STUDY OF PRESSURE AND COMPOSITION EFFECT ON MULTICOMPONENT MEMBRANE SEPARATION INVOLVING HEAVY HYDROCARBON GAS PENTANE

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By

Tan Et Kuan

Dissertation submitted in partial fulfillment of

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CERTIFICATION OF APPROVAL

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Approved by,

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(DR LAU KOK KEONG)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2013

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.

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TAN ET KUAN

ABSTRACT

This work study the performance and characterize polyimide hollow fiber membranes for the separation of CO_2-CH- C_5H_{12} at difference pressure and feed composition as well as the effect of heavy hydrocarbon gas C_5H_{12} on membrane performance. In Malaysia, approximately 13 trillion ft³ of high CO_2 natural gas field are uneconomical to be developed. Development of high CO_2 gas fields requires prudent management of carbon dioxide capture, transportation, and storage to enable commercialization of these fields. Research conducted on CO_2 separation using membrane is limited especially on multicomponent and involving heavy hydrocarbon gas. Scope of experimental study focus on pure gas, gas mixture with and without heavy hydrocarbon gas C_5H_{12} as well as varies the feed pressure from 10 bar to 18 bar and CO_2 feed composition from 10% to 90%. Research methodologies include fabrication of membrane module, membrane characterization using FTIR, FESEM, and performances testing with CO_2SMU and GC. FTIR finding show that membrane matrix's polar sites enhance the preferential interaction and solubility of CO_2 gas molecules, resulting in higher CO_2 permeates flow compare to CH_4 & C_5H_{12}. Decrease in flux, permeance and CO_2 relative permeance is observed in gas mixture feed especially with present of heavy hydrocarbon gas C_5H_{12}. C_5H_{12}. As feed pressure increase, driving force increase preferentially sorbed of CO_2 gas increase CO_2 flux significantly, while CH_4 and C_5H_{12} flux only increase marginally. Furthermore, membrane layer compaction and plasticization increase CO_2 permeance and relative permeance. As CO_2 feed composition increase, membrane plasticize more, increasing preferentially sorbed of CO_2 gas at matrix's polar sites, thus increasing CO_2 flux and permeance while, CH_4 and C_5H_{12} flux and permeance remain constant. So, CO_2 relative permeance increases. In the nutshell, polyimide hollow fiber membranes show promising performance for separation of CO_2-CH-C_5H_{12} and experimental findings can be used for Multicomponent Hollow Fiber Membrane Module Performance Prediction Program (HFM3P).

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ABBREVIATIONS AND NOMENCLATURES

CO_2SMU	Carbon dioxide separation membrane unit
H_2S	Hydrogen sulfide
SO_2	Sulphur dioxide
CO_2	Carbon dioxide
CH_4	Methane
C_5H_{12}	Pentane
CAPEX	Capital Expenditure
OPEX	Operating Expenditure
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
GC	Gas chromatography

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Background Of Study

1.1.1 Membrane Technology

Varieties process of carbon dioxide removal had been developed over years. Major processes available are group into absorption process, adsorption process, physical separation and hybrid solution separation [4]. Selection of the optimum technology for carbon dioxide removal is specific for each application. Factors that need to be considered including reservoir conditions, feed gas rate and composition, operating pressure, operating temperature, cost of product gas, availability and cost of utilities and environmental regulations [8]. But still, membrane technology which excellent in term of economy, size, and process simplicity can be a good choice especially in offshore platform where the available space for equipment is limited.

Membrane is a thin, film-like structure that functions as selective barrier which allowing some particles to pass through, but impermeable to specific particles [9]. The concept of a membrane has been known since the eighteenth century, however first application of membrane technology only start in 1981. Since then, more researches had been done on membrane technology. The rapid development is because of membrane benefits which do not require major phase changes thus consume less energy, easy in handling, simplicity of equipment and small in size.

Membranes can be categorized based on morphology into dense membranes, porous membranes, and asymmetric membranes [10]. Dense membrane consists of

thin layer of dense material and applied in the separation processes of small molecules. While, porous membranes are designed for separation of larger molecules such as solid colloidal particles. As for asymmetric membranes, consists of a dense surface layer and supported by a thicker porous layer. The separation properties and permeation rates are determined by the dense surface layer; while the thicker porous layer functions as mechanical support.

Synthetic membrane can be constructed from many type of material and divided into 3 groups which are liquid, polymeric and ceramic membranes [10]. Liquid membranes refer to synthetic membranes made of non-rigid materials. Polymeric membrane which is made from polymer is most widely used in industry due to its competitive in performance and economics. While, ceramic membranes which made from inorganic materials are used in corrosive and high temperature application.

1.1.2 Hollow Fiber Membrane

In membrane technology, membrane modules designs are important factor to determine the membrane performance. Membrane modules are design base on packing density, cost-effective manufacture, and easy access for cleaning and cost effective membrane replacement.

Hollow-fiber module's design are a bit similar to shell and tube heat exchanger. Fine hollow fibers are wrapped in tube shaped in a highly dense pattern. Feed gas flows over and between the fibers, and some components permeate into the fiber tube. The permeated gas then travels within the fibers tube until it reaches the open end of the fiber tube, mixes with permeates from other fiber tubes and come out as permeate stream. While the gas that does not permeate eventually recollected as non-permeate stream. Hollow-fiber membranes have higher packing density, thus usually smaller in size, but hard for cleaning. Figure 1 illustrate hollow fiber module [6].
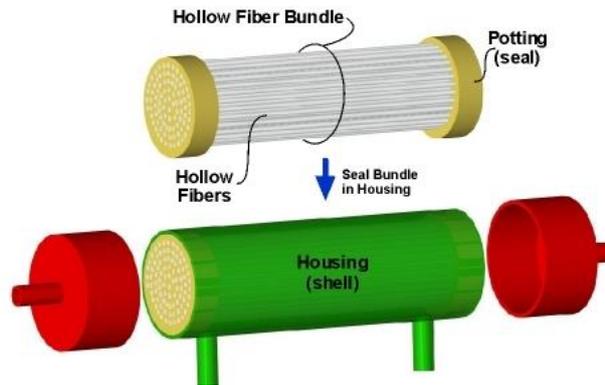
Figure 1: Hollow Fiber Membrane [6]

Table 1 show the comparisons of hollow fiber modules with other type of membrane module such as tubular module, capillary module, and spiral wound module [1].

Table 1: Comparison of membrane modules [1]

Type	Hollow fibre	Tubular	Capillary	Spiral wound
Diameter (mm)	<0.5	5–15	0.5–5 .0	50–200
Packing density, m2/m3	500 to 9000	30 to 200	600 to 1200	200 to 800
Ease of cleaning	Poor	Excellent	Fair	Fair
Relative cost	Low	High	Low	Low

1.1.3 Membrane Performances

Membrane performance can be affected by few factors which include feed composition, pressure gradient, temperature, and concentration polarization [1]. According to sorption-diffusion principle, feed composition will affect the sorption property of membrane, thus affecting the flow and composition of permeate stream. As for the pressure gradient across the membrane, it acts as driving force for the feed component to permeate the membrane. Higher partial pressure at feed over permeate

stream will result in more component pass through the membrane. While, temperature increase will increase the membrane diffusivity but reduce solubility, thus temperature adjustment will affect the relative permeance and rate of permeation. In membrane separation, lower permeation component (large component) will collect at feed side boundary layer of membrane, which can inhibits the rate of permeation of the more permeable species and affect the relative permeance of membrane.

1.2   Problem Statements

Natural gas contains mixture of organic hydrocarbon and inorganic compounds which their compositions are varying from source to source. Large gas fields discovered in Brazil have carbon dioxide concentration greater than 10 %. While, in some other places such as Australia and South East Asia, carbon dioxide concentration are greater than 20% [37]. In the other hand, natural gas at Platong and Erawa fields in Thailand have high carbon dioxide content up to 90% [38].

Development of high carbon dioxide gas fields offshore will indisputably give significant new challenges for all exploration and production companies worldwide. High carbon dioxide content natural gas reservoirs make most of the gas field development uneconomical and has remained undeveloped. Development of these high CO2 gas fields will requires prudent management of carbon dioxide capture, transportation, and storage to enable commercialization of these gas fields [8]. In Malaysia, 13 trillion cubic feet of natural gas field are still undeveloped due to high carbon dioxide content. Same case goes to Indonesia, where 46 trillion cubic feet of natural gas at Greater Sarawak Basin are not economically to be developed [38].

Carbon dioxide when combine with water can be extremely corrosive and rapidly damages pipelines and equipment if not pre-treated. Carbon dioxide also reduces the heating value of a natural gas stream, wastes pipeline capacity, decrease compression power and can cause freezing in low temperature equipment [2]. Thus, the pipeline grid transportation specification for natural gas is limited to less than 2% carbon dioxide, 120ppm water, 4ppm hydrogen sulfide and 4% inert gas [3, 34, 35]. So, most of natural gas required pretreatment to removed carbon dioxide, water and other impurities.

From the literature review conducted [11-29, 32-38], it is found that membrane technology in carbon dioxide separation is still new and not many studies had been done on it. Most of these literary works also focus on basic 2 component separation, and there are still huge gap in 3 component carbon dioxide removal study. Research conducted on ternary (or higher) feed component membrane separation are very limited. In fact, study that focus on separation of carbon dioxide from heavy hydrocarbon gas (pentane) are even less. Figure 2 illustrate corrosion in piping [2].
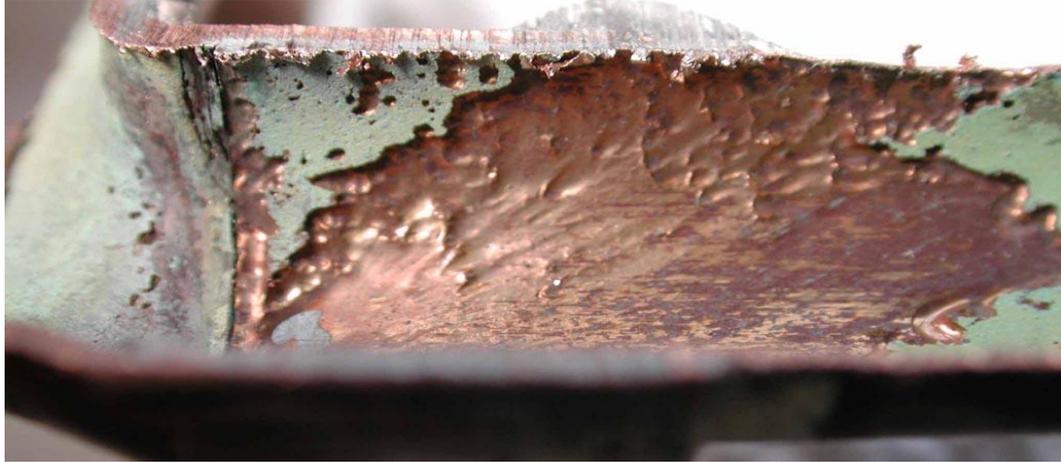
Figure 2: Piping corrosion [2]

1.3   Objectives

1.3.1 Main Objective

The main objective of this project is

- To characterize and study the performance of polyimide hollow fiber membranes for the separation of carbon dioxide-methane-pentane at difference pressure and feed composition as well as the effect of heavy hydrocarbon gas C_5H_{12} on membrane performance

1.3.2 Sub-Objectives

To achieve the main objective above, few sub-objectives are outlined:

- To develop hollow fiber membrane module using commercial fiber

- To characterize hollow fiber membrane with bonding and morphology analysis

- To study the effects of heavy hydrocarbon gas (Pentane) on membrane performance

- To evaluate the flux, permeance and relative permeance of carbon dioxide – methane – pentane separation on hollow fiber membrane at difference pressure

- To evaluate the flux permeance and relative permeance of carbon dioxide – methane – pentane on asymmetric hollow fiber membrane at difference feed composition

1.4   Scopes Of Study

This work emphasis on multicomponent membrane separation involving Carbon dioxide (CO_2), Methane (CH_4) and heavy hydrocarbon gas Pentane (C_5H_{12}). Membrane used for the study is a counter flow asymmetric hollow fiber membrane. Membrane is characterizing using Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). Then, effect of heavy hydrocarbon gas pentane on membrane is investigated by feeding pure CO_2 gas, pure CH_4 gas, Pure C_5H_{12} gas, Binary mixture of CO_2 and CH_4 gas and multicomponent mixture of CO_2, CH_4, C_5H_{12}.

For studies of feed pressure effect on membrane performance, feed gas pressures are scope from 10 bar to 20 bar. 5 set of experiments with pressure of 10 bar, 12 bar, 14 bar, 16 bar, and 18 bar are designed. Flow rate and composition of CO_2, CH_4, C_5H_{12} at feed, retentate and permeate are then recorded and membrane performance are studies according to their flux, permeance and relative permeance.

For studies of feed gas composition effect on membrane performance, Pentane composition is set at 4%, while methane composition ranges from 10% to 90%, and carbon dioxide composition range from 10% to 90%. The 10% CO_2 feed composition indicate the natural gas produce from low CO_2 content natural gas field, while 90% CO_2 feed composition indicate the natural gas produce from high CO_2 content natural gas field. 5 set of experiments with CO2 feed composition of 9.6%, 28.8%, 48%, 67.2%, 86.4% are designed. Flow rate and composition of CO_2, CH_4, C_5H_{12} at feed, retentate and permeate are then recorded and membrane performance are studies according to their flux, permeance and relative permeance.

1.5 Relevancy of Project

This project which study on membrane characterization and performance testing such as effect of pressure, temperature and feed composition on hollow fiber membrane are relevant to the students as it increases the knowledge on current technology used in separation system. Separation system is one of major field in chemical engineering.

Other than that, this project also gives an overview on removal of carbon dioxide from natural gas. These applications are widely used in both onshore and offshore platform. Natural gas stream contain large composition of carbon dioxide which are corrosive to piping and equipment. Thus pre-treatment are needed before transferring natural gas to processing plant. Benfield process requires high capital, high operating costs, and high energy usage for striping. Besides, there are also concerns of corrosion, erosion, and column instability at process unit especially hot potassium carbonate absorber [7].

Amine absorption technology can effectively separate carbon dioxide from methane and pentane; however the process is expensive and large in equipment size. The use of membrane for carbon dioxide – methane – pentane separation can provide a new alternative which are cheaper and space saving. Membrane separations are simple and have high reliability, adaptability and environmental friendly. The only drawback is that with current study and technology, membrane separations are hard to achieve high separation which separate up to 99% of carbon dioxide.

This drawback can be resolved by installing a small Benfield or amine absorption unit to further purify the methane – pentane stream from carbon dioxide. By conducting this project, student can enhance their knowledge on current available technology for separation process which range from membrane filtration, physical separation to adsorption and absorption.

In short, this project evaluates the flux, permeance and relative permeance of carbon dioxide – methane – pentane separation on hollow fiber membrane at difference feed temperature, pressure and composition to enhance the membrane performance for purer separation of carbon dioxide – methane – pentane. To conclude, this project is relevant as it improves student's knowledge on separation system as well as carbon dioxide removal technology.

1.6 Project Feasibility

The project requires lab works on hollow fiber membrane under difference feed temperature, pressure and composition. Hollow fiber membrane used for the experimental purpose need to be fabricated for the purpose of study on Carbon Dioxide – Methane – Pentane Separation. The feasibility of the project needs to be explored in terms of membrane flux, permeance and relative permeance.

This project is schedule to be completed in 2 semesters which is 8 months. Research work is allocated to be done in first semester while the experimental works are schedule to be start on middle if first semester. Project work process and timeline are scheduled planned by using Gantt chart. Lab equipment, membrane and chemicals needed are available for experimental work, thus there should be no issues on project feasibility within time frame.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2 LITERATURE REVIEW AND THEORY

2.1 Literature Review

2.1.1 Carbon Dioxide Separation Technology

Natural gas is widely used as feed for petrochemical industry, sales gas, and other uses. Total worldwide natural gas consumption amount for 100 trillion cubic feet per year. Natural gas contains mixture organic hydrocarbon and inorganic compounds and the composition are vary from source to source. Methane is the main compound in natural gas which is around 50% to 90%. Ethane, propane, butane, pentane and higher molecular weight hydrocarbon have composition around 1% to 3 %, and the rest are inorganic compounds such as water, nitrogen, carbon dioxide and hydrogen sulfide. Inorganic compound amount of 5% to 50% and are impurities and undesired [3]. Carbon dioxide can cause lot of problems in transferring and processing of natural gas such as corrosion in pipelines and equipment, reduces the heating value of a natural gas; wastes pipeline capacity, decrease compression power and cause freezing in low temperature operated equipment [2]. Thus, carbon dioxide needs to be separated from natural gas stream.

