

Study of CO₂/CH₄ Solubility in Liquid Octane

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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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.

TUNKU OZAIR BIN TUNKU MAHMUD

ABSTRACT

Carbon dioxide (CO₂) separation from natural gas is a crucial process in purifying the gas stream to meet customer's requirement. With the present technology of physical solvents requires higher energy to be operated mostly at low temperature, the operation is quite costly and expensive. Development of solvent has been considered in improving gas absorption economically such that having a higher CO₂ loading at higher temperature decreasing the energy requirement for refrigeration purposes & reduces cost. As CO₂ content in natural gas is increasing nowadays, a hydrocarbon solvent which is liquid alkane specifically octane (C₈H₁₈) is used as an alternative in providing more capacity in absorption purposes. Hence, this research project will study more on the solubility of CO₂/CH₄ in octane in determining its feasibility in the industry, in terms of different pressure and temperature conditions. The scope of study of this work includes creating a simulation of the solubility test using Aspen HYSYS software to obtain theoretical results. Experiments of gas solubility test using equilibrium cell were also conducted within the time frame of this project. The solubility of CO₂/CH₄ was determined based on two main parameters which are pressure and temperature. HYSYS simulation has been done simulating the equilibrium cell with the results being obtained at a range of pressure from 30 up to 50 bar. Experiments were done at pressure 30 bar with different temperatures of 308.15K, 318.15K and 328.15K for both CO₂ and CH₄ gases respectively. In accordance with the principle theory of absorption of gases, it is found that the solubility of CO₂ and CH₄ components increases with the increasing in pressure with the decreasing in temperature for both experimentally and through simulation.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Background of study

Carbon dioxide (CO₂) is the largest contaminant found in natural gas and contributes mainly as one of the causes for the global greenhouse gas emissions. As one of the major contaminants in natural gas feeds, carbon dioxide must optimally be removed as it reduces the energy content of the gas and affect the selling price of the natural gas. Moreover, it is corrosive and can become acidic in the existence of water that has a potential to damage the pipeline and the equipment system. Therefore, to meet the pipeline quality standard specifications, the impurities must be removed, thus, enhancing the calorific value of the natural gas and avoid corrosion. [1]

The techniques applied in the gas treating or separating industry today are adsorption, gas permeation through membrane, absorption and cryogenics distillation. Within these methods, technology for improvement has been developed throughout the years for a more optimized and efficient process in purifying natural gas to meet customer's specification demand. Figure 1 below shows the type of CO₂ capture technologies applied today.

As for the case of today, natural gas is usually produced at high pressure (for example, around 10 MPa) and in extreme cases may have a CO₂ concentration of up to 70 mol%. This CO₂ reduces the calorific value of the natural gas, and the mole fraction of CO₂ must be reduced to below 3%, the requirement of standard commercial gas grade, before the gas to be introduced into distribution pipelines. [2]

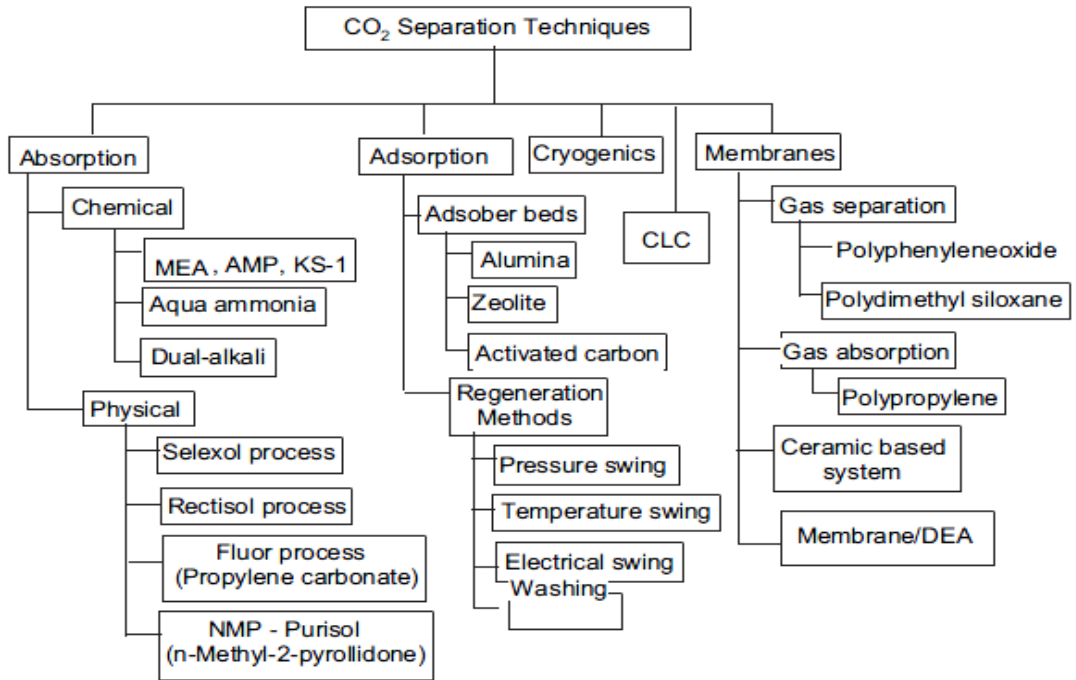


Figure 1.1: CO₂ capture technologies [3]

Among these separation techniques, adsorption is economical for comparatively small-scale purification, typically reducing the CO₂ content from 3% down to 0.5%. Chemical absorption method has been successfully used for low pressure gas streams containing from 3% to 25% of CO₂ but with a downside of larger solvent regeneration cost. The use of gas membranes involve compact and flexible unit that could easily adapt to the changes in CO₂ content but natural gas contaminants could lead to the deterioration to the membranes. [4]

As the implementation of the Kyoto protocol requires the capture of large quantities of CO₂, the injection of CO₂ into depleted, or near-depleted, reservoirs for enhanced oil/gas recovery operations will become increasingly frequent [3]. This will results in even richer CO₂ in natural gas streams. Hence, with this value of CO₂ concentration in the natural gas, it will be one of the challenging gas separation problems in process engineering for CO₂/CH₄ systems. Thus, the removal of CO₂ from the natural gas is vital for an improvement in terms of the quality of the product as well as economic viability. [1]

This favours for the physical absorption processes to be implemented where it is most efficient and economical when it is operated at higher pressure and lower temperature. [5] As according to Burr and Lyddon [6], in order to treat feed gas with very high CO₂ concentration, the leading physical absorption technologies include the Selexol and Rectisol processes, some of the common physical solvent that is being used today. With a higher demand for cost reduction benefits for the industry, newer technologies are being researched into and developed for future commercial usage.

