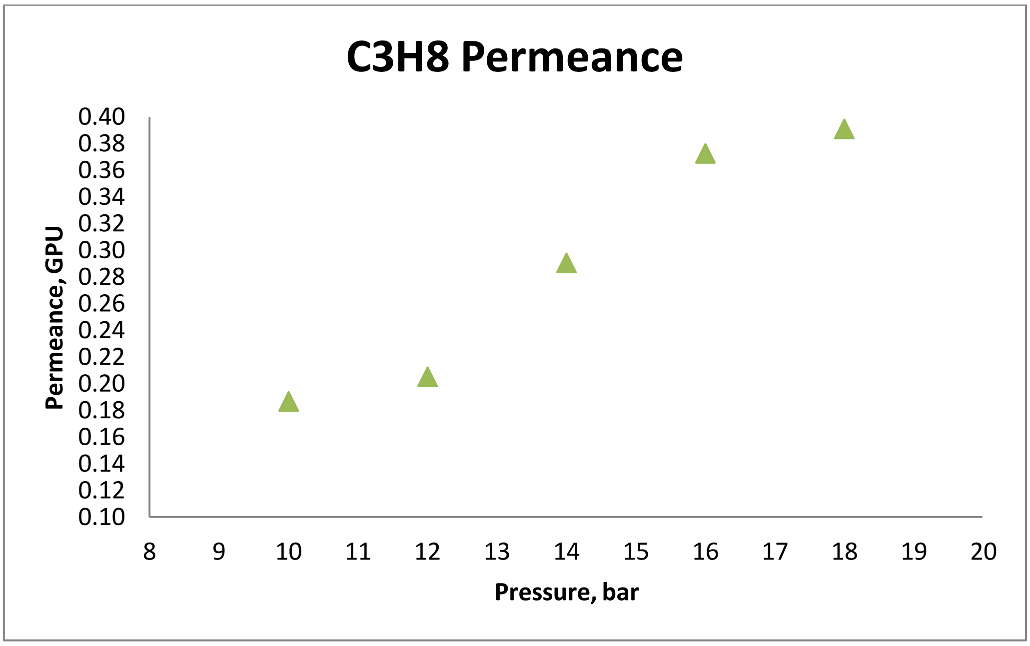


Figure 11 Graph of C3H8 Permeance vs. Pressure

Based on Figure 9Figure 10 and Figure 11 the permeability of CH_3, CO_2 and C_3H_8 are increasing with pressure. A flow of a component across the membrane can only occur if the partial pressure of the component on the feed side of the membrane is greater than the partial pressure on the permeate side of the membrane. The ratio of the partial pressure on feed side to permeate side is always less than or equal to the pressure ratio. Hence with an increased pressure difference the flow of component across the membrane increases as well. Thus it increases the permeability of each gas. Hence when the pressure increases the pressure the permeance of each gas increases.

However, Jusoh et al. reported that increase in pressure will cause a reduction in diffusivity due to polymer matrix loosening phenomena. As it is proven otherwise, it can be assumed that the membrane has a structural strength to withstand its properties in the range of 10 bar to 18 bar.

Although the permeability of all the components increases, the degree of increment differs between the components. The difference in the relative permeability of the component is the selectivity. Based on Figure 12, CO_2 has the highest permeance, and it increases exponentially with pressure.