Varieties process of carbon dioxide removal had been developed over years to meet the gas specification at lower cost while meeting environmental regulation. Major processes available are group into absorption process, adsorption process, physical separation and hybrid solution separation [4]. Solvent absorption separation using Benfield solution or amine solution and physical separation using membrane separation are most common among those processes. Selection of the optimum technology for carbon dioxide removal is specific for each application. Factors that need to be considered including reservoir conditions, feed gas rate and composition,

operating pressure, operating temperature, cost of product gas, availability and cost of utilities and environmental regulations [8].

Abu Dhabi Gas Liquefaction Ltd. [7] has done a study to compare the technical and economic performances of Benfield and amine absorption process for removing CO_2 and H_2S from sour natural gas. The findings show that Benfield technology capital cost and power consumption are 50% and 48% higher than amine absorption process. Comparison of amine absorption and membrane for carbon dioxide removal are tabulated in table 2 [1].

Table 2: Comparison of absorption and membrane for carbon dioxide removal [1]

Factor	Amines Absorption Process	Membranes Process
Equipment Size	Huge	Small
Hydrocarbon losses	Very low	Losses depends on conditions
Meet low CO_2 specif.	Yes (up to ppm level)	No (2% is tough)
Energy consumption	Moderate to high	Low
Operating cost	Moderate	Low to Moderate
Maintenance cost	Low to moderate	Low
Ease of operation	Moderate	Simple
Environmental impact	Complex	Low
Capital cost	Expensive	Low
Pre-treatment costs	Low	Low to moderate
Ease for future expansion	Hard	Easy

Membrane technologies can be used for carbon dioxide removal in both onshore and offshore environment. Membrane offer advantages of lower weight and smaller footprint as compare to other technology which make it very suitable for

offshore application [35, 37]. Offshore platform have limited space and equipment need to be designed as compact as possible. Furthermore, the carbon dioxide composition in natural gas are high, thus amine absorption required large amount of amine solvent and huge equipment. So, the costs are high as compare with membrane.

First application of membrane technology starts in 1981 and since then, researches on membrane technology had increased. Most of the researches focus on the binary feed composition of membrane separation. Overview of current use and future prospects for natural gas treatment using membrane were developed by Baker et al [36]. Membranes are the technology of choice for carbon dioxide removal systems on offshore platforms, and they are beginning to compete head to-head with amine systems at onshore plants [27, 36-37]. PETRONAS studies on carbon dioxide removal application also found that membrane is the most effective and economical way to date for offshore carbon dioxide removal due its compact size, moderate utility consumption, easy operation and reliability [8]. Figure below show technology screening of difference carbon dioxide removal process by considering CAPEX, OPEX, operating flexibility, reliability, expandability, environment friendly, weight, foot print, carbon dioxide removal efficiency, and carbon dioxide purity. Figure 3 show the technology screening of difference carbon dioxide removal process [8].

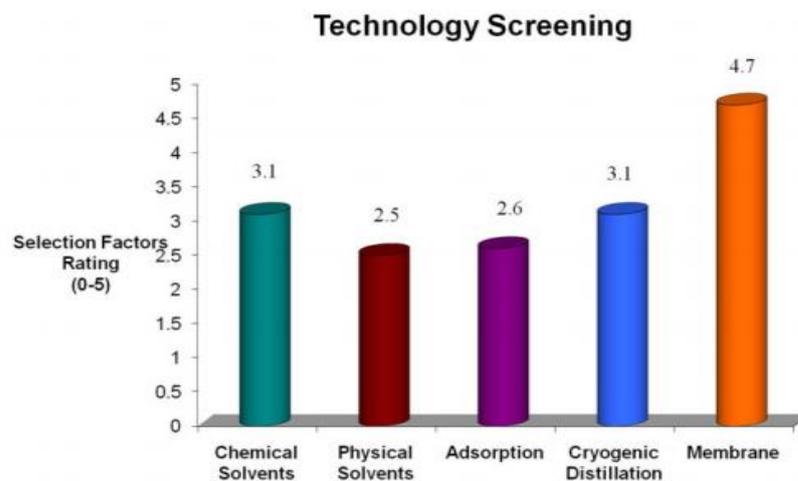Figure 3: Technology screening of difference carbon dioxide removal process [8]

In view of research make by Baker et al [36], Zhanga et al [27] had overview on different types of membrane's working principles, current status and development which form the primary determinants of separation performance and efficiency. The emphasis of overview is on carbon dioxide and methane separation, considering its

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substantial and direct relevance to the gas industry. Zhanga et al [27] stated that polymeric membranes generally exhibit selectivity of 5 to 10 fold lower than those of inorganic membranes. Polymeric membranes, however, currently dominate the gas separation membrane market as it has low manufacturing cost and can be easily processed into both flat sheet and hollow fiber configurations. Whilst, inorganic membranes are attractive for carbon dioxide separation processes at high temperatures; considering their robust thermal, chemical and mechanical stability. However, more studies need to be performed to improve the reproducibility, reliability and reduce cost. Besides, hollow fiber membranes contactors with simultaneous high flux and selectivity have huge potential for industrial application.

2.1.2 Ternary Feed Components Membrane Separation

AI-Falahy et al [29] have develop a scheme for separating sulphur dioxide, nitrogen and carbon dioxide using series of liquid membrane cells. Separation factors as high as 244 and 140 can be obtained for carbon dioxide and sulphur dioxide respectively when PEG400 and *DEA/PEG400 liquid* membrane cells are used. Separation factors were found to be strong functions of partial pressures across the membrane with declining efficiency at high pressure values.

Similarly, M. Hedayat et al (2011) study on simultaneous separation of hydrogen sulfide and carbon dioxide from natural gas represented by methane with hollow fiber membrane contactor using mixture of alcohol-amines. Taguchi method was used to systematically investigate the effect of operating parameters including temperature, pressure, gas-liquid velocities, feed gas concentration and solvent concentration on polysulfone (PSf) and poly vinylidene fluoride (PVDF) hollow fiber membrane. M. Hedayat et al [32] found out that presence of carbon dioxide in feed gas will decreased the efficiency of hydrogen sulfide removal. Furthermore, increase in pressure will have better separation of hydrogen sulfide and carbon dioxide from natural gas (methane). Whilst, increase in operating temperature will reduce carbon dioxide separation thus reduce carbon dioxide selectivity and increase hydrogen sulfide selectivity.

A 2D mathematical model was developed for the simultaneous absorption of carbon dioxide and hydrogen sulfide from natural gas using aqueous carbonate solution while utilizing hollow fiber membrane contactors by using reversible reaction schemes. Faiz et al [33] mention that lower concentrations of carbonate solutions resulted in higher absorption rates, while the presence of high bicarbonate concentrations in the solution was the main incentive for the enhanced reversible reactions and thus, lower absorption rates were achieved. Moreover, complete removal of carbon dioxide and Hydrogen sulfide in a gas mixture containing 5% carbon dioxide, 5% Hydrogen sulfide and 90% methane was possible by using two 1 M carbonate solution membrane modules in series. The first module removes all Hydrogen sulfide in the system and small amounts of carbon dioxide, while the second module removes the remaining carbon dioxide coming out from the first module. This scheme is favorable than using only one membrane module, because the majority of bicarbonate ions that favors the reversible reaction, are generated from the consumption of Hydrogen sulfide with carbonate solution. Therefore in the second module, carbon dioxide can be consumed significantly due to the absence of bicarbonate ions.

2.1.3 Binary Feed Components Membrane Separation

Shuji Himeno [16] has incorporated the synthesis and permeation properties of DDR-Type Zeolite Membrane for carbon dioxide and methane separation study. DDR-type zeolite membrane showed high selectivity for carbon dioxide and methane separation and high carbon dioxide permeance. The study was further expanded by Ainul [22] using polysulfone membrane. Ainul [22] presented non solvent effect on polysulfone membrane for carbon dioxide removal from natural gas by determines the separation performance of the membrane through calculating the selectivity and the permeability of polysulfone membrane. Polysulfone membrane used 100% ethanol as the non-solvent showed the promising performance in term of selectivity and permeability. The results showed that the polymer and the non-solvent pair controlled the morphology of the membrane and eventually affect the performance of the polysulfone membrane.

In addition, Leppin D. et al [35] test on hybrid systems of amines with membranes for carbon dioxide removal justify on the large potential of economic feasibility. Atchariyawut [17] extended Leppin [35] findings on carbon dioxide separation from methane by explore into effect of gas-liquid velocity, concentration of NaOH liquid solution, absorbent temperature, and NaCl liquid concentration on carbon dioxide flux by using gas–liquid membrane contacting process. The experimental data obtained illustrate that carbon dioxide flux was enhanced by the increase of NaOH solution concentration, NaOH solution temperature and the carbon dioxide volume fraction in the feed stream. However, increase of water temperature will resulted in decreasing of carbon dioxide flux [15, 17]. This finding is comparable with Chenar's research [15] on the effect of water vapor on the performance of commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes in carbon dioxide-methane separation application. The presence of water vapor in the feed stream significantly reduced the permeation rates of both carbon dioxide and methane. It was observed that the initial permeance could not be fully recovered after the membrane was exposed to water vapor. Both findings demonstrate that water can reduce the performance of membrane, thus, pre-dehydration may be considered before membrane separation. However, further studies on others membrane type are needed to verify this finding, as difference membrane type may exert different property and performance [15,17].

Norwahyu et al [26] applied duo mode model to study the gas sorption, permeability and selectivity of membrane process for carbon dioxide-methane separation. The result shows that sorption, permeability and diffusion property of carbon dioxide-methane exhibit classical duo model behavior. Ghasem [23] comprehensive the findings on carbon dioxide separation from natural gas by investigate the effect of quenching temperature on characteristics and gas absorption performance of polyvinylidene fluoride micro porous hollow fiber membranes. The membrane was fabricated via thermally induced phase separation technique. A prepared hollow fiber membrane was used as a membrane contactor to absorb carbon dioxide from natural gas using liquid absorbent. It was observed that, high quench bath temperature improves the percent removal of carbon dioxide compared to hollow fiber membrane prepared at low quench bath temperatures. Results revealed that, as the quench temperature increased pore radius and effective surface porosity

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increased and hence gas permeability and water permeability increased accordingly. It was also experiential that the percent crystallinity increased with quenching temperature. Gas absorption results revealed that complete removal of carbon dioxide from natural gas was possible.

From 2009 to 2010, a series of carbon dioxide-natural gas separation studies were conducted using polycarbonate membrane [18], silica-based membrane [19,20], inorganic membrane [21], and Polysulfone membrane [22]. This 4 studies focus on difference type of membrane and their performance where flux, permeability, and selectivity of carbon dioxide through membrane were studied and experimented [18-22]. It is found out that for polycarbonate membrane, porosity of substructure and transport mechanism of solution diffusion played important role in carbon dioxide permeance [18]. Silica membranes managed to separate Carbon dioxide and methane with a significant permeance value but with poor perm selectivity of carbon dioxide over methane. This is due to the formation of micro cracks during calcinations process. However, the selectivity can be improved through modification of the silica membrane by applying multiple separation layers on the porous alumina support by sequences of dipping-drying-calcinations steps [19, 20]. For inorganic membrane, higher feed flow gave higher permeability. As for the pressure increase, membrane permeability will increase until it reaches its limitation due to constant permeation transport in Knudsen diffusion. Carbon dioxide has higher selectivity than methane with average value of 3.5 [21].

Recently, Changhai et al [28] research on the performance of ester-cross linked hollow fiber membrane for natural gas separations. They had successfully enhanced carbon dioxide permeance and carbon dioxide-methane selectivity significantly by operates at lower temperature. The cross linked hollow fibers also able to maintain high carbon dioxide permeance under high feed pressures up to 800 psi without CO_2 plasticization.

A paper on assessment of carbon dioxide and methane gas permeations in polyimide hollow fiber membrane after conducting thermal annealing and chemical cross-linking using 1-Naphthyl ethylene-diamine hydrochloride was presented by Grace [25]. Grace [25] demonstrates that modification of commercially available membrane can be a convenient technique to tailor polyimide membrane properties

for specific applications. Both thermal and chemical modifications remarkably improved the polyimide hollow fiber membrane performance in terms of carbon dioxide permeance and carbon dioxide-methane selectivity.

Mathematic model for predicting the permeability of pore carbon dioxide and methane across y-alumina membrane has been presented by Mukthar et al [12]. Permeability of pure carbon dioxide and methane at the y-alumina membrane was found to be dependent toward membrane pore size, operating pressure and temperature. Permeability of carbon dioxide highest at pore of 0.2nm and decrease as the pore size increase, but permeability of methane increase with increase of pore size due to Knudsen diffusion. Moreover, Mukthar et al [12] also state that permeability of carbon dioxide and methane increase with increase of operating pressure and decrease in temperature due to decrease effect on surface diffusion. Similarly, another model which study on carbon dioxide and nitrogen removal from natural gas using membrane processes was developed [14].

This in line with F. Ahmad et al [24] study on process simulation and optimal design of membrane separation system for carbon dioxide separation from natural gas by incorporating a two dimensional cross flow mathematical model using Aspen HYSYS. It has establish that, increment in carbon dioxide feed composition will increases gas processing cost up to a composition, then further increase in composition will reduce the gas processing cost. Gas processing cost can further reduced by increase the feed pressure or selectivity of the membrane. F. Ahmad et al [38] broaden their research on hollow fiber gas separation system by considering non-ideal effect. Temperature and pressure dependence of hollow fiber membrane permeance and its effect on process economics were studied with non-ideal model. It was found out that higher CO_2 retentate composition, lower stage cut and methane loss in comparison to ideal model for the same fiber length. These findings contribute to decrease in compression, power requirements and gas processing cost for the non-ideal hollow fiber membrane model. So, non-ideal effects of membrane need to be considered in assessment of performance and economics of gas separation system as it have significant effect on carbon dioxide retentate-product composition, product quality, methane loss, stage cut, compressor power and gas processing cost of hollow fiber separation systems.

Qi et al [11] to optimize the design of membrane systems for carbon dioxide and methane separations found out that a two-stage configuration with permeate recycle and a three-stage configuration with residue recycle is suitable for natural gas treatment. Furthermore, Qin et al [13] have claim that the carbon dioxide-methane selectivity of copolyimide dense film decreased significantly with an increase in temperature and the pressure durability of the resultant hollow fiber membranes could reach 1000 psia at room temperature. Besides, Tierling et al [37] study on construction, operation and maintenance of membrane in offshore environment focus on membrane pretreatment requirement, membrane layout considerations, and membrane integrated work process highlight.

2.1.4 Research Gap

Table 3 and 4 summarize the recent published literature on carbon dioxide separation using membrane. Table 3 is the binary separation literature whiles, Table 4 is the multicomponent separation literature

Table 3: Published Literature On Binary Membrane Separation [12,13,16-22]

Author	Findings
H. Shuji (2007) [16]	DDR-type zeolite membrane showed high selectivity for CO_2/CH_4 and high CO_2 permeance
Y. Ainul (2010) [22]	PSF membrane that used 100% Ethanol as the non-solvent showed the promising performance in term of selectivity and permeability for CO_2/CH_4 separation.
S. Atchariyawut et al (2007) [17]	separation of CO_2 from CH_4 using gas-liquid membrane contacting process show that increase of temperature resulted in decreasing the CO_2 flux
M. P. Chenar et al (2006) [15]	Study on effect of water on Cardo-type polyimide hollow fiber membranes in CO_2/CH_4 separation applications. The presence of water vapor in the feed stream significantly reduced the permeation rates of both CO_2 and CH_4. The separation factor and selectivity, however, remained the same because the permeation rates of both gases were declined to the same extent.

N. Ahmad(2009) [18]	for polycarbonate (PC) membrane, porosity of substructure and transport mechanism of solution diffusion play important role in carbon dioxide permeance in CO2/CH4 separation.
Farhana (2010)[19]	evaluate permeability of carbon dioxide and methane on the fabricated alumina silica membrane. membrane managed to separate CO2/CH4 with a significant permeance value for both CO2 and CH4 (CO2 permeance > CH4 permeance) but with poor permselectivity of CO2 over CH4.
N. Safiah (2010) [20]	evaluate the performance of membrane for CO2/CH4 separation. flux increases when the inlet flow rate and inlet pressure are increased. permeability decreases as the inlet pressure is increased due to concentration of gas molecules approaches saturation in the inlet side. as the inlet ressure is increased, the pressure drop is increases, the flux increases and permeability decreases.
M. Jefri (2010)[21]	study on carbon dioxide separation from natural gas using inorganic membrane. Higher feed flowrate and higher feed pressure gave higher permeability, Carbon dioxide has higher selectivity than methane, selectivity both gases reduced as feed pressure increased. increase carbon dioxide concentration from 15% to 30%, based on analysis, has lower methane recovery in retentate stream
H. Mukthar and C.H. Lim (2004)[12]	Permeability of carbon dioxide and methane increase with increase of operating pressure. Increasing temperature would decrease the peamebility due to decrease effect on sufface diffusion.
J.J. Qin et al (2005) [13]	CO2/CH4 selectivity of the copolyimide dense film decreased significantly with an increase in temperature.