In this project, liquid octane is used as the alternative physical solvent to test the solubility of CO₂/CH₄ system based on different pressures and temperatures as higher CO₂ partial pressure and lower temperature increases the solubility of CO₂ in the solvents.

1.2 Problem Statement

Large volume of CO₂, which is termed as ‘acid gas’, will forms carbonic acid when react with water. This component is corrosive and could damage the downstream equipment that could cause an increase in maintenance cost. Steps to remove these major contaminants are crucial to sustain good asset integrity of the plant.

The use of physical solvent today is applied to separate CO₂ from natural gas at high pressure. The usage of this may have been proven to be successful but only that it brings a few drawbacks. Most of the physical solvents are operated at a very low temperature which required higher energy resulting in an increase in operating cost. The absorption capacity is also less effective due to having high affinity to heavy hydrocarbon. These solvents used will also create waste products that have high environmental effect. Considering this, the need for an alternative solvent could provide higher performance in terms of absorption capacity with low cost technologies and low energy requirements.

Therefore, liquid octane is chosen as the solvent for CO₂ removal from natural gas. Octane shall be tested with CO₂/CH₄ solubility to assess the effectiveness of the solvent which could be beneficial in minimizing these problems or even eliminating them. Hence, this research project should be carry out as it reflects the real life composition of the natural gas with octane might be a possible solvent for CO₂ removal for future term benefits.

1.3 Objectives

To evaluate the equilibrium performance of CO₂/CH₄ solubility in liquid octane acting as a physical solvent for absorption based on two parameters; differences in pressure and temperature.

1.4 Scope of Study

This project will utilize the basic and fundamental knowledge of solubility and thermodynamics with subject to absorption of gas to liquid phase. The scope of study includes:

- Create a simulation using ASPEN Hysys software to obtain the results of the project theoretically
- Conduct an experiment of gas solubility test using equilibrium cell
- Perform calculations to achieve the CO₂/CH₄ solubility in liquid octane
- Investigate the CO₂/CH₄ solubility in liquid octane (C₈H₁₈) in terms of two parameters; pressure and temperature
- Study the effect of pressure and temperature on the solubility of CO₂/CH₄

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Separation Techniques

CO₂ removal process has been widely implemented in the oil and gas industry over the years as an early precaution to avoid any damages to the plant equipment. With carbon dioxide also known as ‘acid gas’, CO₂ is separated in several ways to maintain the asset integrity such as through adsorption, membrane separation, cryogenic distillation and absorption. The differences between these methods are basically suitability of operating parameters, separation effectiveness and operational cost of the process. These methods are discussed further as below:

2.1.1 Adsorption

Adsorption is described as the adhesion or retention of selective components of feed gas stream as in this case, carbon dioxide, brought into contact to the surface of certain solid adsorbent. [1] This method is divided into two which are temperature swing adsorption (TSA) and pressure swing adsorption (PSA). With desorption in TSA is accomplished by raising the temperature & desorption in PSA is accomplished by lowering the partial pressure, both processes possess same feature which is efficient in purification purposes of the feed gas. Adsorption is not yet being considered for large scale of CO₂ removal due to the low capacity of the sorbents. Therefore, it is not suitable for high pressure gas condition.

2.1.2 Membrane Separation

The transport phenomenon through permeation also promotes CO₂ capture in the industry. The permeability of gases in a membrane is related as a function of membrane properties (physical and chemical structure), the nature of permeant species and the interaction between membrane and permeant species. [1] Mostly today, depending on the materials of the membrane, it may lead to very low permeability of gases in a large scale because of the thickness of membrane. A thin membrane will affect its strength to withstand the CO₂ separation process resulting in deterioration of the membrane. Thus, both strength and membrane permeability should be balanced out in the development of a new membrane for the application towards CO₂ rich natural gas.

2.1.3 Cryogenic distillation

Cryogenic separation is a process of removing CO₂ at a very low temperature down to -75°C. It uses this technique where gases will be cooled and condense below its boiling point, separated and transformed into liquid state. Different gases have different boiling points and it uses this as a benchmark for gas removal with only facing a downside of high energy demand for cooling purposes. [1] Although this method is also suitable for high pressure conditions, it requires higher energy demand and will have an increase in operating cost that might not be economically feasible.

2.1.4 Chemical Absorption

Absorption is the most common method used in gas separation processes where natural gas will interact and become soluble with the liquid solvent. It is mainly divided into two; chemical and physical absorption. For chemical solvents, it provides a high driving force necessary for selective capture from streams with low CO₂ partial pressure. [7] However, the absorption is limited by the stoichiometry of the chemical reaction so that the use of this process for CO₂-rich gas streams will lead to large amounts of solvents, high solvent circulation flow rates and high energy requirements which is not appropriate for large levels of CO₂. [4]

2.2 Physical Absorption Theory

The solubility of gases relies on two main parameters which are pressure and temperature. According to Henry's law, concentration of dissolved gas at a particular temperature is directly proportional to the partial pressure of the gas in equilibrium with the liquid. With a rise in temperature, molecules will gain kinetic energy and tend to escape liquid phase to enter vapour phase up to a point where rate of evaporation equals to the rate of condensation; saturated liquid. The saturated vapour pressure will becomes equal to the partial pressure leading to a decrease in solubility. [8]