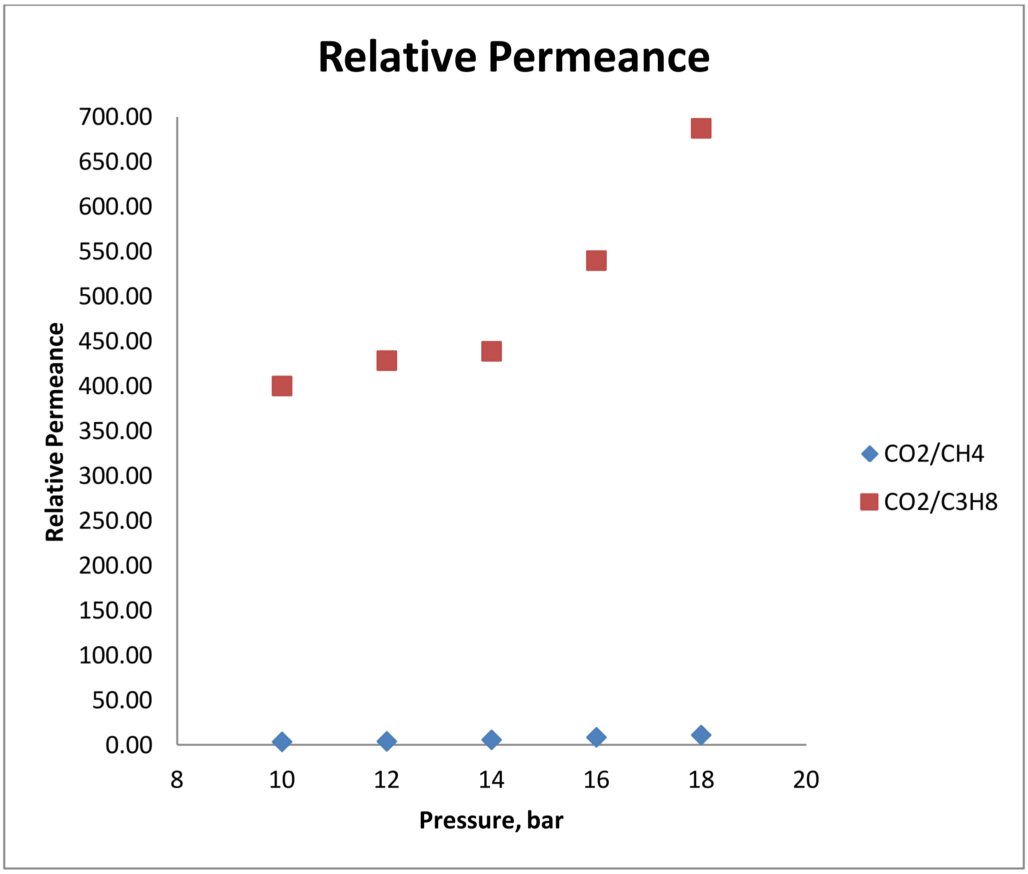


Figure 12 Relative Permeance of CO2 over CH4 and C3H8 at different pressure.

The increase in CO_2 permeance is strongly related to the selectivity of the membrane. Membrane selectivity for component A over component B is the ratio of permeability of A over the permeability of B.

$$\alpha_{AB} = \frac{P_A}{P_B}$$

The formula can be replaced and rearranged to give:

$$\alpha_{AB} = \frac{K_A}{K_B} \frac{D_A}{D_B}$$

K_A is the sorption coefficient. It is an equilibrium term linking the concentration of a permeating component in a fluid phase with its concentration in the membrane polymer phase. It accounts for the solubility of the component in the membrane.

D_A is the diffusion coefficient. It is a kinetic term that reflects the effect of the surrounding environment on the molecular motion of the permeating component. It accounts for the diffusion of the component through the membrane.

The ratio D_A/D_B is the ratio of the diffusion coefficients of the 2 gases and can be viewed as the mobility selectivity, reflecting the different sizes of the 2 molecules. The ratio K_A/K_B is the ratio of the sorption coefficients of the 2 gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of the 2 gases.

In the case of polymer membrane, the diffusion coefficient decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than small molecules do. Hence the mobility selectivity always favours the passage of small molecules over large ones. The molecular size of CO_2 is smaller than CH_4 and C_3H_8.

The mobility term is usually more dominant, thus small molecules permeate preferentially. When used to segregate CO_2, the membrane preferentially permeates CO_2. As the pressure increases, the rate of CO_2 moving across the membrane increases more rapidly than other gases. Thus it increases the permeance of CO_2.