Table 4: Published Literature On Multicomponent Membrane Separation [29,32]

Author	Findings
M.A. AIFalahy et al (1998)[29]	Had develop sulphur dioxide, nitrogen and carbon dioxide separation scheme. Separation factors as high as 244 and 140 can be obtained for CO2 and SO2, respectively when PEG400 and DEA/PEG400 membranes are used. Separation factors were found to be strong functions of partial pressures across the membrane with declining efficiency at high pressure values
M.Hedayat et al (2011) [32]	Study on separation of hydrogen sulphide and carbon dioxide from methane. Presence of CO2 in feed gas decreased the H2S removal. Pressure had a positive effect on the removal efficiency. Temperature had no significant effect on H2S removal, but decreased the CO2 removal and thus enhanced H2S selectivity.

Most of literature review published [11-28, 35, 37, 38], are focus on binary feed component where, carbon dioxide are separated from natural gas which represented by methane. Even literature reviews available on binary feed component are not much but still more than ternary feed component. This is because membrane separation technology industrial application only started on 1981. Figure 4, show the amount of study on carbon dioxide removal by membrane done up to year 2005.
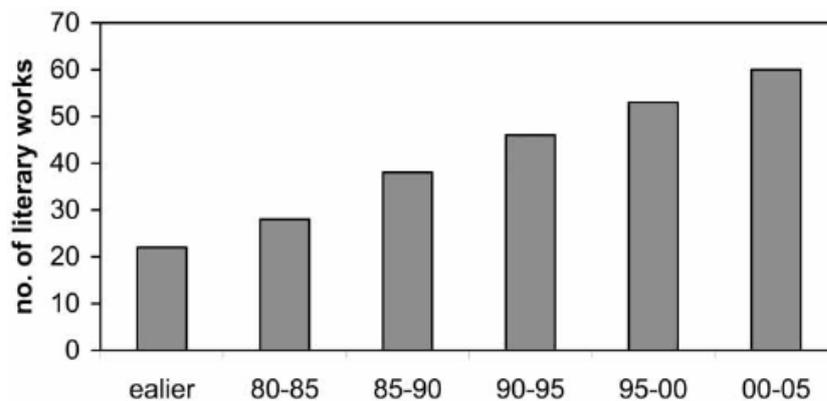

Figure 4: Overview of rate of advancement in research occurring in the field of CO_2 separation from CH_4 [1]

The number of literary work shows an increment over years. However the study conducted still far from adequate and still had huge potential for study especially on ternary feed component membrane separation.

Based on published literature [29, 32, 33], it can be concluded that there is limited study done on membrane separation for ternary feed component. Very few of the above literature review studies on ternary feed component membrane separation that investigates on carbon dioxide separation from methane and pentane. There are limited number of study had been done on carbon dioxide, hydrogen sulfide, sulphur dioxide separation from methane. Although M. Hedayat et al [32] have investigated on the effect of operating parameters such as temperature and pressure but the research was investigated on mixture of alcohol-amines hollow fiber membrane instead of polyimide hollow fiber membrane. Moreover most studies does not scope on carbon dioxide separation from heavy hydrocarbon gas (pentane).

2.2 Theory
2.2.1 Transport Mechanism

Solution diffusion that explained the transport mechanism for gas separation through polymer membrane states that permeates dissolve in membrane material and then diffuses through the membrane with effect of concentration gradient. Thus, separation is achieved as a result of difference in CO_2-CH_4-C_5H_{12} that dissolves in and rate of CO_2-CH_4-C_5H_{12} diffusion through the membrane. Fick's law of diffusion is applied in governing of permeates flux and permeance as a function of pressure difference across the membrane as driving force.

$$\text{Flux, } J_i = \frac{q_{p,i}}{A_m} = \frac{q_p \times y_{p,i}}{A_m} \quad (1)$$

$$Permeance, P_i = \frac{J_i}{P_h X_i - P_l y_i} \quad (2)$$

where, $J(cm^3_{STP}/cm^2.s)$ is component gas i flux, $q_p(cm^3_{STP}/s)$ is total volume of permeating gas, $y_{p,i}$ is component gas i volume%, $A_m(cm^2)$ is membrane area required for permeation, P_i $(cm^3_{STP}/cm^2.s.bar)$ is the permeance of gas component i, P_h and P_l (bar) are feed and permeate side pressure. X_i and y_i are component i fraction on feed and permeance side.

The ratio of permeance, P_i and P_j give the membrane relative permeance.

$$Relative\ Permeance \propto = \frac{P_i}{P_j} \tag{3}$$

2.2.2 Vapor-Liquid Equibrium

Vapor–liquid equilibrium is a condition where a liquid and its vapor (gas phase) are in equilibrium with each other. It is a condition or state where the rate of evaporation equals the rate of condensation on a molecular level such that there is no net vapor–liquid interconversion. A substance at vapor–liquid equilibrium is generally referred to as saturated fluid. The concentration of a vapor in contact with its liquid at equilibrium is depending on its vapor pressure. The equilibrium vapor pressure of a liquid is dependent on temperature.

Dalton's law states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.

$$P_{tot} = P_{CO2} + P_{CH4} + P_{C5H12} \tag{4}$$

With each component in the vapor phase:

$$y_{CO2} = P_{CO2} / P_{tot} \tag{5}$$

$$y_{CH4} = P_{CH4} / P_{tot} \tag{6}$$

$$y_{C5H12} = P_{C5H12} / P_{tot} \tag{7}$$

Where P_i = partial pressure of component i

y_i = mole fractions of vapor components i

Raoult's law states that the vapor pressure of an ideal solution is directly dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution.

$$P_{CO2} = x_{CO2}\, P^{o}_{CO2} \tag{8}$$

$$P_{CH4} = x_{CH4} \, P^{o}_{CH4} \tag{9}$$

$$P_{C5H12} = x_{C5H12} \, P^{o}_{C5H12} \tag{10}$$

Where P^{o}_{i} = Vapor pressures of components i

x_{i} = mole fractions of liquid components i

As vapor pressures of liquids are very dependent on temperature, the P^{o} pure vapor pressures for each component are a function of temperature (T). For example, commonly for a pure liquid component, the Clausius–Clapeyron relation may be used to approximate how the vapor pressure varies as a function of temperature. This makes each of the partial pressures dependent on temperature also regardless of whether Raoult's law applies or not. When Raoult's law is valid these expressions become:

$$P_{CO2}T = x_{CO2} \, P^{o}_{CO2}T \tag{11}$$

$$P_{CH4}T = x_{CH4} \, P^{o}_{CH4}T \tag{12}$$

$$P_{C5H12}T = x_{C5H12} \, P^{o}_{C5H12}T \tag{13}$$

At boiling temperatures if Raoult's law applies, the total pressure becomes:

$$P_{tot} = x_{CO2} \, P^{o}_{CO2}T + x_{CH4} \, P^{o}_{CH4}T + x_{C5H12} \, P^{o}_{C5H12}T \tag{14}$$

At a given P_{tot} and a given liquid composition, T can be solved for to give the liquid mixture's boiling point or bubble point, although the solution for T may not be mathematically analytical. For a ternary mixture at a given P_{tot}, the bubble point T can become a function of x_1 (x_2 or x_3). At boiling temperatures if Raoult's law applies, a number of the preceding equations can be combined to give the following expressions for vapour mole fractions as a function of liquid mole fractions and temperature:

$$y_{CO2} = x_{CO2} \, P^{o}_{CO2}T / P_{tot} \tag{15}$$

$$y_{CH4} = x_{CH4} \, P^{o}_{CH4}T / P_{tot} \tag{16}$$

$$y_{C5H12} = x_{C5H12} P^{o}_{C5H12}T / P_{tot} \tag{17}$$

Once the bubble point T's as a function of liquid composition in terms of mole fractions have been determined, these values can be inserted into the above equations to obtain corresponding vapour compositions in terms of mole fractions. When this is finished over a complete range of liquid mole fractions and their corresponding temperatures, one effectively obtains a temperature T function of vapour composition mole fractions. This function effectively acts as the dew point T function of vapour composition. In the case of a ternary mixture,

$$X_{CO2} = 1 - x_{CH4} - x_{C5H12} \tag{18}$$

$$x_{CH4} = 1 - x_{CO2} - x_{C5H12} \tag{19}$$

$$x_{C5H12} = 1 - x_{CO2} - x_{CH4} \tag{20}$$

and the above equations can be expressed as:

$$y_{CO2} = x_{CO2}\, P^{\circ}_{CO2} T / P_{tot} \tag{21}$$

$$y_{CH4} = (1 - x_{CO2} - x_{C5H12})\, P^{\circ}_{CH4} T / P_{tot} \tag{22}$$

$$y_{C5H12} = (1 - x_{CO2} - x_{CH4})\, P^{\circ}_{C5H12} T / P_{tot} \tag{23}$$

From above equation, it shows that:

y_i is proportional with $1/P_{tot}$, which mean yi is inversely proportional with P_{tot}.

y_i is proportional with T

The equations are agreed with calibration graph at Figure 5 [26] where pentane composition increases with pressure decrease or temperature increase.
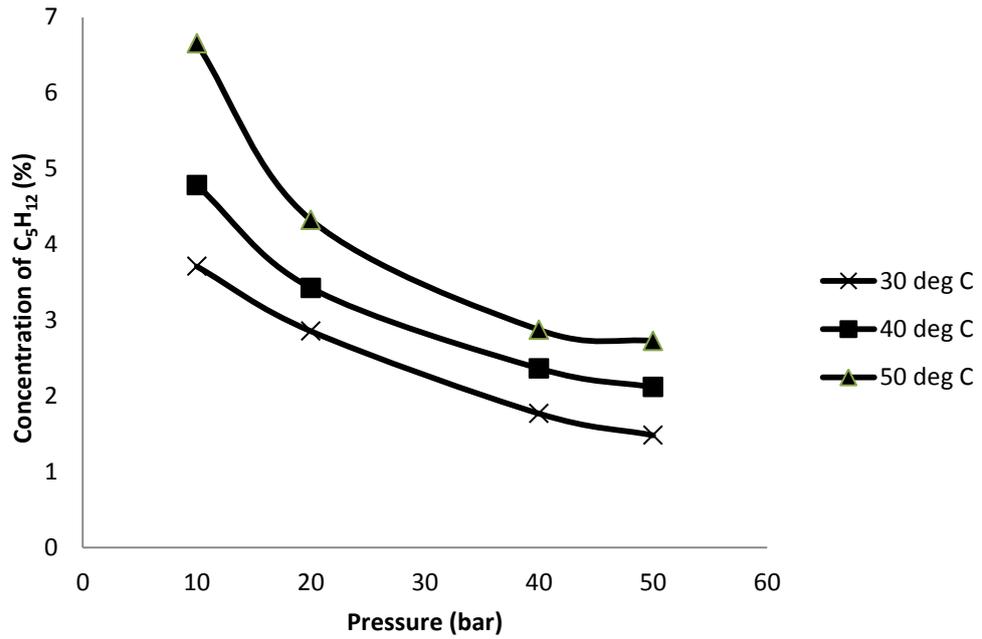
Figure 5 Calibration graph for concentration of pentane at different
pressure and temperature [26]

Figure 5 show pentane composition at difference temperature and pressure in manifold 2 (feed stream). The calibration graph can be used at operating temperature range from 30 degC to 50 degC and pressure range from 10 bar to 50 bar.

Calibration graph at Figure 5 [26] are used to determine the pentane composition in membrane feed stream, which is at manifold 2. Calibration graph above supplement the pentane composition data collected during CO_2SMU experiment. There are 2 mass flow controller and infrared gas analyzer attached to CO_2SMU. However, both mass flow controllers and infrared analyzers are used to control flow rate and measure the composition of carbon dioxide and methane. Thus, to control the flow rate of pentane and determine the pentane composition in feed gas at manifold 2, calibration graph are used.

Calibration graph from Figure 5 can be obtained from CO_2SMU experiment and gas chromatography. Figure 6 illustrate the gas chromatography analyses on CO_2-CH_4-C_5H_{12} gas sample.
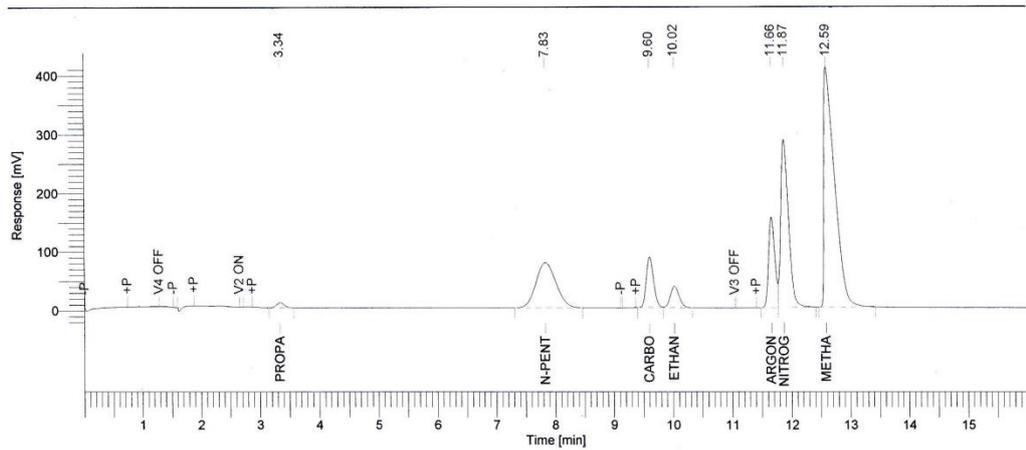
Department of Chemical Engineering, UTP

Figure 6 Gas chromatography analyses on CO_2-CH_4-C_5H_{12} gas sample

Carbon dioxide and methane are mixed at manifold 1, then feed to manifold 2 at 10 bar. Manifold temperature is control at 30 degC. After the gas had well mixed, the gas at manifold 2 are collected with sample bag and send for gas chromatography to determine the composition of pentane. Similar procedure are repeated with feed & manifold 2 pressure at 20 bar, 30 bar, 40 bar and 50 bar. The experiments are then repeated with temperature at 40 degC and 50 degC. From the pentane composition measure using gas chromatography, we can obtain the data above which show the pentane composition in feed stream (manifold 2) at certain temperature and pressure.

CHAPTER 3

METHODOLOGY

3 METHODOLOGY

3.1 Research Methodology and Project Activities

Methodologies are divided into two main phases which are literature review and experimental study. Figure 7 illustrate summarize flow chart of methodology
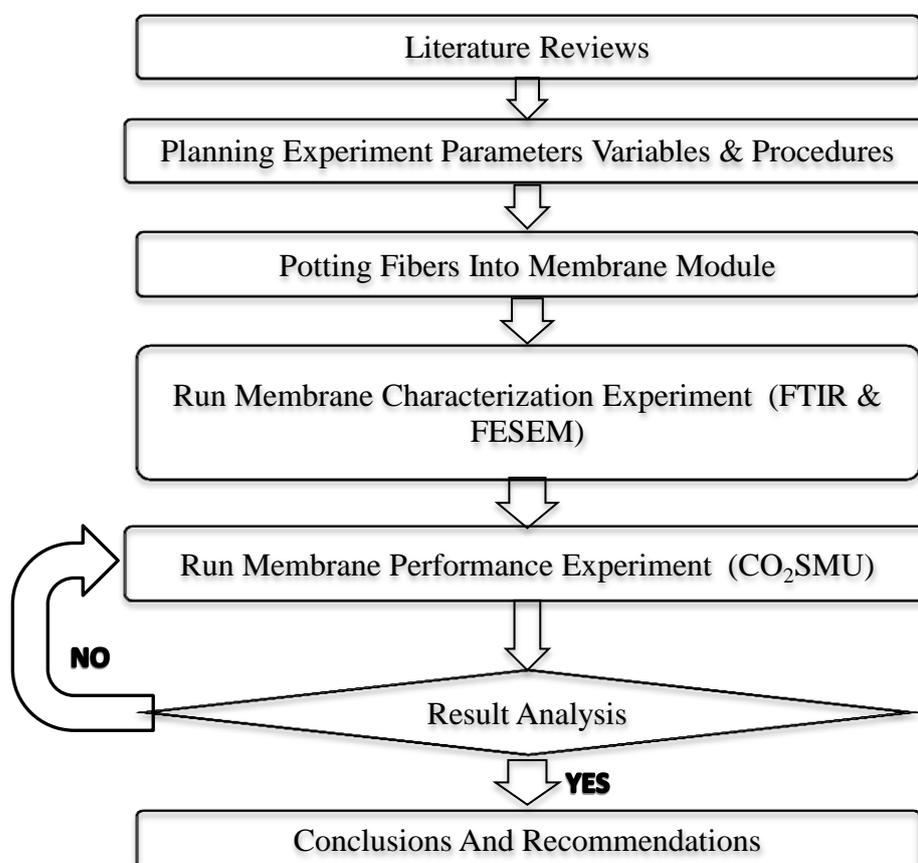
Figure 7: Flow chart of methodology

3.1.1 Literature Reviews

• Define objectives, scope of study, and problem statement

• Gathering as much information as possible from various sources such as journals and websites on pressure & composition effect, carbon dioxide – methane – pentane separation, hollow fiber membrane

• Identify research gap and potential base on compilation of literary works

• Study of parameters that will be used for experimental study

• List all chemicals and equipment required for experimental study

3.1.2 Pre-experimental Work

Table 5 lists out the pre-experimental activities that need to prepared before conducting experiment.