Physical absorption has greater absorption limits of physical solvents with respect to CO₂. The loading that can be achieved depends thermodynamically upon the solvent being used, the partial pressure of CO₂ in the gas stream, and the temperature, with higher partial pressures and lower temperatures being more favourable [9]. At high CO₂ partial pressure, the CO₂ loading capacity of the solvent has the potential to be higher for a physical solvent than for a chemical solvent. Moreover, the interaction between CO₂ and the solvent is relatively weak; decreasing the energy requirement for regeneration process. With that, physical absorption processes are particularly appropriate for the treatment of CO₂-rich gas streams. [4]

It is confirmed by a recent study of various chemical and physical absorbents for acid gas removal in coal gasification plants that physical solvents tend to be favoured when treating gases with high partial pressures of acid gas. The results of the study are summarized in Figure 2.1. [10]

From the figure below, it is clearly shown that CO₂ in natural gas with a high partial pressure containing high CO₂ content will have the tendency to be absorbed frequently by physical solvent. Therefore, an alternative in separating CO₂ from natural gas stream is found to be suitable through physical absorption as it has larger absorption capacity and less energy intensive compared to chemical absorption which will need more energy for regeneration of its solvent.

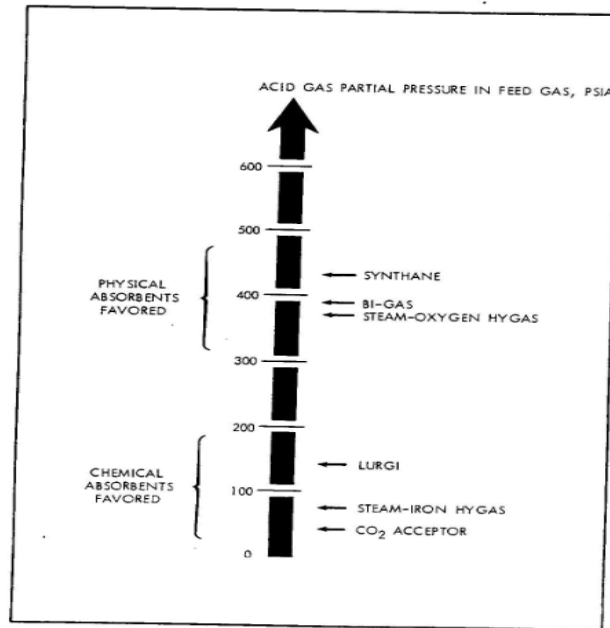


Figure 2.1: Level of chemical and physical absorbents in coal gasification plants according to differences in partial pressure. [10]

2.3 Conventional Physical Solvent

Physical solvents scrubbing of CO_2 are commercially available which are Selexol, Rectisol, and Fluor. Selexol process uses dimethylether polyethylene glycol as solvent taking place at low temperature around $0 - 5^\circ\text{C}$. It is able to remove CO_2 simultaneously with H_2S and water. The process is economical when high acid gas partial pressures exist and having an absence of heavy ends in the gas. Some of the drawbacks are having high affinity to heavy hydrocarbon which will be coabsorbed in the solvent resulting in hydrocarbon losses [3]. The process as well can be expensive where the chilling option could increase the process cost.[11]

According to Rufford et al., to produce a sweet gas containing less than 50 ppmv CO_2 for feed to a LNG plant, the Rectisol process using a chilled methanol solvent operating at temperatures as low as -35 to -75°C has been applied successfully [12]. The solvent will have no degradation problems and is non-corrosive which leads to the usage of carbon steel for the equipment material. This reduces the material cost but the need to refrigerate the solvent result in high capital and operating cost of the plant.[3]

Fluor solvent process is based on the physical solvent propylene carbonate which is a polar solvent with high affinity of CO₂. It is mainly used for gas treating when the feed gas CO₂ partial pressure is high up to more than 60 psig, when the sour feed gas is primarily CO₂. Only that the solvent is expensive and requires high solvent circulation rate. [3]

Physical solvent processes use organic solvents to physically absorb acid gas components rather than reacting chemically. Higher CO₂ partial pressure and lower temperature will favour the solubility of CO₂ in the solvent. With these solvents have been used for decades in the physical absorption process of separating CO₂, research and development (R&D) pathways are explored for more improvements include modifying regeneration conditions to recover CO₂ at higher pressure, improving selectivity to reduce H₂ losses and developing a solvent that has a high CO₂ loading at a higher temperature [9]. An alternative solvent that could provide higher performance in terms of absorption capacity with less costly technologies and energy requirements should be looked into for a future term benefits.

2.4 Octane Solvent

There are a range of physical solvents that has been used today in the physical absorption method of CO₂ separation purposes. A choice of solvent is certainly a factor in getting the best performance of this process depending on the condition as in this case; treating a CO₂-rich gas streams.

Modern technological physical solvents are characterized with a relatively high ability to dissolve acid gases and low ability in dissolving other gaseous components. [13] Formulations of tributyl phosphate, polycarbonate, methylcyanoacetate, and n-formyl morpholine have been used for the absorption processes today. Unfortunately, the major drawbacks with such solvents for practical operations; the solvents are not easily disposable and may be involved in side reactions with other natural gas constituents. A hydrocarbon solvent is more suitable, which is relatively inert and can easily be handled in an oil and gas environment; n-butane that has been used in the Ryan-Holmes process. [4]

Ryan-Holmes process is a cryogenic separation process to natural gas treatment through cooling and condensation of gas. It is commercially applied to the streams that have high CO₂ content but having a disadvantage of high energy requirement for refrigeration purposes. [14]

Based on the success of n-butane as a solvent in the Ryan-Holmes process, longer n-alkanes with correspondingly high boiling points are investigated in order to develop a non-cryogenic process. Considering the range of solvents which possess suitable volatility and viscosity, n-alkanes between n-heptane (C₇) and n-tetradecane (C₁₄) is selected; as octane is used in this work. Longer n-alkanes are likely to be viscous while shorter n-alkanes are likely to be too volatile for temperature range of interest [4]. As expected by Wang et al., octane has a lower that could offer smaller diffusion resistance as compared with tetradecane. [15]

With octane being in the range of C₇ to C₁₄, it is a suitable selection among other hydrocarbon to be tested with CO₂ solubility in the search of an alternative solvent. Octane as well has a higher boiling point which is 126°C and will certainly help in developing a non-cryogenic process eliminating the uses high energy requirements.