4.2. Experiment 2: Effect of CO_2 composition in feed on Permeance and Relative Permeance

Based on the permeance, a graph of permeance versus CO_2 composition is plotted for each gas in Figure 13Figure 14 and Figure 15 respectively.

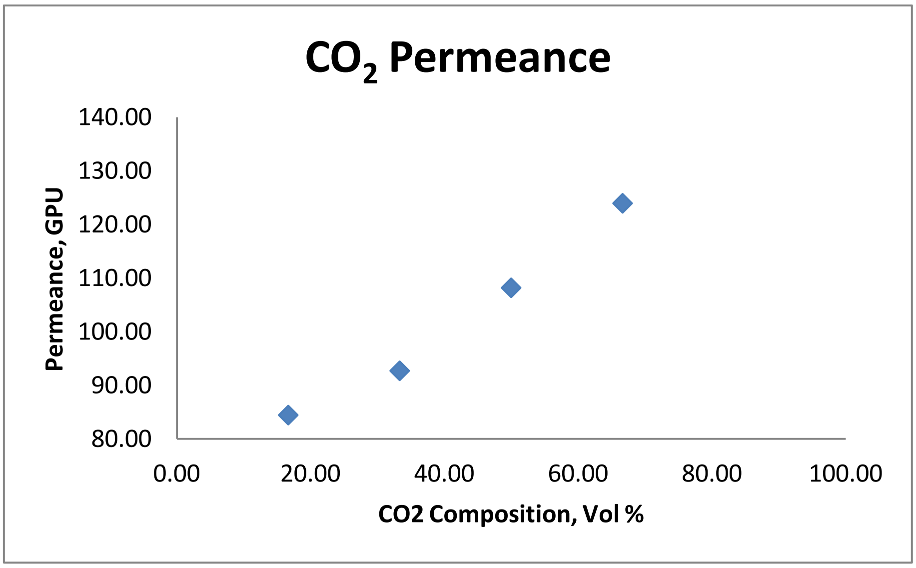


Figure 13 Graph of CO_2 Permeance vs. CO_2 Composition

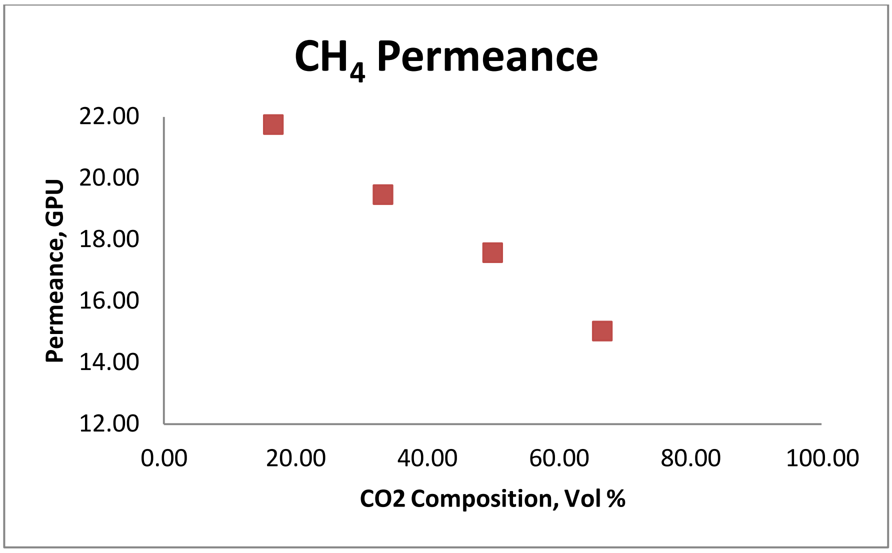


Figure 14 Graph of CH_4 Permeance vs. CO_2 Composition

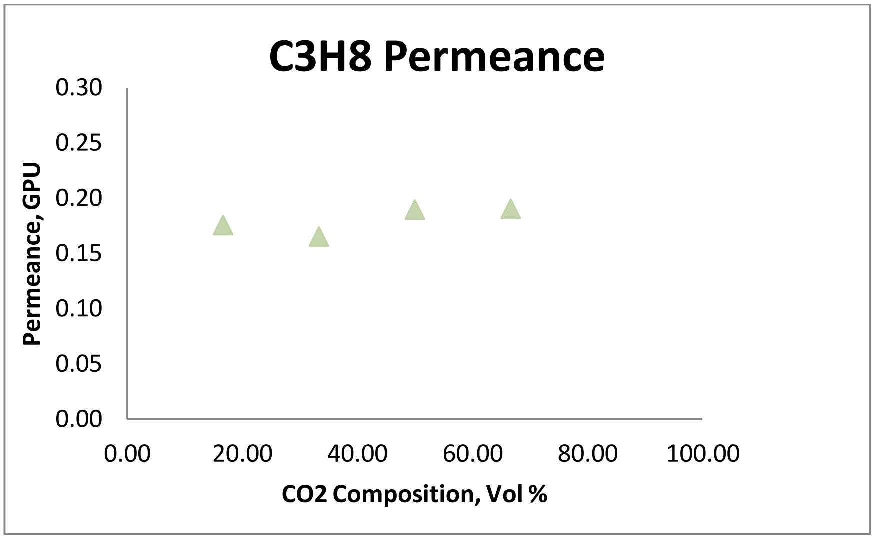


Figure 15 Graph of C3H8 Permeance vs. CO2 Composition

As seen in Figure 13, the permeance of the CO_2 increases as the CO_2 composition is increased in the feed. On the other hand, the permeance of CH_4 decreases as the feed gas gets richer in CO_2. Figure 15 shows that there is not any significant changes in C_3H_8 permeance.

Permeance of CO_2 is higher than CH_4 because CO_2 sorption in these microvoids is favorable and CO_2 has a higher affinity towards free volume defect sites than CH_4. As the CO_2 composition increases, the transport mechanism favors the surface diffusion This mechanism is achieved when one of the permeating molecules is adsorbed on the pore wall. This type of mechanism can reduce the effective pore dimensions obstructing the transfer of other molecular species. As the CO_2's affinity is higher towards the membrane, larger surface area in adsorbed by CO_2 leaving very little space for CH_4 or C_3H_8.

A graph of relative permeance versus CO_2 composition was plotted in Figure 16.