Table 5: Pre-experimental activities

Phase	Activities
Pre-experiment	Identifying the problems and purpose of experiments
	Study related journal on membrane experiment as well as relation between composition and pressure with membrane performance.
	Study of parameters and variables that will be used in the experiments
	Checking availability of equipment and chemicals
	Prepare laboratory documentations such as job safety analysis, material safety data sheet, and experimental procedures

3.1.3 Potting Fiber into Membrane Module

A counter flow configuration hollow fiber module needs to be fabricated following the procedure from published literature [45,46]. Figure 8 illustrate the membrane potting conducted in lab and the membrane module.

Figure 8: Membrane fiber potting

The detail procedure for membrane potting was as below [45,46]:

1.   Membrane packing density were set as 50% packing density, then the required fiber numbers and fiber length were calculated based on the diameter of hollow fibers and the length of membrane module.

2.   Membrane fibers were cut into a desired length and visibly defective fibers were removed.

3.   The remaining fibers were arranged in parallel order and put together as a fiber bundle

4.   A piece of Parafilm barrier film was cut with a dimension of about 40 mm long and 10 mm wide. The paper backing were removed and the Parafilm was slowly stretched to four or five times of its original length, wrap on one end of the fiber bundle before it relaxes back to natural status

5.   The wrapped end of the fiber bundle was cut with razor blade to yield smooth cross-section, then this end was encircle with a thin string

6. Membrane module shell was then placed vertically on a holder and a long string was lay through the shell lumen. The string was tie with to the roped fiber bundle

7. The string was pulled 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, so that the fibers become ordered and packed naturally when being pulled into the shell.

8. Step 4 and 5 were repeated with the other end of fiber bundle

9. A layer of Araldite 5 min curing adhesive was applied 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

10. Shell side of membrane was blow with compress air to ensure the passageway is unblocked till the epoxy resin is fully cured

11. The lower end of the module was wrapped with flexible heating tape to cure the epoxy resin

12. Epoxy resin and hardener was mixed using epoxy gun to get the correct epoxy mixture composition

13. The epoxy resin mixture was then slowly fill into a syringe and the syringe piston was continuously push till the liquid-like epoxy mixture touches the fiber bundle. The syringe was continually applied until the epoxy resin can be observed from the lower outlet of module shell. Then, Teflon or cotton bud was put inside the lower outlet of membrane module to prevent the membrane fiber from epoxy contamination.

14. The membrane was keep for 24 hours for the epoxy resin to be fully cured.

15. Step 12, 13 and 14 was repeated on other side of membrane

16. Lastly, the solidified epoxy resin located outside the module tube sheets was removed and residual epoxy resin on the thread area was clean up

Figure 9 show the process flow of membrane fabrication and potting procedure.

| Module shell preparation | → | Calculate required fiber numbers and length | → | Cut fibers to the desired length | → | Wrap one end of the fiber bundle and cut to smooth cross-section |

| Attach this end with a thin string | → | Pull the string through membrane shell lumen to house fiber bundle | → | Wrap and clean cut other end of fiber bundle | → | Apply adhesive on the cross-sections ends of bundle |

| Blow shell side with compress air | → | Heat up epoxy, mixed with hardener and degas under vacuum | → | Filled epoxy mixture to syringe and applied to fiber bundle | → | Applied epoxy at another end of module |

| Keep module at 60 degC for 2 hours then 80degC for 1 day | → | clean-up residual epoxy and seal the module | → | Membrane module testing, re-potting if needed |

Figure 9: Flow chart of membrane fiber potting procedures

3.1.4 Membrane Characterization

Table 6 shows the equipment that used for membrane characterization.

Table 6: Membrane Characterization

No.	Facilities	Descriptions	Pictures
1	Fourier transform infrared spectroscopy (FTIR)	• Spectra are collected based on measurements of the coherence of radioactive source, using time or space-domain measurements of the electromagnetic radiation • Use infrared (IR) portion of the electromagnetic spectrum • For characterization of chemicals bonding for the membrane	
2	Field Emission Scanning Electron Microscopy (FESEM)	• Use ultra-high-resolution imaging • For analysis of membrane nano scale surface structure and its morphology	

3.1.5 Membrane Performance Test

Table 7 shows the equipment that used for membrane performance testing.

Table 7: Membrane Performance Test

No.	Facilities	Descriptions	Pictures
1	Infrared Gas Analyser	• Measures trace gases by determining the absorption of emitted infrared light source through a certain air sample. • Trace gases found in the Earth's atmosphere get excited under specific wavelengths found in the infrared range.	
2	Gas Chromatography (GC)	• Sample gas flow-through column, which different chemical constituents pass in carrier gas stream at different rates and identified electronically as they exit the column	
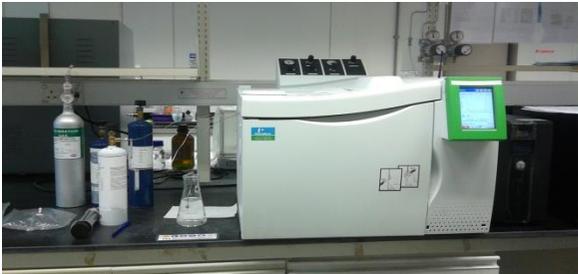
3.1.6 CO$_2$SMU Experiment Procedure

The detail procedure for CO$_2$SMU experiment was as below [44]:

1   For system start up, main power supplied inside the control panel MCCB and computer power supplied are switched on. Then NI lab view is activated and analyzer switch is turn on

2   For hot water system heat up, the main power is power up and the heater temperature is set to 50 degC. The water pump was turn on to to circulate the hot water inside the heat exchanger

3   For feed gas set up, correct type of feed gas cylinder is choose, and the gas cylinder valve is opened. Another valve at heat exchanger valves which related to CO$_2$SMU test rig was open too.

4   For gas feeding at feed panels set up, the inlet and outlet of valve for CO$_2$, CH$_4$, and C$_5$H$_{12}$ was open. The feed pressure regulator is set at 10 bars and the flow rate is set at NI interface.

5   For mass flow controller set up and data acquisition, the value of both mass flow controller are set up and the toggle ON is tap to start collecting data for data acquisition.

6   For backpressure regulator set up, high pressure regulator is used to regulate the system back pressure. The knob is turn clockwise up to set pressure.

7   For compressor start up, compressor switch at control panel, "START" button at compressor and inlet COMP1 valve is turned on. The inlet pressure is set up to 0.4 bars.

8   The experimental readings are monitor via National Instrument Interface and instrument indicator at test rig.

9   For sample analyzing, needle valve is opened, the "START" button at compressor is pressed and inlet COMP1 valve is open. Inlet pressure is set up to 0.4 bars.

10   After the sample analyzing, the inlet ball valve to compressor 1 is closed and the " STOP" button at compressor and "Comp1 switch" of compressor are pressed to stop compressor 1

11   Step 3 to 10 are repeated with different feed gas of pure carbon dioxide, pure methane, pure pentane, carbon dioxide (50%) methane (50%) gas mixture, carbon dioxide (48%) methane (48%) pentane (4%) gas mixture at 16 bar

12   Step 3 to 10 are repeated with different feed pressure which is 12 bar, 14 bar, 16 bar, 18 bar and 20 bar

13   Step 3 to 10 are repeated with difference feed composition where carbon dioxide composition is set at 10%, 30%, 55%, 65%, 85%

CO$_2$SMU experimental procedures discuss above are illustrating with flow diagram at Figure 10. While, CO$_2$SMU test rig flow sheet are shown in Figure 11.
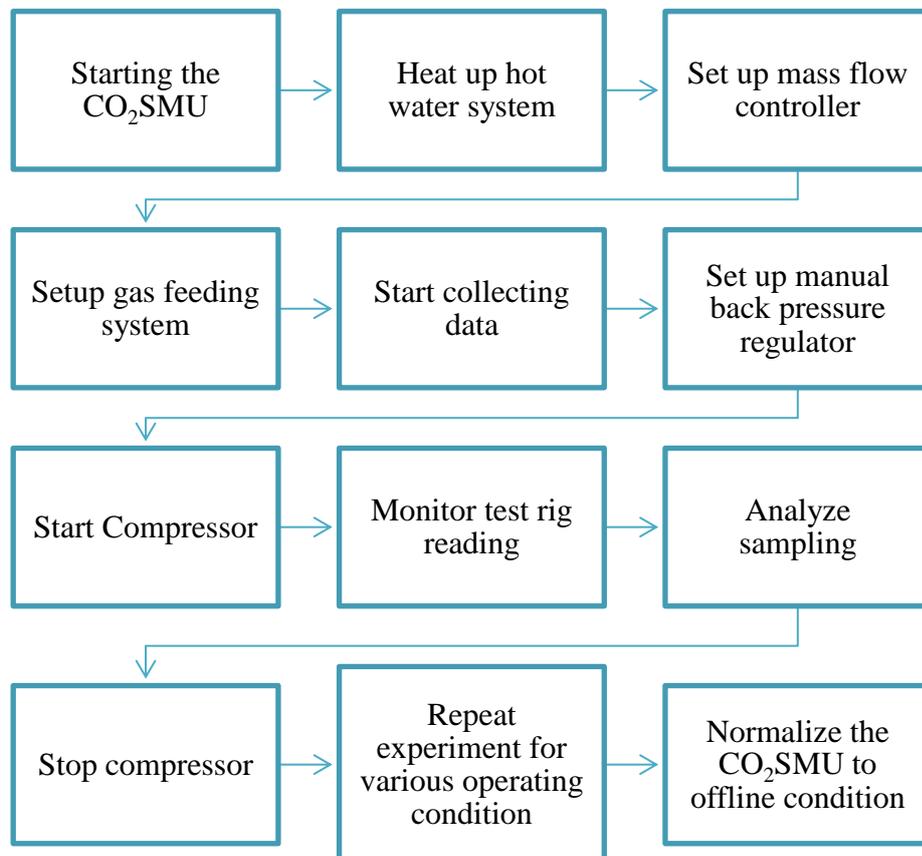
Figure 10: Flow chart of detail CO$_2$SMU experimental procedures
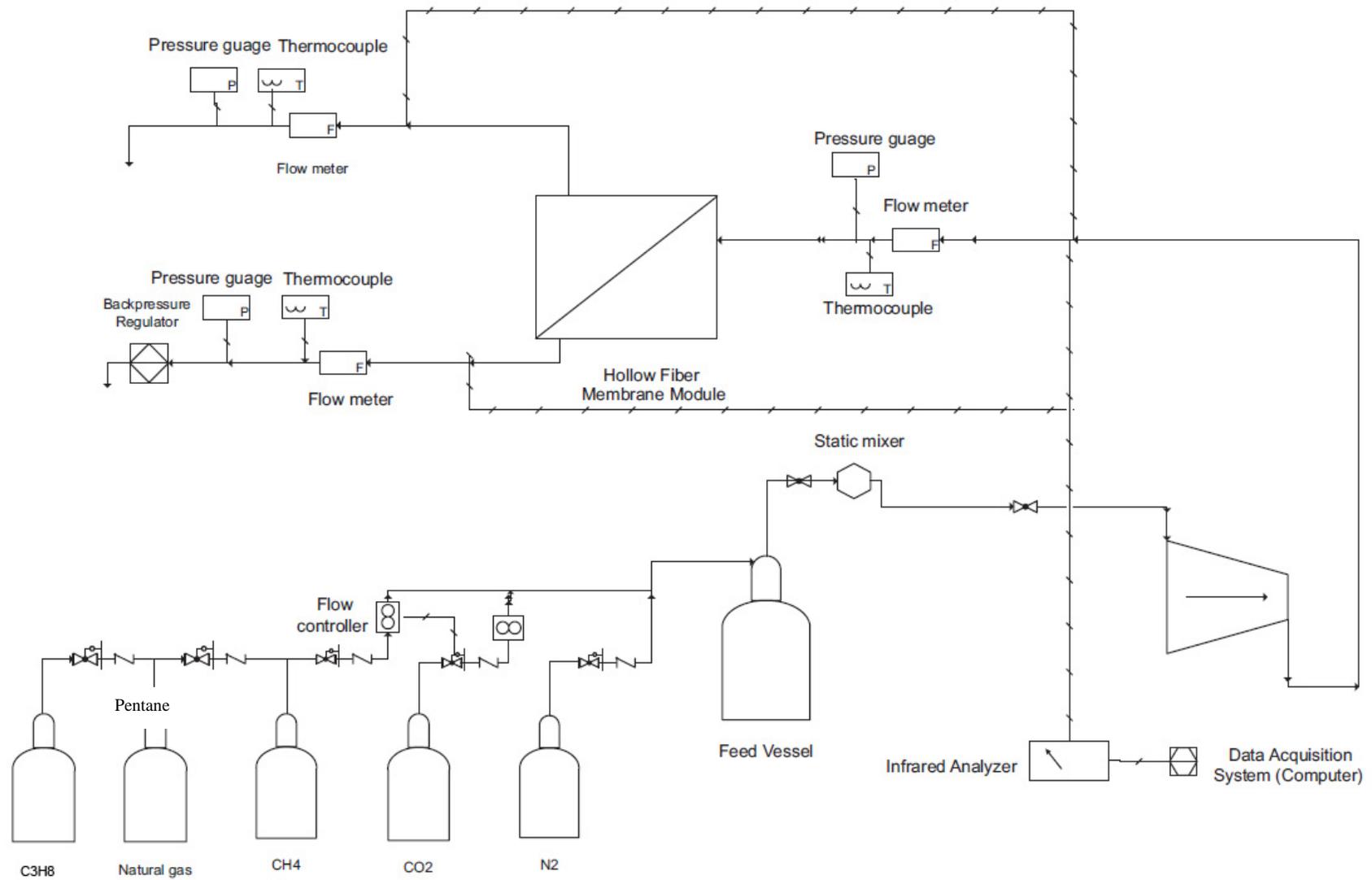
Figure 11 Flow sheet of gas separation testing unit for experimental work [38]

3.1.7 Post-experimental Work

Table 8 lists out the post-experimental activities after finish conducting experiment.

Table 8: Post- experimental activities

Phase	Activities
Post-experiment	Review experimental results
	Plot experiment result graph and interpret the data
	Conclude findings of the experiment and recommendations
	Compare and support experimental findings with related literature reviews
	Documentation and reporting

3.2 Key Milestones

Several key milestones need to be achieved for this research project and shown in Table 9

Table 9: Key milestones

No	Key Milestones	Timeline
1	Familiarized with FYP topic	FYP 1 Week 1
2	Conducted literature reviews	FYP 1 Week 6
3	Visited CO_2SMU lab visit	FYP 1 Week 7
4	Booked lab equipment and chemicals	FYP 1 Week 8
5	Reviewed CO_2SMU experimental procedures	FYP 1 Week 9
6	Fabricated hollow fibre membrane	FYP 1 Week 13
7	Conducted lab works using FTIR, GC, FESEM	FYP 2 Week 3
8	Conducted experiment using CO_2SMU	FYP 2 Week 6
9	Analysed experimental results	FYP 2 Week 9
10	Concluded experimental findings	FYP 2 Week 10
11	Compared experimental findings with literature reviews and theories	FYP 2 Week 10
12	Concluded FYP finding	FYP 2 Week 10
13	FYP viva and project dissertation submitted	FYP 2 Week 13

3.3 Gantt Chart

Gantt chart is scheduled to plan work activities for this study. Gantt charts for FYP 1 and FYP 2 are shown in Figure 12 and 13 respectively.