The solubility of hydrocarbons in organic solvents increases with the molecular weight of the hydrocarbon. Although special designs for the recovery of these compounds have been proposed, physical solvent processes are generally not economical for the treatment of hydrocarbon streams that contain a substantial amount of pentane-plus hydrocarbon. [5] Like n-butane, other alkanes such as n-decane, are known to absorb CO₂ preferentially to CH₄ [16]. The n-alkane solvent absorbs CO₂ preferentially to CH₄ so that the gaseous stream is consequently stripped of CO₂ as it makes way to the top of the absorber column. [4]

Commonly, physical solvent will have higher affinity in heavier hydrocarbon that may lead to hydrocarbon losses when applied to physical absorption of CO₂ capture. Comparing to the lighter hydrocarbon such as methane, CO₂ will be much more soluble in octane making it suitable for lighter gas streams. [5] Therefore, octane will be used in this project to further observe the performance and efficiency of CO₂ to dissolves in the solvent from methane stream at a lesser energy demand; energy required for operating temperature eliminating the need to refrigerate.

2.5 Previous Solubility Study

Research study of CO₂ solubility in various types of solvent particularly in alkane has been explored to determine its performance and capability of CO₂ absorption. The solubility measurement or prediction of the binary mixtures of both CO₂ and octane has also been done by several researchers throughout the years. Commonly, similar type of equipment of equilibrium cell was used to run the solubility test. The differences are only the range of pressure and temperature performed at with different way of exhibiting the final data and results. In this work, the solubility of CO₂/CH₄ system with different composition will be tested using the same apparatus.

According to Wang et al [15], experiments have been done in studying the transport process of CO₂ in n-octane at 290K and 311K with pressure up to 3.67MPa. The solubility of CO₂ in liquid octane was measured, collected and proceed with evaluating the Fick's diffusion coefficient of the system. From this study, the diffusion coefficient of carbon dioxide in liquid octane depends on temperature and pressure.

Yu et al [17] have made a research work of experimental determination of CO₂ + octane to high temperature and high pressure ranging from 313.15K – 393.15K and pressure from 1 – 14MPa. It is found that the solubility increment under high pressure is less than that under low pressure indicates that the effect of pressure on solubility is more obvious under low pressure.

Another experiment made by Tochigi et al [18] predict and measured high pressure vapour – liquid equilibria for binary mixture of CO₂ + n-octane at 313.14K from 0.52 – 3.52MPa. Apart from other researches, the measured data have been correlated using modified Soave-Redlich-Kwong (MSRK) equation and the SAFT-VR equation despite having some deviation in predicting its phase behaviour.

Gallegos et al [19] also run a similar experiment of vapour – liquid equilibria (VLE) for the CO₂ + octane system with a different range of temperature from 322 – 372K. The measured data was correlated using Peng – Robinson equation of state to represent the best VLE with an average deviation less than 1.8%.

The solubility measurement study of tertiary mixture system are relatively scarce and very limited to be found with most researchers still focused on binary mixture system for CO₂ solubility. They were only a few that made the study on liquid octane solvent as mentioned as others did experiments on various type of solvent. The equilibrium cell are often used for gas solubility test purposes not only in physical solvent but for chemical solvents as well such as Sako et al [20] and Tourneux et al [21]. Table 2.1 shows the summary of previous solubility study on octane solvent.

Table 2.1: Previous solubility study experimental details

References	Gas component	Solvent	Temperature (K)	Pressure (MPa)
Wang et al [15]	Carbon dioxide	Octane	290 & 311	0.9 – 4
Yu et al [17]	Carbon dioxide	Octane	313.15 – 393.15	1 – 14
Tochigi et al [18]	Carbon dioxide	Octane	313.14	0.52 – 3.52
Gallegos et al [19]	Carbon dioxide	Octane	322 – 372	2 - 16
Wilcock et al [22]	Carbon dioxide	Octane	293 -313	0.1

Based on Table 2.1 above, 5 research papers have been referred to for this particular project. All of the studies were made on the solubility of carbon dioxide in liquid octane at a various range of pressure and temperature. The equipment used to run the experiment which is the solubility cell was similar that is also being proceeded in this project. As Wang et al [15], compares their results with previous studies for validation purposes, HYSYS simulation is used in this project with the same intention.

CHAPTER 3

METHODOLOGY

3. METHODOLOGY

3.1 Research Methodology & Project Activities

The methodology for conducting this research project can be achieved through laboratory experiments approach aided with the application of simulation. The area and scope of this research is narrowed down to the solubility test of CO₂/CH₄ gases in liquid octane solvent for a development of a new solvent for CO₂ separation so that it is feasible and could be completed within the allocated time frame. After a critical literature review has been done on the issue of concern and physical absorption process using physical solvents, the laboratory experiments can be conducted to achieve the objective of this research which is to test the solubility of CO₂/CH₄ system in liquid octane solvent.

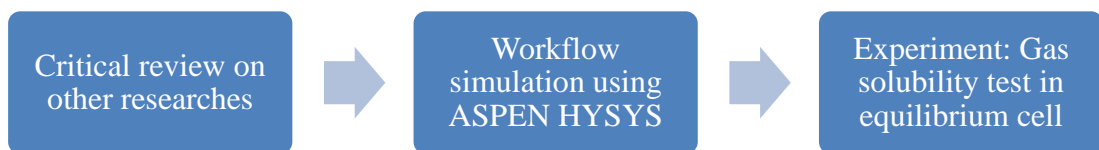


Figure 3.1: Research methodology for final year project

1. **Critical literature review:** Review on physical absorption concept which is highly manipulated by two parameters; pressure and temperature. Analyse on physical solvents, gap in the existing technology, improvement of technology and experiments conducted by other researches.
2. **HYSYS Simulation:** A simulation of the solubility cell experiment where the theoretical results will be compared with the expected experimental data to check on the accuracy and precision of the equipment.