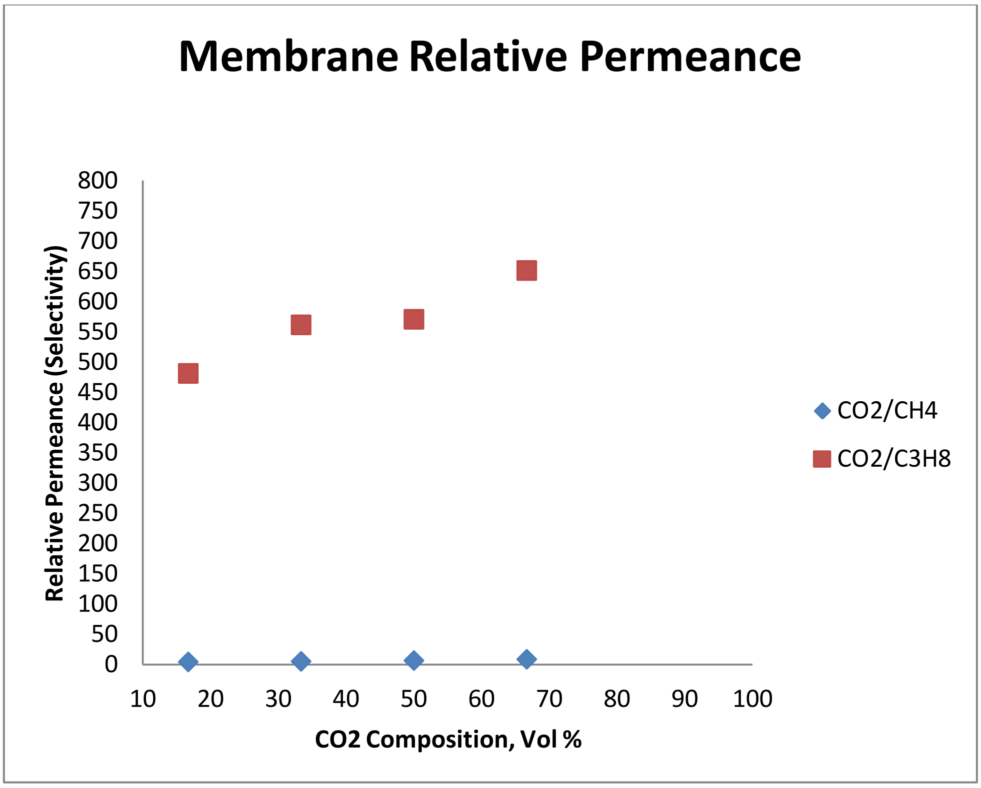


Figure 16 Relative Permeance of CO_2 over CH_4 and C_3H_8 at different CO_2 composition.

Another reason that can be associated with the CO_2 permeance is the diffusion mechanism. Diffusion occurs across a semi permeable membrane. The driving force of diffusion is the concentration gradient. When a CO_2 rich feed gas is used, the driving force for CO_2 is higher compared to the other gases. Hence it moves across the membrane more readily than other gases.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A hollow fiber membrane module was successfully prepared. The module prepared was used to conduct the experiments for the study to obtain the reading.

Module was successfully used to study the effect of feed pressure on the selectivity and permeability on the membrane in the range of 10 bar to 18 bar. From the analysis of the results obtained, it clearly shows that CO_2 has the highest permeance even in the presence of other gases. Hence, as the feed pressure increases the selectivity of the CO_2 increases.

The module was also used to study the effect of CO_2 composition on the permeability and selectivity of the membrane in the range of 16 Vol % CO_2 to 67 Vol % CO_2. The analysis of the results obtained shows that permeance of CO_2 increases as its composition increases. The permeances of other gases are inversely proportional to the CO_2 composition. Hence the selectivity of CO_2 increases as its composition increases.

5.2 Recommendations

Among the possible recommendations for this project is relating to improving this study by incorporating additional elements.

i. Future work can assimilate the counter current flow and cross flow model
ii. Future research can be done by using multiple stages to reduce hydrocarbon loss
iii. To fabricate a new module to that can house higher number of fibers
iv. To install a 3^{rd} mass flow meter to ease the experiment for multicomponet

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APPENDICES

Appendix A: Experimental Data for Experiment 1: Effect of Feed Pressure

	M1 Feed	**M2 Feed**	**M3 Rentate**	**M4 Permeate**
Pressure (bar)	3.67	10.07	8.98	0.03
Temp (˚C)	27.66	52.14	47.57	41.98
Flow (kg/Hhr)	0.60	0.66	0.65	0.01
CO2 Composition (Vol %)	44.98	45.60	44.63	90.50
CH4 Composition (Vol %)	45.02	45.05	45.83	9.13
C3H8 Composition (Vol %)	10.00	9.35	9.54	0.37

	M1 Feed	**M2 Feed**	**M3 Rentate**	**M4 Permeate**
Pressure (bar)	5.58	12.13	11.07	0.03
Temp (˚C)	28.48	53.72	46.43	40.16
Flow (kg/Hhr)	0.57	0.63	0.61	0.02
CO2 Composition (Vol %)	44.95	44.90	43.40	91.65
CH4 Composition (Vol %)	44.92	45.08	46.27	8.00
C5H12 Composition (Vol %)	10.03	10.02	10.33	0.35