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	FYP topic familiarization	■													
1.1	Identification of problem statement	■													
1.2	Define FYP objectives	■													
1.3	Outline scope of study	■													
2	Literature Reviews		■	■	■	■	■								
2.1	Binary feed component membrane separation		■	■											
2.2	Ternary and higher feed component membrane separation				■	■									
2.3	Membrane separation of CO_2 from heavy hydrocarbon gas C_5H_{12}						■								
3	Lab visit and briefing by lab technician							■							
4	Checking availability of equipment and chemicals							■							
5	CO_2SMU lab and chemicals booking								■						
6	Review CO_2SMU experimental procedures									■					
7	Fabricate hollow fiber membrane										■	■	■	■	
7.1	Learning fabrication procedures										■				
7.2	Remove old membrane fiber											■			
7.3	Potting new fiber into membrane module												■	■	
8	Documentation and reporting														■

Figure 12 Gantt chart for FYP 1

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Conducted lab works using FTIR, GC & FESEM	█	█													
2	Conduct experiment using CO_2SMU			█	█	█	█									
2.1	Membrane performance testing			█												
2.2	Manipulating operating pressure			█	█											
2.3	Manipulating feed composition					█	█									
3	Result analysis							█		█	█					
3.1	Review and organize experimental data							█								
3.2	Plot inter-relation graph									█						
3.3	Interpret experiment data										█					
4	Conclude experimental findings											█				
5	Compare experimental findings with literature reviews and theories											█				
6	Draw FYP conclusion and recommendation											█				
7	Documentation and reporting												█			
8	Pre-SEDEX & SEDEX													█		
9	FYP viva and submission of FYP project dissertation														█	

Figure 13 Gantt chart for FYP 2

3.4 Tools Required

Chemicals, equipment, and software required for this study are listed as tabulated at Table 10, 11 and 12 respectively:

Table 10: List of Chemicals

No.	Chemical(s)	Function
1.	Natural gas cylinder	Feed
2	Carbon dioxide gas cylinder	Feed
3	Methane gas cylinder	Feed
4	Pentane liquid	Feed
5	Nitrogen gas cylinder	Feed

Table 11: List of Equipment

No.	Equipment	Function
1.	Carbon Dioxide Separation Membrane Unit (CO_2SMU)	Test rig to study membrane performance
2.	Hollow Fibre Membrane	Separate carbon dioxide, methane and pentane
3.	Fourier Transform Infrared Spectroscopy	For characterization of chemicals bonding for the membrane
4.	Field Emission Scanning Electron Microscopy	To analysis membrane surface structure and its morphology
5.	Gas chromatography	To analysis feed, retentate and permeate gas composition

Table 12: List of Software

No.	Software	Function
1.	National Instrument (NI) Labview	Collect experiment data
2.	TC SMART Modbus V1.0	Set temperature

Equipment and software required for this study are shown at Figure 14, 15, 16, 17.
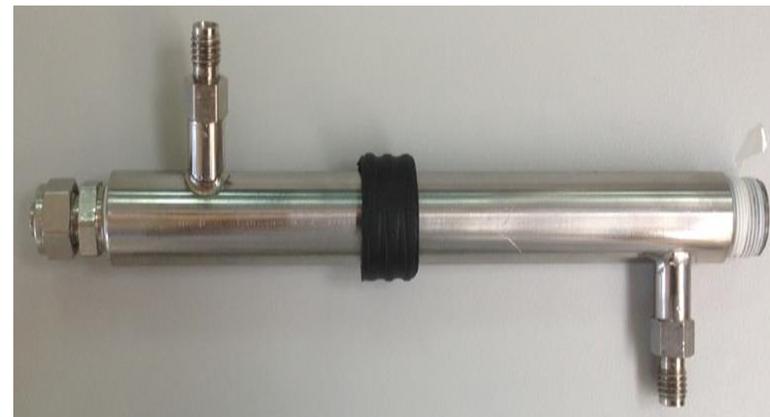

Figure 14 CO_2SMU equipment configurations
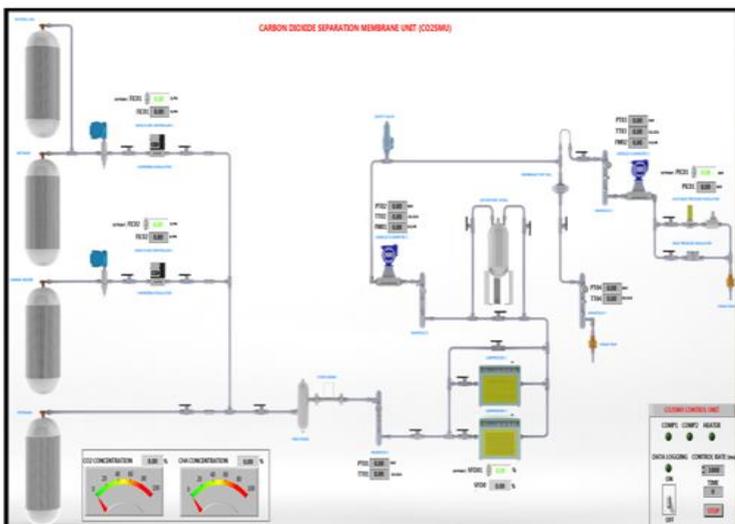

Figure 15 Hollow fiber membranes in CO_2SMU
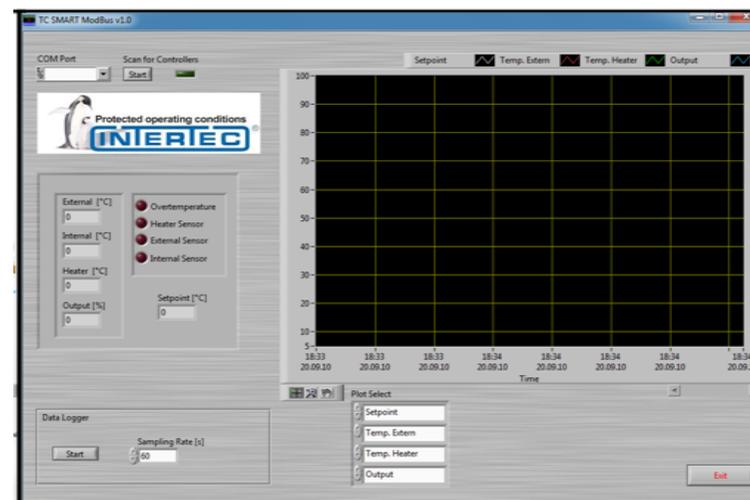

Figure 16 National Instrument (NI) Labview

Figure 17 TC SMART Modbus V1.0

CHAPTER 4

RESULTS AND DISCUSSION

4 RESULTS AND DISCUSSION

4.1 Membrane Characterization

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared (FTIR) spectral measurements were performed on the membrane to characterize on chemical bonding of the membrane. This analysis can provide information on membrane functional group as to identify the chemical structure of the membrane. Hollow fiber membrane FTIR spectrum is shown in Figure 18. Base on the frequency, membrane characteristic bond and functional group are identified and tabulated in Table 13.
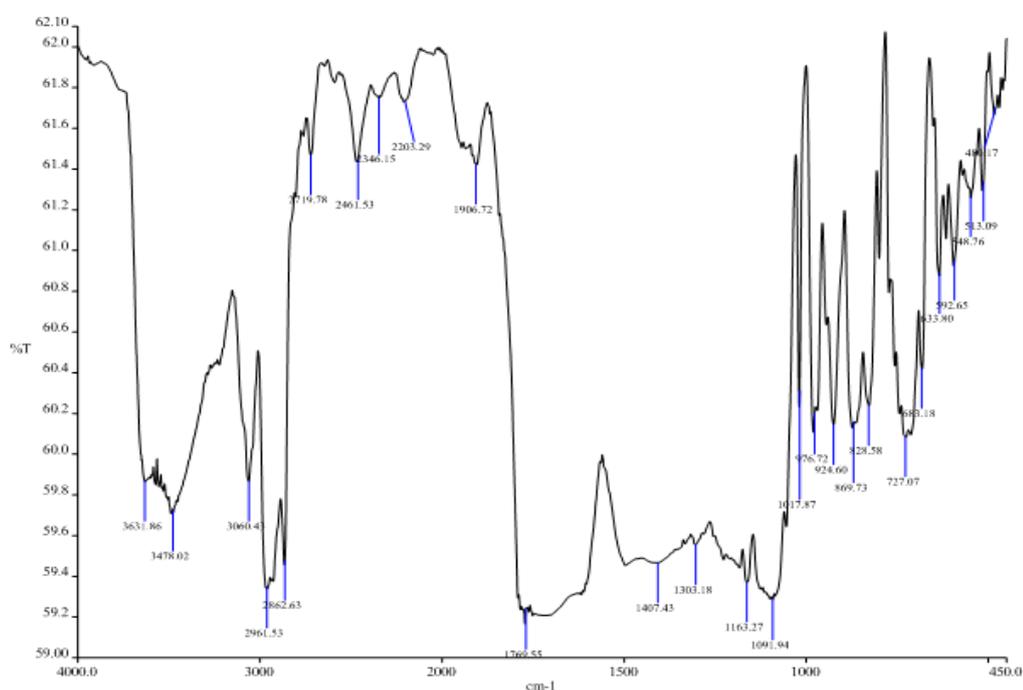

Figure 18 Membrane's FTIR Spectrum

Table 13: FTIR Analysis

Frequency (cm-1)	Bond	Functional group	Spectrum Band Detected (cm-1)
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols	3631.86
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols	3478.02
3300–2500 (m)	O–H stretch	carboxylic acids	3060.43
3100–3000 (s)	C–H stretch	aromatics	3060.43
3100–3000 (m)	=C–H stretch	alkenes	3060.43
3000–2850 (m)	C–H stretch	alkanes	2961.53, 2862.63
2830–2695 (m)	H–C=O:C–H stretch	aldehydes	2719.78
1785-1760	Symmetric C=O stretching	Imide	1769.55
1500–1400 (m)	C–C stretch (in–ring)	aromatics	1407.43
1335–1250 (s)	C–N stretch	aromatic amines	1303.18
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers	1017.87, 1091.94, 1163.27, 1303.18
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides	1163.27
1250–1020 (m)	C–N stretch	aliphatic amines	1091.94, 1163.27
1000–650 (s)	=C–H bend	alkenes	683.18, 727.07, 828.58, 869.73, 924.60, 976.72
910–665 (s, b)	N–H wag	1°, 2° amines	683.18, 727.07, 828.58, 869.73

900–675 (s)	C–H "oop"	aromatics	683.18, 727.07, 828.58, 809.73
700–610 (b, s)	–C≡C–H: C–H bend	alkynes	633.80, 683.18

FTIR spectrum above represents spectrum of the hollow fiber obtained at room temperature in the range of 450 to 4000 cm^{-1}. Firstly, bands at 3631.86 and 3478.02 cm^{-1} indicate the presence of O-H stretch. Next, the C-H aromatics stretch is present at 3060.43 cm^{-1}, while bands at 2961.53, 2862.63, and 2719.78 cm^{-1} indicate C-H stretch for alkane's functional group. Bands observed at 1769.55 cm^{-1} show the presence of Symmetric C=O stretching, whereas the C–O stretch is indicated at 1017.87, 1091.94, 1163.27, 1303.18 cm^{-1}. C–C stretch (in aromatic ring) and C–H aromatics ring stretch are represented, respectively, by the bands observed at 1407.43 cm^{-1} and 683.18, 727.07, 828.58, 809.73 cm^{-1}. The characteristic bonds appearing around 1303.18, 1163.27, and 1163.27 cm^{-1} are assigned, respectively to the C–N stretch, C–N stretch, and C–H wag (–CH_2X). =C–H bend and C–H bend are represent respectively at 683.18, 727.07, 828.58, 869.73, 924.60, 976.72 cm^{-1} and 633.80, 683.18 cm^{-1} bands. Aside from that, N–H wag also identified at 683.18, 727.07, 828.58, 869.73 cm^{-1} bands.

From the characteristic bond and functional group identified, the FTIR spectrums above are characterize as matrimid polyimide membranes. The chemical structure of matrimid polyimide monomer unit is as below:
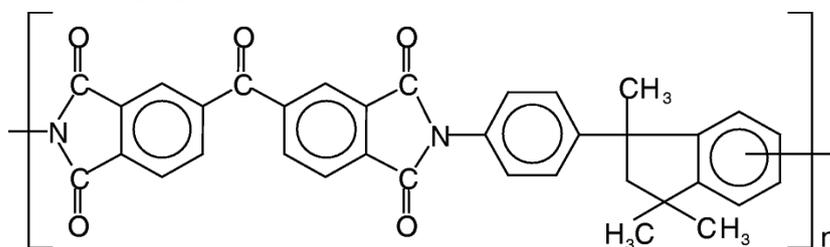

Figure 19 Chemical structure of matrimid imide monomer unit

The result shows that polar sites in the membrane matrix could aid the preferential interaction and solubility of CO_2 gas molecules, thus resulting in higher flux flow of CO_2 across the membrane as compare to other components such as CH_4 and C_5H_{12}. This will increase the relative permeance of CO_2.

4.1.2 Field Emission Scanning Electron Microscopy (FESEM) Analysis

Field Emission Scanning Electron Microscopy (FESEM) Analysis was performed on the membrane to analysis of membrane nano-scale surface structure and its morphology. Membrane cross sectional view, outer surface view and inner surface view are shown in Figure 20, 21 and 22.
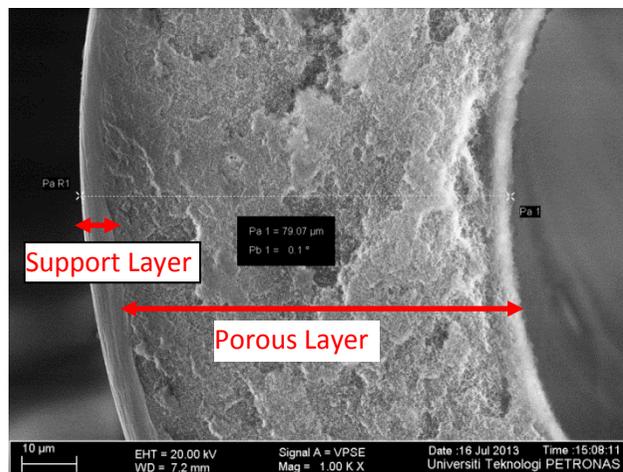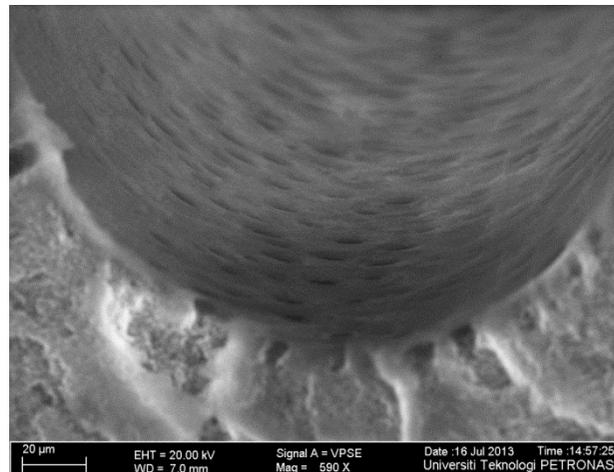

Figure 20 Cross Sectional View
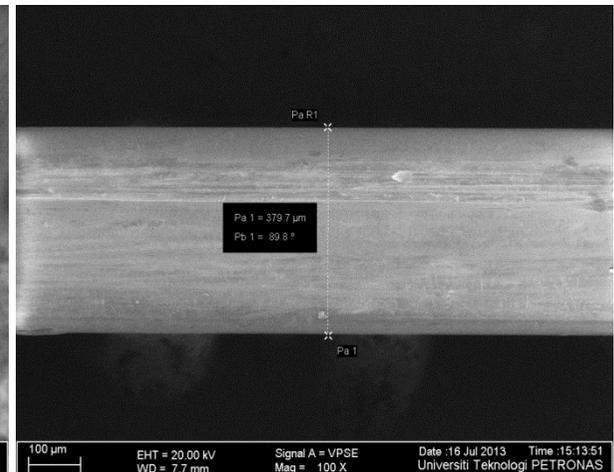
Figure 21 Inner Surface Views

Figure 22 Outer Surface Views

Figure 20 show the membrane cross sectional view at 1kX magnification. While, Figure 21 and Figure 22 show the inner surface view at 500X magnification and outer surface view at 100X magnification . Figure 20 show that membranes have asymmetric configuration with outer and inner layer. The inner parts (76 micrometer) as shown in Figure 21 consist of high porosity, permeability, spongy and soft matrimid membrane. The membrane inner layer consists of high porosity material which allow selective component to pass through the membrane while blocking others. These porous layers are formed by elongated pores. The huge amount of membrane pore is distributed all around the membrane surface. These dense surface films determine the separation properties of the membrane. Aside from that, the membrane outer diameter and membrane thickness are measured, and the result show 380 micrometer and 80 micrometer respectively. In the other hand, the outer part (4 micrometer) as shown in Figure 22 is shinny and has excellent mechanical strength which act as mechanical support of membrane. These parts have good thermal stability, good chemical resistance, light weight, flexible and characteristic yellow color of polyimide as well as low creep and high tensile strength. Figure 23 illustrate membrane dimension base on finding from FESEM analysis.
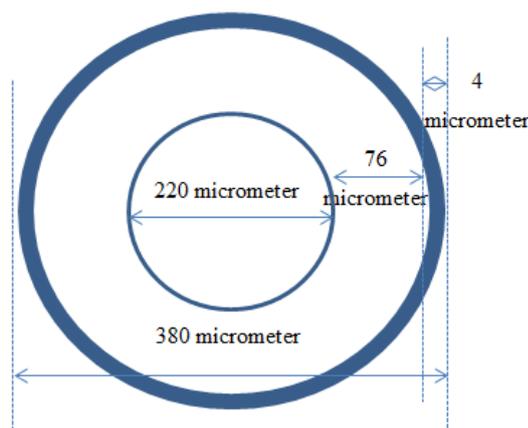

Figure 23 Membrane's Dimension

4.2 Heavy Hydrocarbon Gas (Pentane) Effect On Membrane Performance

Table 14 show membrane flux, permeance and relative permeance data for pure gas and gas mixture with & without heavy hydrocarbon gas pentane at 16 bar.