- Solubility Test Experiment:** An experiment using solubility test will be conducted based on different pressure and temperature. The pressure and temperature to be tested are of 30 bar and of 308.15, 318.15, & 328.15K respectively.

3.2 Experimental Work

3.2.1 Setup of experiment

CO₂ with purity of 99.8% and CH₄ with purity of 99.95% obtained from MOX – Linde Gases were used in this test. The experiment was conducted using SOLTEQ BP22 High Pressure Gas Solubility Cell located in Unit Operation Laboratory of Chemical Engineering Department at Block 03-00-06 as per figure 3.2 below.

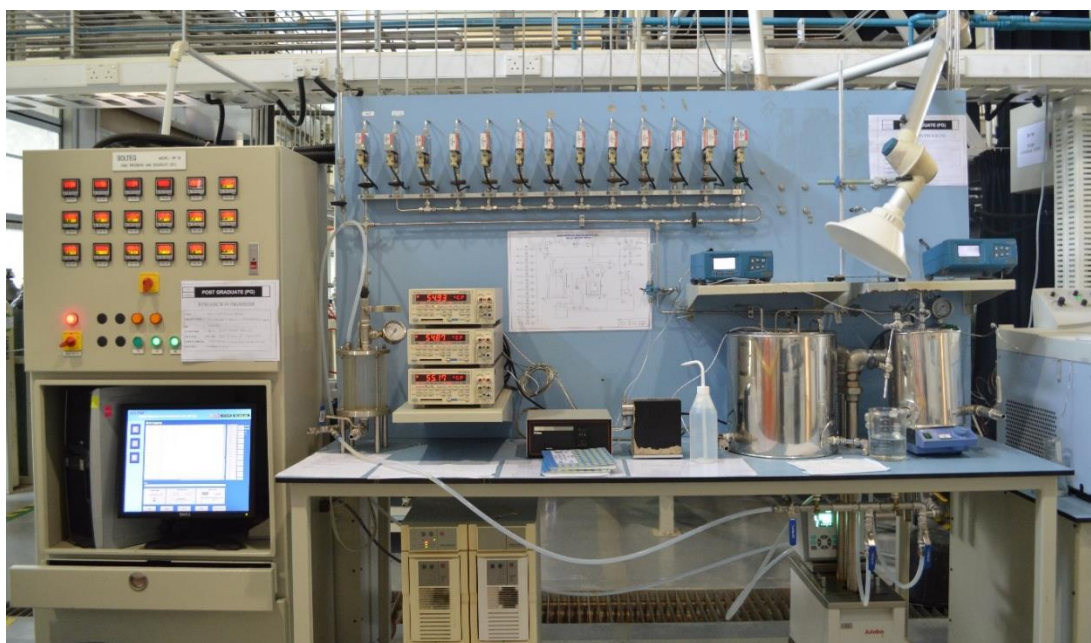


Figure 3.2: High Pressure Gas Solubility Cell equipment

Two pressure vessels are mainly used in this experiment which are the mixing vessel (MV); where the CO₂/CH₄ gas pressure was raised, and the equilibrium cell (EC) where the mixing of the gas and the solvent takes place. The temperatures of both vessels are maintained with a circulating water bath set at desired value. For the elevation of the pressure, a gas booster pump is used. A metering pump is used to introduce the octane solvent inside the equilibrium cell.

3.2.2 Experimental Procedure

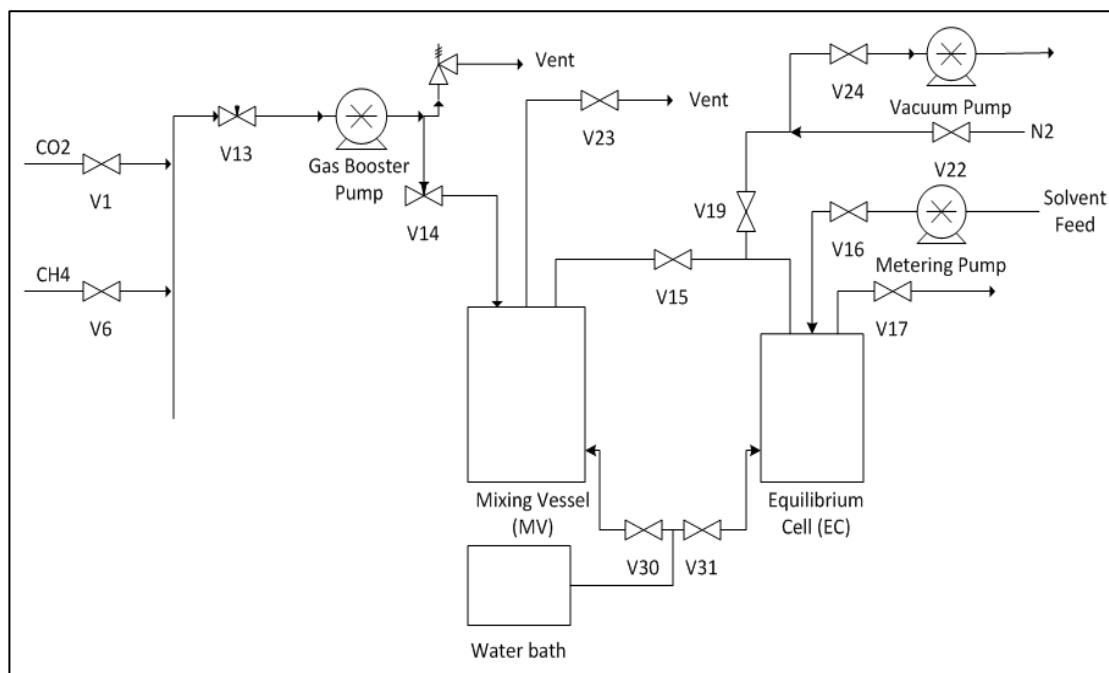


Figure 3.3: Schematic diagram of the equipment

Where, MV : Mixing Vessel (3L)

EC : Equilibrium Cell (50mL)

V1 : CO₂ inlet

V6 : CH₄ inlet

V22 : N₂ inlet

V30 : Water inlet to MV

V31 : Water inlet to EC

V19 : Gas inlet to EC

V17 : Sample outlet valve

V24 : Gas outlet to vacuum

V13 : Gas inlet to gas booster pump

V14 : From gas booster pump to mixing vessel

V15 : MV to EC valve

V16 : Solvent inlet to EC

V23 : Vent valve

Figure 3.3 above shows a schematic diagram of the equipment involved. The following are the step-by-step procedure to conduct the experiment using the solubility cell.