	M1 Feed	**M2 Feed**	**M3 Rentate**	**M4 Permeate**
Pressure (bar)	7.28	14.11	12.89	0.03
Temp (˚C)	29.17	54.43	47.18	41.59
Flow (kg/Hhr)	0.58	0.64	0.61	0.03
CO2 Composition (Vol %)	44.75	44.90	42.30	93.88
CH4 Composition (Vol %)	44.73	44.36	46.41	5.77
C5H12 Composition (Vol %)	10.52	10.74	11.29	0.35

	M1 Feed	**M2 Feed**	**M3 Rentate**	**M4 Permeate**
Pressure (bar)	9.13	16.28	15.04	0.03
Temp (˚C)	29.58	53.71	48.52	42.96
Flow (kg/Hhr)	0.57	0.65	0.59	0.06
CO2 Composition (Vol %)	44.52	44.80	39.79	95.70
CH4 Composition (Vol %)	44.47	44.19	48.06	4.01
C5H12 Composition (Vol %)	11.01	11.01	12.15	0.29

	M1 Feed	**M2 Feed**	**M3 Rentate**	**M4 Permeate**
Pressure (bar)	11.59	18.21	16.94	0.03
Temp (˚C)	28.71	51.58	46.93	43.64
Flow (kg/Hhr)	0.60	0.67	0.58	0.09
CO2 Composition (Vol %)	44.37	44.30	37.65	96.62
CH4 Composition (Vol %)	44.40	44.45	49.60	3.15
C5H12 Composition (Vol %)	11.23	11.25	12.75	0.23

Feed Pressure (Bar)	**Pemeability (GPU)**		
	CO_2	CH_4	C_3H_8
10	74.73	20.73	0.19
12	87.92	21.10	0.21
14	127.54	21.56	0.29
16	201.24	23.19	0.37
18	268.78	24.10	0.39

Appendix B: Experimental Data for Experiment 2: Effect of CO_2 composition

	M1 Feed	M2 Feed	M3 Rentate	M4 Permeate
Pressure (bar)	11	11.0	10.0	0.03
Temp (˚C)	30	41	41	40
Flow (kg/Hhr)	0.613	0.613	0.588	0.025
CO2 Composition (Vol %)	16.67	16.67	13.50	91.16
CH4 Composition (Vol %)	65.82	65.82	68.26	8.53
C3H8 Composition (Vol %)	17.51	17.51	18.24	0.31

	M1 Feed	M2 Feed	M3 Rentate	M4 Permeate
Pressure (bar)	11	16.0	15.0	0.03
Temp (˚C)	30	41	41	40
Flow (kg/Hhr)	0.647	0.647	0.620	0.027
CO2 Composition (Vol %)	33.45	33.45	30.87	92.66
CH4 Composition (Vol %)	64.88	64.88	67.40	7.07
C3H8 Composition (Vol %)	1.67	1.67	1.73	0.27

	M1 Feed	M2 Feed	M3 Rentate	M4 Permeate
Pressure (bar)	11	16.0	15.0	0.03
Temp (˚C)	30	41	41	40
Flow (kg/Hhr)	0.663	0.663	0.632	0.031
CO2 Composition (Vol %)	44.23	44.23	41.78	94.17
CH4 Composition (Vol %)	54.10	54.10	56.48	5.56
C3H8 Composition (Vol %)	1.67	1.67	1.74	0.27

	M1 Feed	M2 Feed	M3 Rentate	M4 Permeate
Pressure (bar)	11	16.0	15.0	0.03
Temp (˚C)	30	41	41	40
Flow (kg/Hhr)	0.687	0.687	0.652	0.035
CO2 Composition (Vol %)	66.67	66.67	65.12	95.55
CH4 Composition (Vol %)	31.66	31.66	33.14	4.21
C3H8 Composition (Vol %)	1.67	1.67	1.74	0.24

CO_2 Composition, Vol %	**Permeance (GPU)**		
	CO_2	CH_4	C_3H_8
16.67	84.51	21.75	0.18
33.33	92.77	19.47	0.17
50.00	108.25	17.58	0.19
66.67	124.01	15.03	0.19