Table 14: Membrane Flux, Permeance and Relative Permeance Data for Pure Gas and Gas Mixture with & without Heavy Hydrocarbon Gas Pentane at Pressure 16 bar

No	Description	Flux, cm^3 (STP)/cm^2.S			Permeance, GPU			CO_2 Relative Permeance	
		CO_2	CH_4	C_5H_{12}	CO_2	CH_4	C_5H_{12}	CO_2/CH_4	CO_2/C_5H_{12}
1	Pure (100% CO_2, CH_4, C_5H_{12})	0.2838	0.0294	0.0003	227.41	23.53	0.25	10	903
2	Mixture w/o C_5H_{12} (50% CO_2 & CH_4)	0.1577	0.0237	N/A	126.34	18.97	N/A	7	N/A
3	Mixture with Pentane (4% Pentane, 48% CO_2 & CH_4)	0.1314	0.0213	0.0002	105.28	17.09	0.18	6	571

From the experimental data obtained, comparison and analysis are done on pure gas versus gas mixture and gas mixture with pentane versus without pentane. This analysis can provide information on membrane performance when feed with single component and multiple component, as well as heavy hydrocarbon gas effect on membrane performance.

4.2.1 Effect Of Single Component Feed Gas Versus Multiple Component Feed Gas Mixture In Membrane Separation Performance

From Table 14, Row 1 show membrane performance with pure CO_2, CH_4, and C_5H_{12} feed, whiles, Row 2 & 3 show membrane performance with mixture of CO_2, CH_4, and C_5H_{12} feed.

It is observed that CO_2 flux is 0.2838 cm^3 (STP)/cm^2.S when pure CO_2 gas is feed into the membrane, while the flux decrease to 0.1577 cm^3 (STP)/cm^2.S and 0.1314 cm^3 (STP)/cm^2.S when gas mixture are feed into membrane. Similarly, CH_4 flux is 0.0294 cm^3 (STP)/cm^2.S when pure CH_4 gas is feed into the membrane, while the flux decrease to 0.0237 cm^3 (STP)/cm^2.S and 0.0213 cm^3 (STP)/cm^2.S when gas mixture are feed into membrane. For Pentane, C_5H_{12} flux is 0.0003 cm^3 (STP)/cm^2.S when pure C_5H_{12} gas is feed into the membrane, while the flux decrease to 0.0002 cm^3 (STP)/cm^2.S when gas mixture are feed into membrane. It is concluded that the membrane flux is higher when membrane is feed with pure gas as compare to gas mixture.

It is observed that CO_2 permeance is 227.41 GPU when pure CO_2 gas is feed into the membrane, while the permeance decrease to 126.34 GPU and 105.28 GPU when gas mixture are feed into membrane. Similarly, CH_4 permeance is 23.53 GPU when pure CH_4 gas is feed into the membrane, while the permeance decrease to 18.97 GPU and 17.09 GPU when gas mixture are feed into membrane. For Pentane, C_5H_{12} permeance is 0.25 GPU when pure C_5H_{12} gas is feed into the membrane, while the permeance decrease to 0.18 GPU when gas mixture are feed into membrane. It is concluded that the membrane permeance is higher when membrane is feed with pure gas as compare to gas mixture.

Both flux and permeance change are due to coupling effect between CO_2, CH_4 and C_5H_{12} gases, which resulted in an increased flux of pure gas. With gas mixture feed, the membrane surface have component of CO_2, CH_4 and may be C_5H_{12} trying to permeate through the membrane. CO_2 need to complete with other gases to to reach the membrane surface and pass through the membrane pore. Thus, reduce the component flux and permeance flow. For pure gas, all membrane surface and selective pore are consist of the component, thus increasing the contact between molecule and pore, this increase the component flux and permeance flow through the membrane. Figure 24, 25 and 26 illustrate gas mixture and pure gas flow through

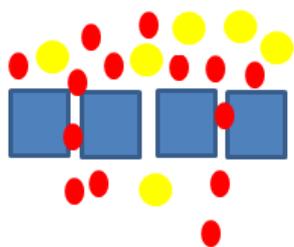membrane. Blue color indicates membrane, while red color indicates CO_2 molecule, and yellow color indicates CH_4 and C_5H_{12} molecule.
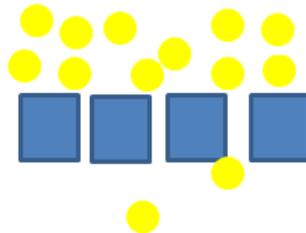

Figure 24 Gas Mixture CO_2/CH_4
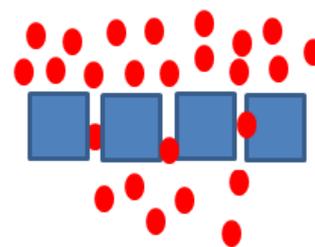
Figure 25 Pure CH_4

Figure 26 Pure CO_2

It is observed that CO_2/CH_4 relative permeance is 10 when pure gas is feed into the membrane, while the CO_2/CH_4 relative permeance decrease to 7 and 6 when gas mixture are feed into membrane. Similarly, CO_2/ C_5H_{12} relative permeance is 903 pure gas is feed into the membrane, while the CO_2/ C_5H_{12} relative permeance decrease to 571 when gas mixture are feed into membrane. It is concluded that the membrane CO_2 relative permeance is higher when membrane is feed with pure gas as compare to gas mixture. Increase in relative permeance for pure gas is due to substantial increase in CO_2 flux and permeance as compare to CH_4 and C_5H_{12}. Substantial increase in CO_2 flux and permeance is because of preferential interaction and solubility of CO_2 gas molecules across the membrane. Thus, the CO_2 permeance flow and its change are more significant as compare to CH_4 and C_5H_{12}.

4.2.2 Effect Of Heavy Hydrocarbon Gas Pentane In Multicomponent Membrane Separation Performance

From Table 14, Row 2 show membrane performance without C_5H_{12} feed, whiles, Row 3 show membrane performance with gas mixture of CO_2, CH_4, and C_5H_{12}.

It is observed that CO_2 flux is 0.1577 cm^3 (STP)/cm^2.S when C_5H_{12} is not feed into the membrane, as compare to 0.1314 cm^3 (STP)/cm^2.S when gas mixture with C_5H_{12} are feed into membrane. Similarly, CH_4 flux is 0.0237 cm3 (STP)/cm^2.S when C_5H_{12} is not feed into the membrane, as compare to 0.0213 cm^3 (STP)/cm^2.S when gas mixture with C_5H_{12} are feed into membrane. It is concluded that the

membrane gas flux is lower when C_5H_{12} is present in the feed, indicate that C_5H_{12} reduce the CO_2 and CH_4 flux, and affect the membrane performance.

It is observed that CO_2 permeance is 126.34 GPU when C_5H_{12} is not feed into the membrane, as compare to 105.28 GPU when gas mixture with C_5H_{12} is feed into membrane. Similarly, CH_4 permeance is 18.97 GPU when C_5H_{12} is not feed into the membrane, as compare to 17.09 GPU when gas mixture with C_5H_{12} is feed into membrane. It is concluded that the membrane gas permeance is lower when C_5H_{12} is present in the feed, indicate that C_5H_{12} reduce the CO_2 and CH_4 permeance, and thus affect the membrane performance.

It is observed that CO_2/CH_4 relative permeance is 7 when gas without C_5H_{12} is feed into the membrane, while the CO_2/CH_4 relative permeance decreases to 6 when gas mixture with C_5H_{12} is feed into membrane. It is concluded that the membrane CO_2 relative permeance is lower when C_5H_{12} is present in the feed, indicate that C_5H_{12} reduce the membrane CO_2 separation performance.

So, experimental result had shown that CO_2, CH_4, and C_5H_{12} flux, permeance, and relative permeance are lower when heavy hydrocarbon gas C_5H_{12} is present in the feed. This cause reduces in membrane separation performance. This phenomenon can be explained with increase of membrane surface damage and pore blockage by large molecular size C_5H_{12}.

4.2.3 Comparison Of Present Data With Literature Review

CO_2SMU result from Table 14 show that membrane flux, permeance and CO_2 relative permeance are lower when membrane is feed with gas mixture as compare to pure gas due to coupling effect and lower membrane surface concentration. In fact, the membrane gas flux, permeance, and relative permeance are even lower when heavy hydrocarbon gas C_5H_{12} is present possibly due to increase of membrane surface damage and pore blockage by larger molecular size C_5H_{12}.

Chenar et al [15] who investigate the effect of third component on the performance of commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes in CO_2-CH_4 separation applications also found out that presence of third component vapor in the feed stream significantly reduced the permeation rates of CO_2. M.Hedayat et al [32] who investigate the separation of hydrogen sulfide, carbon dioxide, methane with membrane found that presence of carbon dioxide in

feed gas decreased the hydrogen sulfide separation from natural gas represent by methane. These findings are similar with result from Chapter 4.2.2 where CO_2 flux and permeace decrease from 0.1577 cm^3 (STP)/cm^2.S to 0.1314 cm^3 (STP)/cm^2.S and 126.3 GPU to 105.28GPU.

4.3 Membrane Performance Test (CO_2SMU)

4.3.1 Pressure Effect On Multicomponent Gas Separation

Figure 27 illustrate CO_2, CH_4 and C_5H_{12} flux at difference feed pressure, varied from 10 to 18 bar for hollow fiber membrane.
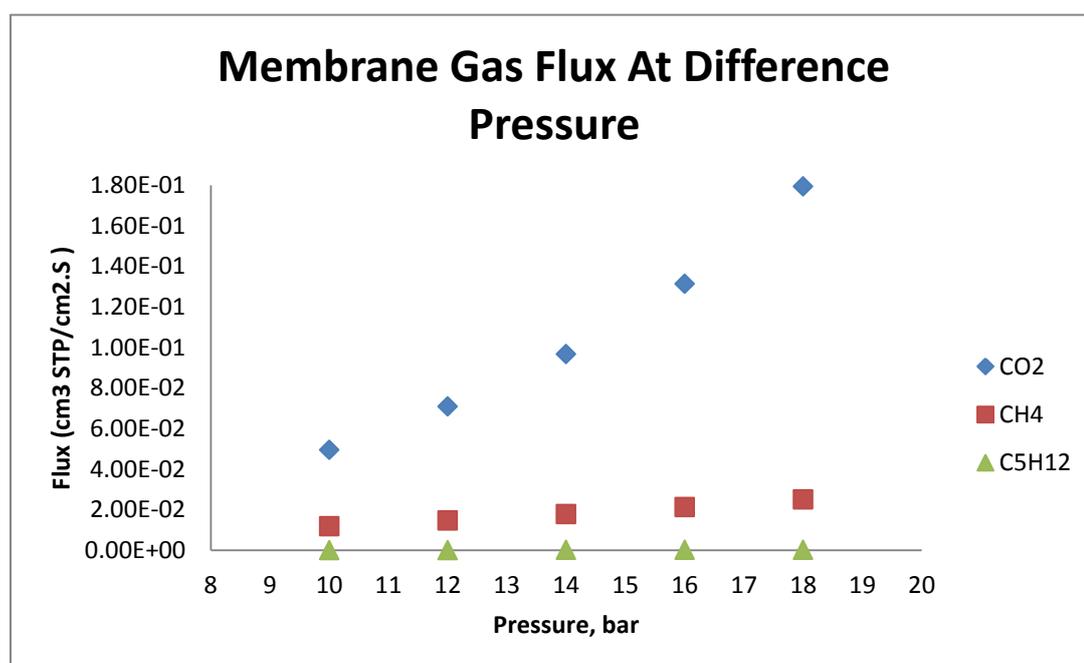

Figure 27 Gas Flux at Difference Feed Pressure

CO_2, CH_4 and C_5H_{12} flux increase with increase in membrane feed pressure. This is because as feed pressure increase (permeate side pressure remain constant), the pressure difference across the membrane increase. This will cause an increase in driving force of CO_2, CH_4 and C_5H_{12} molecule to permeate through the membrane. Thus, the flux of the CO_2, CH_4 and C_5H_{12} gases across the membrane increase.

CO_2 flux increase with increase in membrane feed pressure. CO_2 increase significantly from 0.0495 cm^3 $_{STP}$/cm^2.S to 0.179 cm^3 $_{STP}$/cm^2.S as pressure increase from 10 bar to 18 bar. While, CH_4 and C_5H_{12} flux are only slightly increase with increase in membrane feed pressure. Experimental result show that CH_4 and C_5H_{12}

flux increase from 0.0119 cm^3 $_{STP}$/cm^2.S to 0.0252 cm^3 $_{STP}$/cm^2.S and 0.0001 cm^3 $_{STP}$/cm^2.S to 0.0003 cm^3 $_{STP}$/cm^2.S when pressure increase from 10 bar to 18 bar. These observations are due to membrane matrix's polar sites that enhance preferentially sorbed CO_2 gas. Thus, increasing pressure will increase the driving force and enhance preferentially sorbed CO_2 gas. On the other hand, CH_4 and C_5H_{12} molecule does not have a substantial interaction with the membrane and therefore, effect of increasing membrane feed pressure only marginally improve their flux.