A. Start up

- I. The main power sources of the computer, magnetic stirrer, temperature and pressure indicator are switched on.
- II. The gas cylinders of N₂ and CO₂ (or CH₄) are fully opened.

B. Temperature Setting

- I. V30 and V31 are opened to let water flows into both mixing vessel and equilibrium cell.
- II. The desired temperature for equilibrium cell is set.

C. Purging of Equilibrium Cell (EC)

- I. V22 and V19 are opened to let N₂ flows into equilibrium cell.
- II. V17 is opened to let the gas flows out.
- III. The purging process takes around 45 seconds.
- IV. V22, V17 and V19 are closed.

D. Vacuum of Equilibrium Cell (EC)

- I. V19 and V24 are opened.
- II. Vacuum pump is switched on to make a vacuum state condition inside the equilibrium cell.
- III. When the pressure inside equilibrium cell is around 0.6 bar, vacuum pump is switched off.
- IV. V19 and V24 are closed.

E. Gas Pressurizing

- I. V1 is opened to let CO₂ gas flow into the mixing vessel. (V6 for CH₄ inlet)
- II. V13 and V14 is opened for the gas to flow through the gas booster pump.
- III. Gas booster pump is switched on. Pressure increase is observed through the pressure indicator.

- IV. When the desired pressure is achieved, gas booster pump is switched off.
- V. V1, V13 and V14 are closed.

F. Solvent Transfer

- I. 5ml of octane solvent is put in the solvent inlet.
- II. V16 is opened. Make sure all other valves are closed.
- III. Metering pump is switched on to pump the solvent into the equilibrium cell.
- IV. When all of the solvent is transferred, metering pump is switched off and V16 is closed.
- V. When the pressure stabilizes, pressure reading of mixing vessel is taken as initial pressure, P1.

G. Gas Transfer from MV to EC

- I. At the computer, go to 'Data Logging' and log is started.
- II. V15 is opened to transfer the gas from mixing vessel to equilibrium cell.
- III. When the pressure of both mixing vessel and equilibrium cell are approximately similar to each other, the reading of the stabilized pressure of mixing vessel and equilibrium cell is taken and denoted as P2.
- IV. V15 is closed to let the solubility process takes place.
- V. When there is no or very little change of pressure in equilibrium cell, the equilibrium is achieved. The equilibrium pressure, P_{eqm} is taken.

H. Shut down

- I. Equilibrium cell is washed with distilled water. Instruction in part F is followed.
- II. The software is exit and the computer is shut off.
- III. The power sources on the computer, magnetic stirrer, temperature and pressure indicator are switched off. V30 and V31 are closed.

3.3 Simulation procedure

Simulation work is done using Aspen HYSYS software. The arrangement of the equipment and units simulated in HYSYS will be similar to that of the equilibrium cell as per figure 3.4 below.

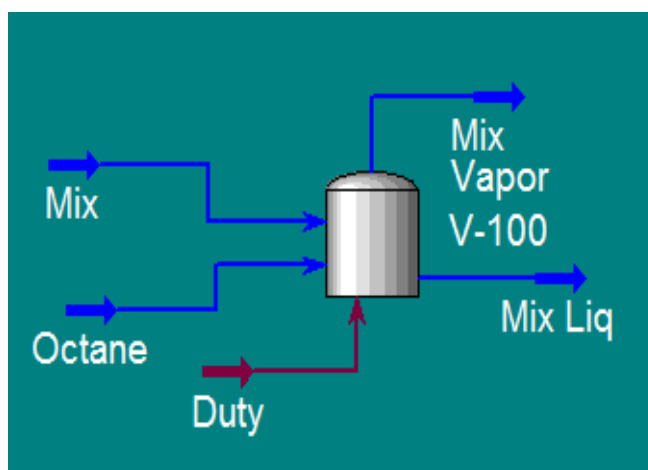


Figure 3.4: The arrangement of units simulated for solubility test

For this work, 30, 35, 40, 45 and 50 bar pressure are simulated by having an inlet stream of CO₂ and CH₄ respectively set at the desired pressure. Another inlet stream to it is the liquid octane solvent coming into the tank which acts as the equilibrium cell where the gas and the solvent interacts with each other. The desired temperature is set at 308K, 318K and 328K. The mole fraction of CO₂ and CH₄ being absorbed by the solvent is observed in the 'Mix Liq' stream whereas the mole fraction of CO₂ and CH₄ that is still in gas phase is observed in the 'Mix Vapor'. Peng Robinson was selected as the fluid package used in the simulation as it is generally the recommended property package for oil, gas and petrochemical applications.