Figure 28, 29 and 30 illustrate CO_2, CH_4 and C_5H_{12} permeance at difference feed pressure, varied from 10 to 18 bar using hollow fiber membrane.
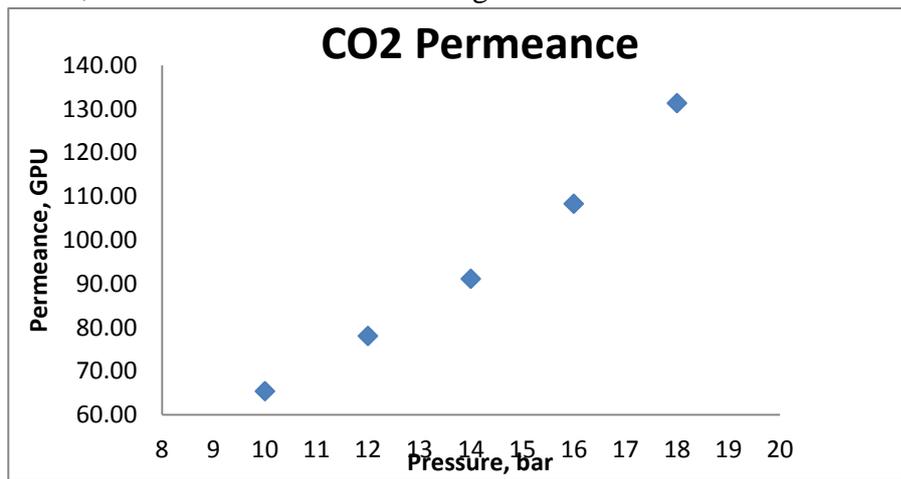

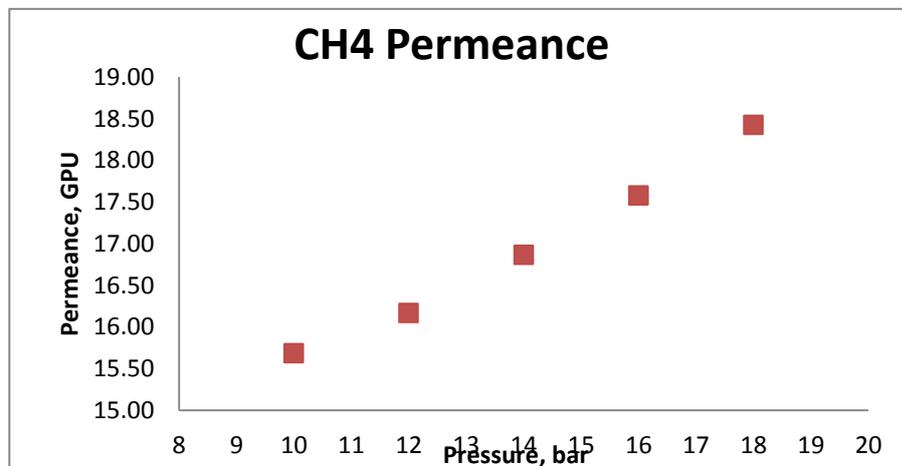Figure 28 CO_2 Permeance at Difference Feed Pressure

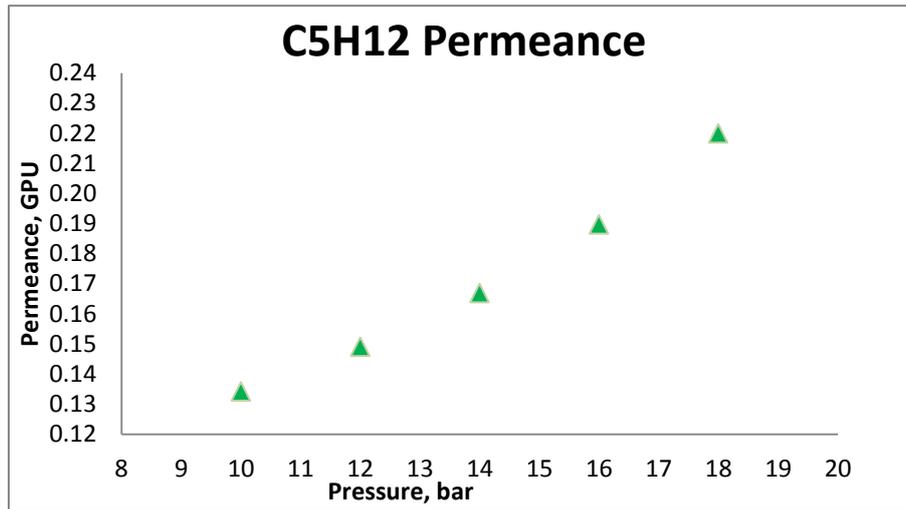Figure 29 CH_4 Permeance at Difference Feed Pressure

C5H12 Permeance

Figure 30 C_5H_{12} Permeance at Difference Feed Pressure

Figure 28 illustrate CO_2 permeance at difference feed pressure. Figure 29 illustrate CH_4 permeance at difference feed pressure. Figure 30 illustrate C_5H_{12} permeance at difference feed pressure.

Figure 28, 29 and 30 shows that all CO_2, CH_4 and C_5H_{12} permeance increase with increase in membrane feed pressure. This is because as feed pressure increase, the membrane being compressed more, thus membrane compaction factor increase. This will result in decrease in membrane thickness, thus gaseous can pass through the membrane easier, and flux increase.

$$Permeance = \frac{Flux}{Pressure} = \frac{Volume_{STP}}{Surface\ Area\ \times Time\ \times Pressure} \quad [24]$$

From Figure 27, it is known that as pressure increase flux increase. Due to significant effect of membrane compaction factor, there is significant increase of flux as pressure increase. As a result, CO_2, CH_4 and C_5H_{12} permeance increase.

Figure 28, 29 and 30 show that CO_2 permeance increase with increase in membrane feed pressure. CO_2 permeance increase from 65.36 GPU to 131.35 GPU as pressure increase from 10 bar to 18 bar. While, CH_4 and C_5H_{12} permeance are only slightly increase (almost constant) with increase in membrane feed pressure. Experimental result show that CH_4 and C_5H_{12} permeance increase from 15.69 GPU to 18.42 GPU and 0.13 GPU to 0.22 GPU when pressure increase from 10 bar to 18 bar. These observations can be explained on the basis of increasing plasticization of the membrane by the preferentially sorbed CO_2 gas with increasing pressure. On the other hand CH_4 and C_5H_{12} molecule does not have a substantial interaction with the

membrane and therefore, effect of increasing membrane feed pressure only marginally improve their permeance.

Figures 31 and 32 illustrate the relative permeance of CO_2 over CH_4 and C_5H_{12} across the hollow fiber membrane at difference feed pressure, varied from 10 to 18 bar for hollow fiber membrane.
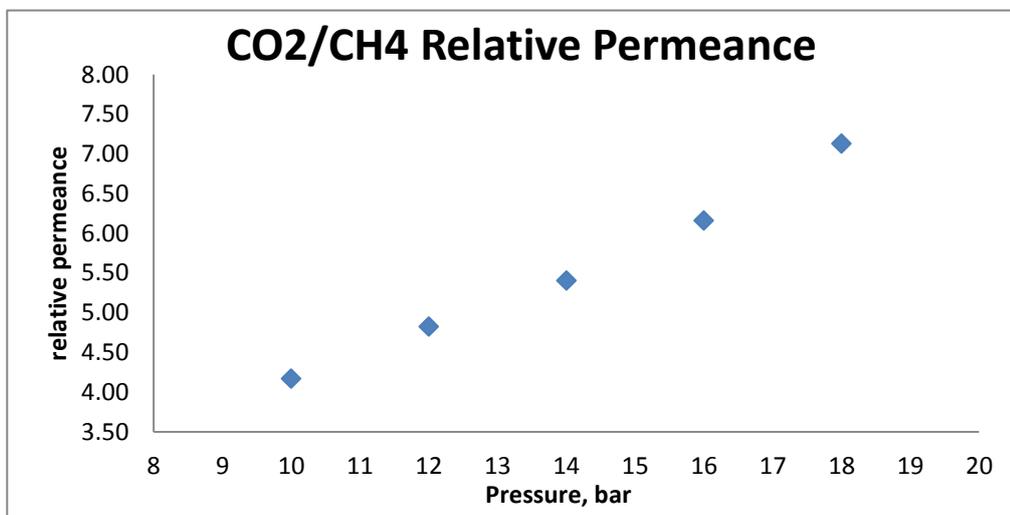
Figure 31 CO_2/CH_4 Relative Permeance At Difference Feed Pressure
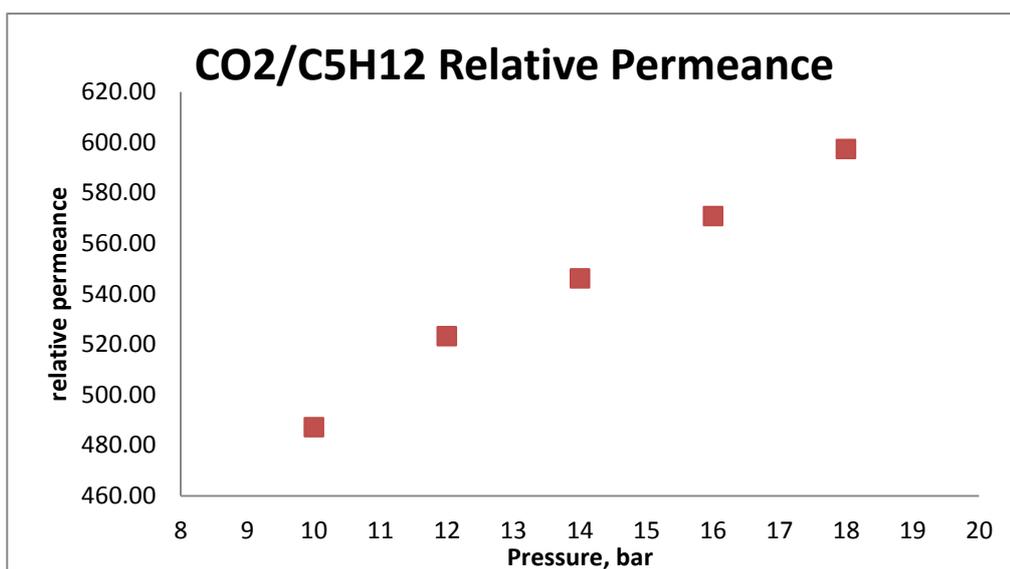
Figure 32 CO_2/C_5H_{12} Relative Permeance At Difference Feed Pressure

Figure 31 and 32 shows that CO_2/CH_4 and CO_2/C_5H_{12} relative permeance increase with increase in membrane feed pressure. CO_2/CH_4 relative permeance increase from 4.17 to 7.13 as pressure increase from 10 bar to 18 bar. While, CO_2/C_5H_{12} permeance relative permeance increase from 487.14 to 597.27 as pressure increase from 10 bar to 18 bar. The increase in CO_2 relative permeance is due to CO_2

permeance across the membrane vary a lot with feed pressure change as shown in figure 30 while CH_4 and C_5H_{12} permeance are almost constant (only increase slightly) when feed pressure increase. Thus as pressure increase, increase in driving force and membrane plasticization together with matrix's polar sites that enhance preferentially sorbed CO_2 gas and membrane compaction factor cause more CO_2 be push to pass through the membrane, while larger size CH_4 and C_5H_{12} does not have a substantial interaction with the membrane.

4.3.2 Feed CO_2 Composition Effect on Multicomponent Gas Separation

Figure 33 illustrate CO_2, CH_4 and C_5H_{12} flux at difference CO_2 feed composition, varied from 10% to 90% using hollow fiber membrane
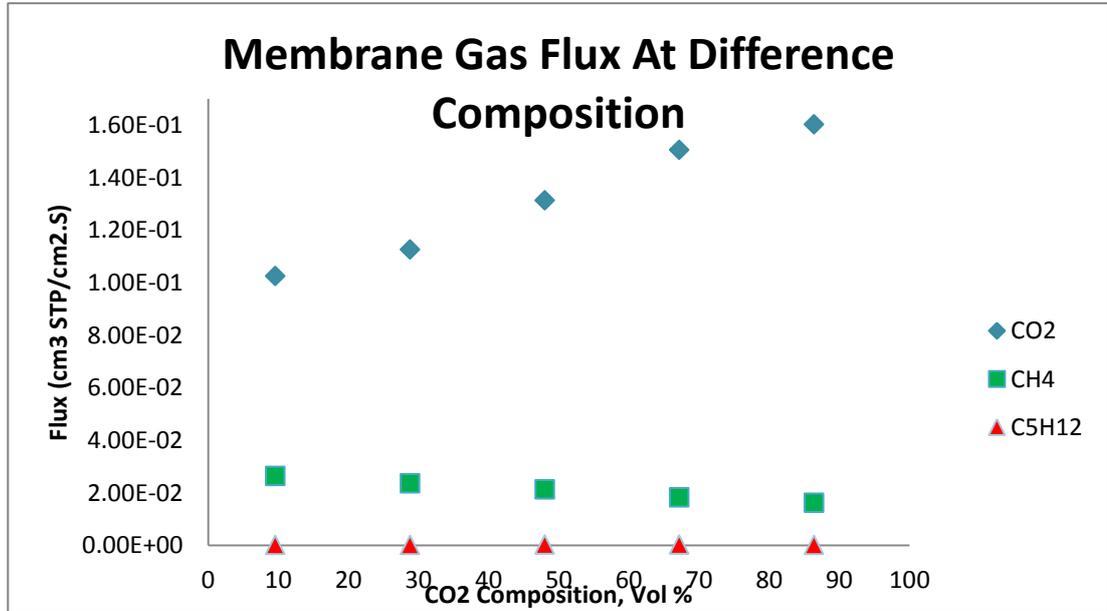

Figure 33 Gas Flux at Difference CO_2 Feed Composition

The 10% CO_2 feed composition indicate the natural gas produce from low CO_2 content natural gas field, while 90% CO_2 feed composition indicate the natural gas produce from high CO_2 content natural gas field. It can be observed that, CO_2 flux increase with increase in CO_2 feed composition, while CH_4 and C_5H_{12} flux are nearly constant. CO_2 flux increase from 0.103 cm^3 STP/cm^2.S to 0.16 cm^3 STP/cm^2.S as CO_2 feed composition increase from 9.6 % to 86.4 %. While, CH_4 and C_5H_{12} flux are almost constant with slightly varies as CO_2 feed composition increase from 9.6 % to 86.4 %. Experimental result show that CH_4 and C_5H_{12} flux varies from 0.0162 cm^3 STP/cm^2.S to 0.0264 cm^3 STP/cm2.S and 0.000201 cm^3 STP/cm^2.S to 0.000231 cm^3 STP/cm^2.S as CO_2 feed composition increase from 9.6 % to 86.4 %.

Theoretically, CO_2, CH_4 and C_5H1_2 flux from 10% to 90% CO_2 feed composition should be constant. Membrane has very low stage cut which is less than 10% and usually can be as low as 1% depends on membrane separation performance, retention time and surface area.

$$Stage\ Cut\ \% = \frac{Pemeate\ Flow}{Feed\ Flow} \times 100\%$$ [25]

So, change in CO_2 feed composition have no effect on gas flux, permeance, and relative permeance except CO_2 composition manipulated at lower than stage cut value. In this experiment, scopes of study are based on actual reservoir CO_2 composition which is higher than membrane stage cut value. Let take stage cut value as 2%. This means that at one time only 2% of feed (mostly CO_2 due to high CO_2 relative permeance) can pass through the membrane. So, vary CO_2 feed composition higher than stage cut %, will not increase the permeate flow, thus flux will be constant.

The difference between experimental results with theory can be explained on the basis of increasing plasticization of the membrane by the preferentially sorbed CO_2 gas with increasing CO_2 feed composition. Thus, CO_2 flux increase. On the other hand, the saturated CH_4 and C_5H_{12} molecule does not have a substantial interaction with the membrane and therefore, effect of increasing CO_2 feed composition only did not have much effect on CH_4 and C_5H_{12} flux. In short, as CO_2 feed composition increase, membrane plasticization increase, CO_2 flux increase while, CH_4 and C_5H_{12} flux remain constant.

Figures 34, 35 and 36 illustrate CO_2, CH_4 and C_5H_{12} permeance at difference CO_2 feed composition, varied from 10 % to 90 % for hollow fiber membrane. The 10% CO_2 feed composition indicate the natural gas produce from low CO_2 content natural gas field, while 90% CO_2 feed composition indicate the natural gas produce from high CO_2 content natural gas field.
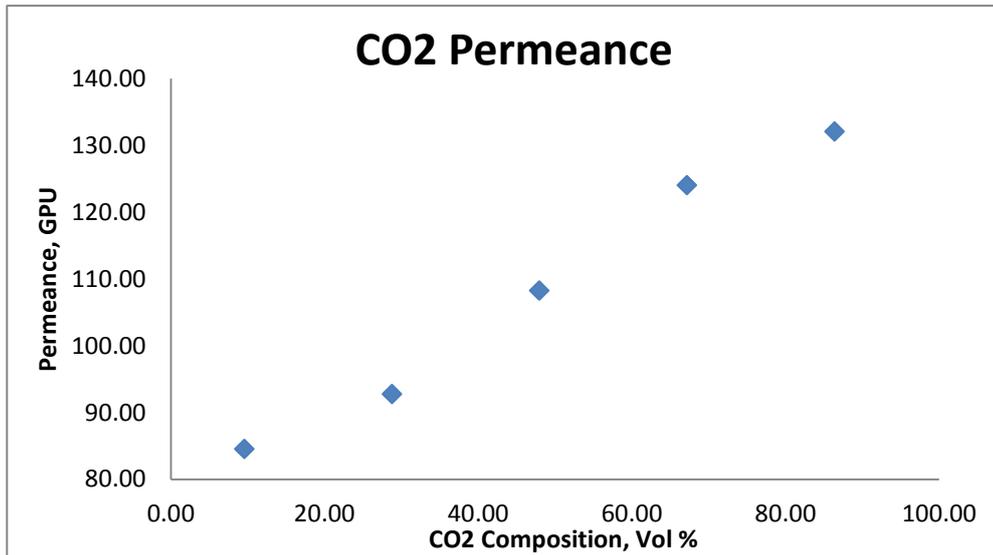
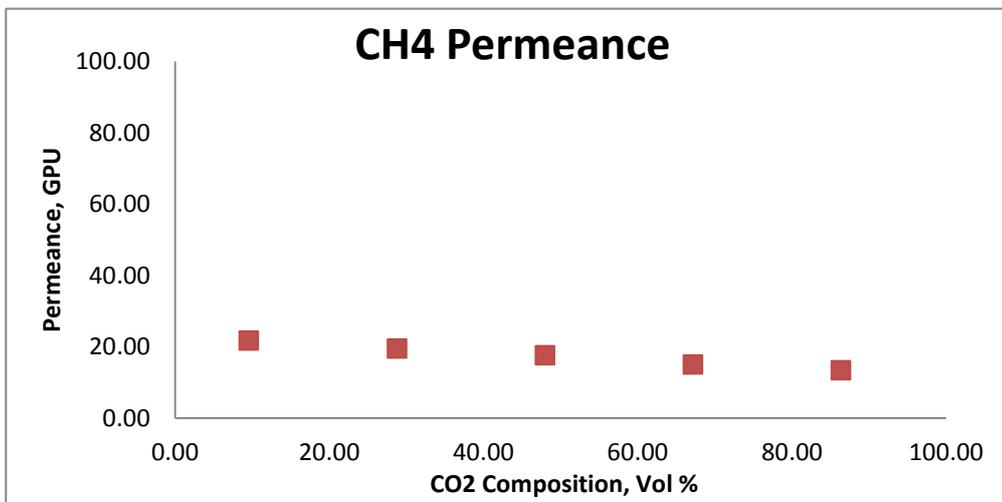Figure 34 CO_2 Permeance at Difference CO_2 feed composition