3.4 Key Milestones

Several key milestones for this research project must be achieved in order to meet the objective of this project:

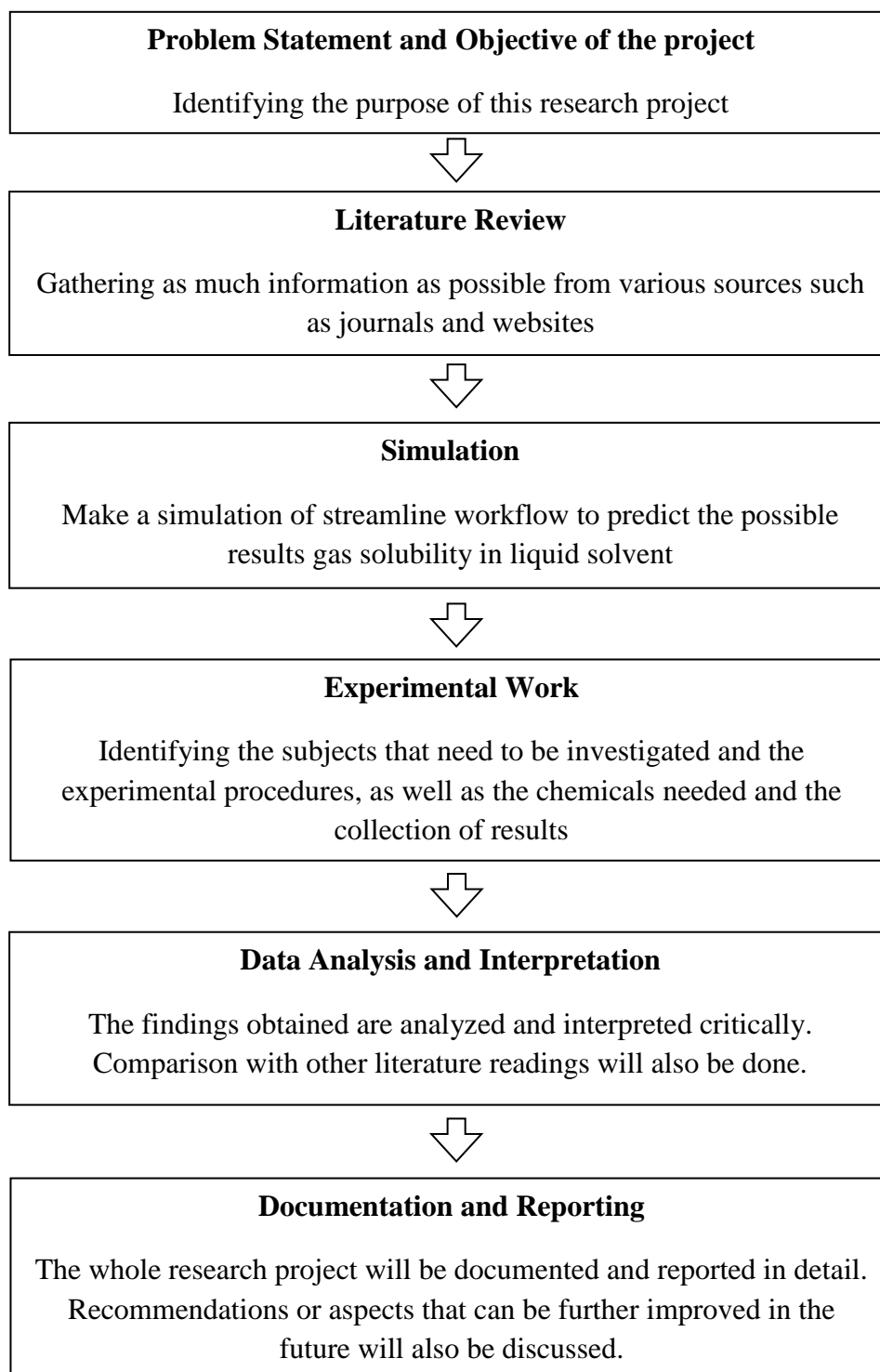


Figure 3.5: Key milestones flow throughout FYP

3.5 Gantt Chart

Table 3.1: Gantt chart for FYP1

No	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Title														
2	Accept Project Title														
3	Preliminary Research Work & Literature Review on														
	• CO ₂ separation issue														
	• Physical absorption principle and concept														
	• Physical solvents and gap in technology														
	• Solubility measurement														
4	Submission of Extended Proposal														
5	Proposal Defence preparation														
6	Proposal Defence Presentation														
7	HYSYS Simulation work (at 10, 20, 30, 40 & 50 bar)														
	• For (0.7 CO ₂ , 0.3 CH ₄) composition (at 298, 308, 318K)														
	• For (0.5 CO ₂ , 0.5 CH ₄) composition (at 298, 308, 318K)														
	• For (0.3 CO ₂ , 0.7 CH ₄) composition (at 298, 308, 318K)														
8	Trending graph of the acquired simulation data														
9	Understand solubility calculation before experiment														
10	Submission of Draft Interim Report														
11	Submission of Interim Report														


 In Progress

Table 3.2: Gantt Chart for FYPII

No	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Gather all apparatus needed	■													
2	Familiarize with the equipment and learn how to operate it	■													
3	Conduct experimental work		■	■	■	■	■	■							
	• Constant temperature at different pressure		■	■	■										
	• Constant pressure at different temperature					■	■	■							
4	Submission of progress report							■							
5	Data analysis and discussion								■	■	■				
	• Behaviour and results of the experiment								■	■					
	• Solubility calculation								■	■					
	• Trending between experimental and theoretical data									■	■				
6	Pre-Sedex										■				
7	Submission of draft report											■			
8	Submission of dissertation (Soft Bound)												■		
9	Submission of technical paper													■	
10	Oral Presentation														■
11	Submission of Project Dissertation (Hard Bound)														■

■ In Progress

CHAPTER 4

RESULTS & DISCUSSION

4. RESULTS & DISCUSSION

4.1 Results

This section will give a clear analysis about the result and calculation based on the solubility experiment. The results were obtained from the CO₂ and CH₄ solubility test using the equipment as discussed earlier. From the equipment, CO₂ and CH₄ loading in octane can be calculated based on the data provided.

4.1.1 Experimental data

Figure 4.1 below shows the CO₂ solubility experiment data over time using the High Pressure Gas Solubility Cell at 30 bar with temperatures of 318.15 and 328.15K as there were technical problems with the data logging of the computer at 308.15K.