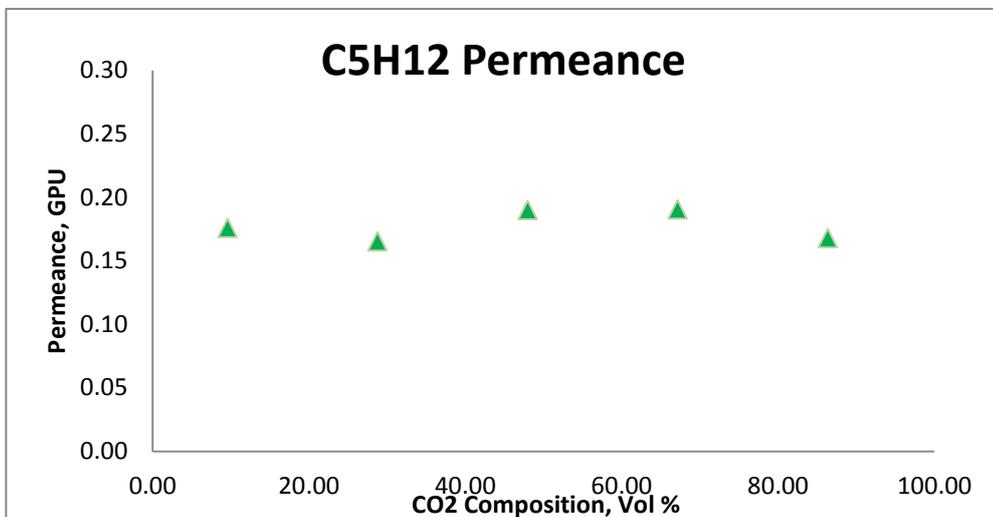Figure 35 CH_4 Permeance at Difference CO_2 feed composition

Figure 36 C_5H_{12} Permeance at Difference CO_2 feed composition

Figure 34 illustrate CO_2 permeance at difference CO_2 feed composition. Figure 35 illustrate CH_4 permeance at difference CO_2 feed composition. Figure 36 illustrate C_5H_{12} permeance at difference CO_2 feed composition. In this experiment, we manipulated CO_2 feed composition while fixed the feed pressure. Thus, when pressure is constant, permeance is proportional with flux.

$$Permeance = \frac{Flux}{Pressure} = \frac{Volume_{STP}}{Surface\ Area\ \times Time\ \times Pressure} \quad [26]$$

$$Permeance \propto Flux \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad [27]$$

It can be observed that, CO_2 permeance increase with increase in CO_2 feed composition, while CH_4 and C_5H_{12} permeance are nearly constant. CO_2 permeance increase from 84.51 GPU to 132.07 GPU as CO_2 feed composition increase from 9.6 % to 86.4 %. While, CH_4 and C_5H_{12} permeance are almost constant with slightly varies as CO_2 feed composition increase from 9.6 % to 86.4 %. Experimental result show that CH_4 and C_5H_{12} permeance varies from 13.36 GPU to 21.75 GPU and 0.17 GPU to 0.19 GPU as CO2 feed composition increase from 9.6 % to 86.4 %.

Theoretically, CO_2, CH_4 and C_5H_{12} permeance from 10% to 90% CO_2 feed composition should be constant. Membrane has very low stage cut which is less than 10% and usually can be as low as 1% depends on membrane separation performance, retention time and surface area.

$$Stage\ Cut\ \% = \frac{Pemeate\ Flow}{Feed\ Flow} \times 100\% \quad\quad\quad [28]$$

So, change in CO_2 feed composition have no effect on gas flux, permeance, and relative permeance except CO_2 composition manipulated at lower than stage cut value. In this experiment, scopes of study are based on actual reservoir CO_2 composition which is higher than membrane stage cut value. Let take stage cut value as 2%. This means that at one time only 2% of feed (mostly CO_2 due to high CO_2 relative permeance) can pass through the membrane. So, vary CO_2 feed composition higher than stage cut %, will not increase the permeate flow, thus flux and permeance will be constant.

The difference between experimental results with theory can be explained on the basis of increasing plasticization of the membrane by the preferentially sorbed CO_2 gas with increasing CO_2 feed composition. Thus, CO_2 flux and permeance increase. On the other hand, the saturated CH_4 and C_5H_{12} molecule does not have a

substantial interaction with the membrane and therefore, effect of increasing CO_2 feed composition only did not have much effect on CH_4 and C_5H_{12} flux and permeance. In short, as CO_2 feed composition increase, membrane plasticization increase, CO_2 flux and permeance increase while, CH_4 and C_5H_{12} flux and permeance remain constant.

Figures 37 and 38 illustrate the relative permeance of CO_2 over CH_4 and C_5H_{12} across the hollow fiber membrane at difference CO_2 feed composition, varied from 10% to 90% for hollow fiber membrane.
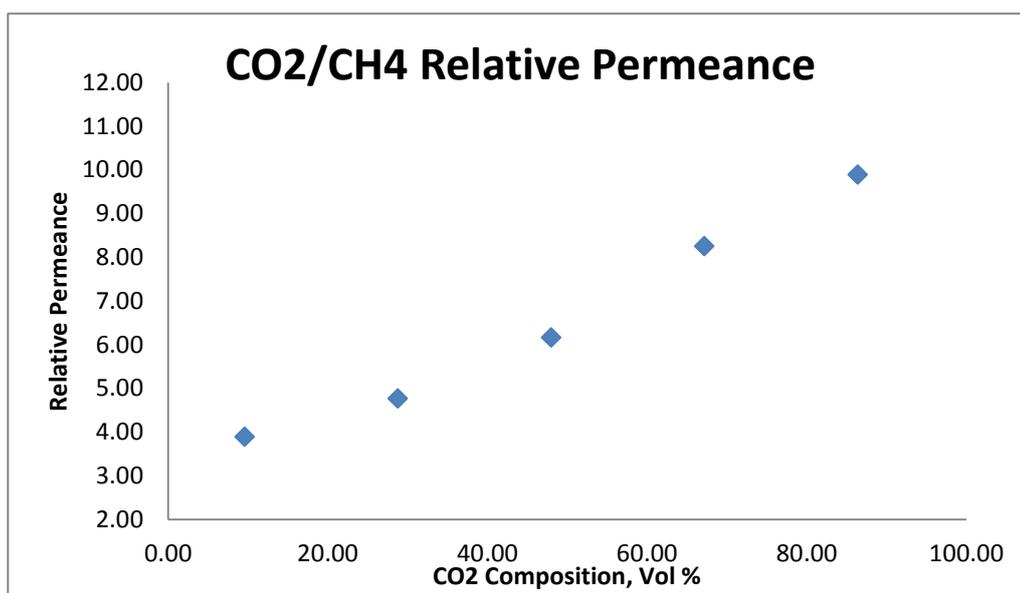

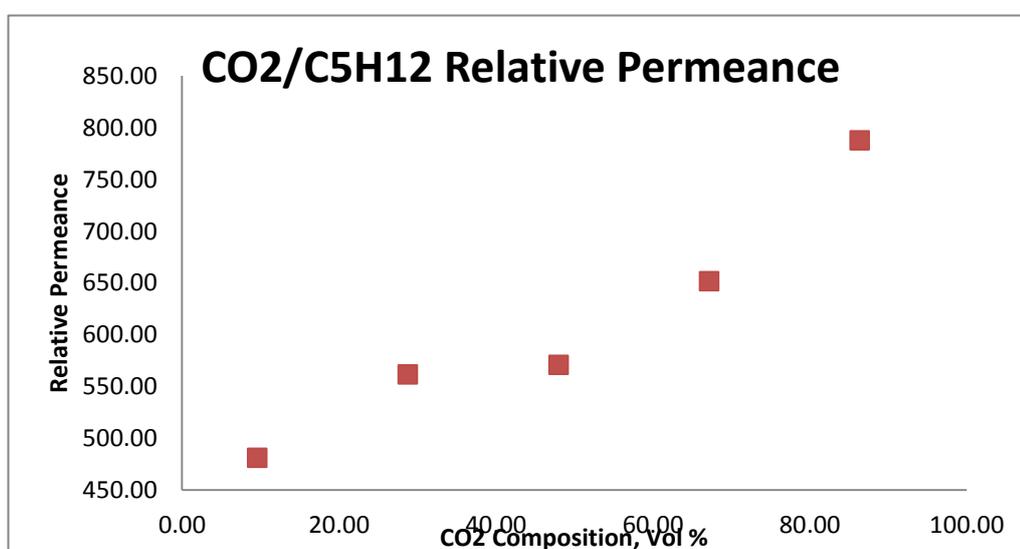Figure 37 CO_2/CH_4 Relative Permeance At Difference CO_2 feed composition

Figure 38 CO_2/C_5H_{12} Relative Permeance At Difference CO_2 feed composition

Figure 37 and 38 shows that CO_2/CH_4 and CO_2/C_5H_{12} relative permeance increase with increase in membrane feed pressure. CO_2/CH_4 relative permeance increase from 3.89 to 9.89 as CO_2 feed composition increase from 9.6% to 86.4%. While, CO_2/C_5H_{12} permeance relative permeance increase from 481.2 to 787.58 as CO_2 feed composition increase from 9.6% to 86.4%. The increase in CO_2 relative permeance is due to CO_2 permeance across the membrane vary a lot with CO_2 feed composition change as shown in Figure 41 while CH_4 and C_5H_{12} permeance are constant (varies slightly) when CO_2 feed composition increase.

Thus as CO_2 feed composition increase, membrane plasticization and matrix's polar sites that enhance preferentially sorbed CO_2 gas cause more CO_2 be push to pass through the membrane, while larger size CH_4 and C_5H_{12} does not have a substantial interaction with the membrane.

4.3.3 Comparison Of Present Data With Literature Review

For membrane performance, when feed pressure increase, driving force increase, CO_2, CH_4 and C_5H_{12} flux increase. Pressure increase and matrix's polar sites enhances preferentially sorbed CO_2 gas and increase CO_2 flux significantly. However CH_4 and C_5H_{12} molecule does not have a substantial interaction with the membrane therefore, only marginally improve their flux. Due to significant effect of membrane compaction factor, there is significant increase in flux as compare to pressure increase. As a result, CO_2, CH_4 and C_5H_{12} permeance increase. Moreover, increasing membrane plasticization by the preferentially sorbed of CO_2 gas, resulting increase in CO_2 relative permeance as pressure increase. Safiah [20] evaluate the performance of membrane for CO_2-CH_4 separation. Similary, Safiah [20] found out that flux increases when inlet pressure is increased. These findings also supported by Mukthar [12] who develop mathematic model for predicting the permeability of pore carbon dioxide and methane across y-alumina membrane. The results show that permeance of carbon dioxide and methane increase with increase of operating pressure. Hedayat [32] also show that pressure had a positive effect on hydrogen sulphide and carbon dioxide removal from methane.

Theoretically, given stage cut less than 10%, as CO_2 feed composition increase, CO_2, CH_4 and C_5H1_2 flux remain constant. When pressure is constant, permeance is proportional with flux. Experimental results show that increase in CO_2 feed

composition, increasing plasticization of the membrane by the preferentially sorbed CO_2 gas at matrix's polar sites, thus increasing CO_2 flux and permeance. On the other hand, the saturated CH_4 and C_5H_{12} molecule does not have a substantial interaction with the membrane and therefore, CH_4 and C_5H_{12} flux and permeance remain constant. Thus CO_2 relative permeance increase as CO_2 feed composition increase. These findings have some similarity with Jefri [21], who study on carbon dioxide separation from natural gas using inorganic membrane. Jefri [21] found that increase carbon dioxide concentration from 15% to 30%, increase carbon dioxide recovery in permeate stream.

CHAPTER 5

CONCLUSION AND RECOMENDATIONS

5   CONCLUSION AND RECOMENDATIONS

5.1 Relevancy To Objectives

Performance of polyimide hollow fiber membranes for the separation of carbon dioxide-methane-pentane at difference pressure and feed composition as well as the effect of heavy hydrocarbon gas C_5H_{12} on membrane performance had been studied. Firstly, hollow fiber membrane module had been successfully potted using commercial fiber. Secondly, hollow fiber membrane bonding and morphology and were characterize with using FTIR and FESEM show that polar sites in the matrimid polyimide hollow fiber membranes matrix could aid the preferential interaction and solubility of CO_2 gas molecules, thus resulting in higher flux flow of CO_2 across the membrane as compare to other components such as CH_4 and C_5H_{12}. Thirdly, the effects of heavy hydrocarbon gas (Pentane) on membrane performance are tested showing that permeate gas flux, permeance, and relative permeance are even lower when heavy hydrocarbon gas C_5H_{12} is present. Fourthly, flux, permeance and relative permeance of carbon dioxide – methane – pentane separation on hollow fiber membrane at difference feed pressure are evaluated showing increase of gas flux, permeance and relative permeance as pressure increase. Last but not least, flux, permeance and relative permeance of carbon dioxide – methane – pentane separation on hollow fiber membrane at difference CO_2 feed composition are tested showing CO_2 flux, permeance, and relative permeance increase, while CH_4 and C_5H_{12} remain constant as CO_2 feed composition increase. In the nutshell, the objectives for FYP are achieved.

5.2 Recommendations

Experimental studies with manipulating heavy hydrocarbon gas pentane feed composition can be conducted to further studies on effect of heavy hydrocarbon gas pentane. Aside from three components, experimental studies can be expanded to more feed component with feed gas that consists of mixture of carbon dioxide, methane, ethane, pentane, butane, pentane, and nitrogen. Aside from that, to further study of membrane performance for natural gas, real natural gas sample from offshore can be considered to be used as experimental gas feed. With the data of real natural gas sample, the project studied will be more compressive and better prove that the membrane can apply on real industries. Real sample of natural gas feed will also give better study on the behavior and characteristics of carbon dioxide removal from natural gas in the oil and gas industry.

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APPENDICES

Table 15: Flux, Permeance and relative permeance at Difference Feed Pressure

Feed Pressure (Bar)	Flux ($cm^3_{STP}/cm^2.S$)		
	CO_2	CH_4	C_5H_{12}
10	4.95E-02	1.19E-02	1.02E-04
12	7.09E-02	1.47E-02	1.36E-04
14	9.67E-02	1.79E-02	1.77E-04
16	1.31E-01	2.13E-02	2.30E-04
18	1.79E-01	2.52E-02	3.00E-04

Feed Pressure (Bar)	Permeance (GPU)			CO_2 Relative Permeance	
	CO_2	CH_4	C_5H_{12}	CO_2/CH_4	CO_2/C_5H_{12}
10	65.36	15.69	0.13	4.17	487.14
12	77.98	16.17	0.15	4.82	523.18
14	91.09	16.87	0.17	5.40	546.02
16	108.25	17.58	0.19	6.16	570.73
18	131.35	18.42	0.22	7.13	597.27

Table 16: Flux, Permeance and relative permeance at Difference CO_2 Feed Composition

CO_2 Composition, Vol %	Flux ($cm^3_{STP}/cm^2.S$)		
	CO_2	CH_4	C_5H_{12}
9.60	1.03E-01	2.64E-02	2.13E-04
28.80	1.13E-01	2.36E-02	2.01E-04
48.00	1.31E-01	2.13E-02	2.30E-04
67.20	1.51E-01	1.82E-02	2.31E-04
86.40	1.60E-01	1.62E-02	2.04E-04

CO_2 Composition, Vol %	Permeance (GPU)			CO_2 Relative Permeance	
	CO_2	CH_4	C_5H_{12}	CO_2/CH_4	CO_2/C_5H_{12}
9.60	84.51	21.75	0.18	3.89	481.20
28.80	92.77	19.47	0.17	4.77	561.58
48.00	108.25	17.58	0.19	6.16	570.73
67.20	124.01	15.03	0.19	8.25	651.48
86.40	132.07	13.36	0.17	9.89	787.58