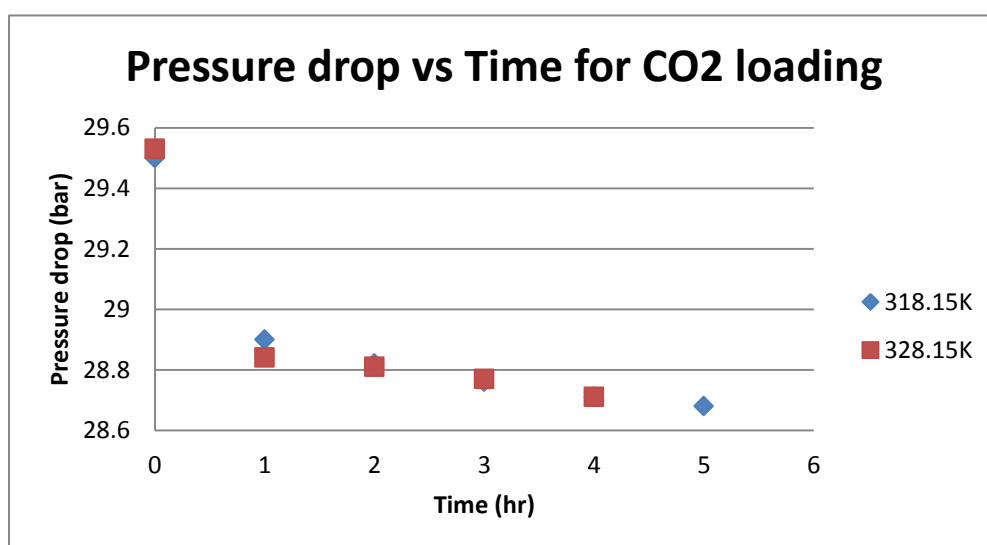


Figure 4.1: Trending of pressure drop over time for CO₂ loading

Figure below shows the CH₄ solubility experiment data over time using the High Pressure Gas Solubility Cell at 30 bar with temperatures of 318.15 and 328.15K as there were technical problems with the data logging of the computer at 308.15K.

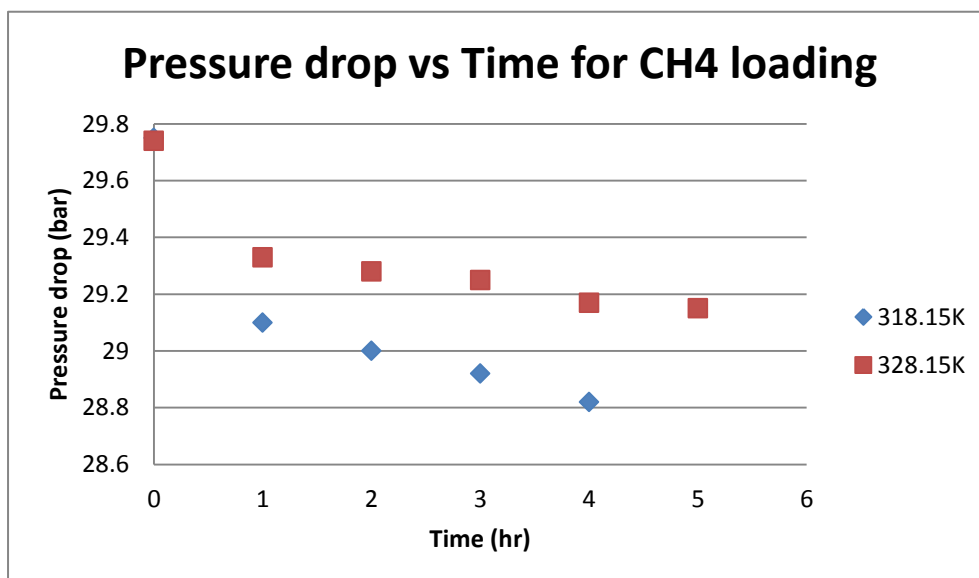


Figure 4.2: Trending of pressure drop over time for CH₄ loading

Table 4.1 below shows the initial data of the CO₂ and CH₄ solubility experiment obtained from the High Pressure Gas Solubility Cell at 30 bar which will be used to calculate the CO₂ and CH₄ loading in octane.

Table 4.1: Data from experimental work

Experiment	Temperature (K)	P1 (bar)	P2 (bar)	P _{eqm} (bar)
CO ₂	308.15	29.88	29.07	27.54
	318.15	30.01	29.20	28.41
	328.15	30.02	29.26	28.44
CH ₄	308.15	30.13	29.35	28.46
	318.15	30.15	29.43	28.51
	328.15	30.13	29.44	28.88

4.1.2 CO₂ and CH₄ Loading Calculation

Data from CO₂ experiment at 308.15K was taken for this calculation. The following must be acknowledged.

$$T = 308.15 \quad R = 0.08314 \text{ L bar/ K mol}$$

$$Z_1 = 0.856 \quad Z_2 = 0.848$$

$$V_t = 3\text{L}$$

Z values above were referred to the compressibility chart as in appendix. The initial number of moles of CO₂ was calculated first based on the information given as below.

$$N_{\text{co2}} = \frac{3\text{L}}{(0.08314)(308.15\text{K})} \left(\frac{29.88 \text{ bar}}{0.856} - \frac{29.07 \text{ bar}}{0.848} \right)$$

Based on the calculation, the initial moles of CO₂, N_{co2} is 0.0733. The number of moles of CO₂ remaining in gas phase is calculated next.

$$T = 308.15 \quad R = 0.08314 \text{ L bar/ K mol}$$

$$Z_{\text{co2}} = 0.863 \quad V_t = 0.045\text{L}$$

$$N_{\text{g}}(\text{co2}) = \frac{(0.045\text{L})(27.43 \text{ bar})}{(0.08314)(308.15\text{K})(0.863)}$$

Based on the calculation, the number of moles of CO₂ remaining in the gas phase is 0.0564. Therefore, number of moles of CO₂ left in octane is calculated as below.

$$N * (\text{co2}) = 0.0733 - 0.0564 = 0.0169$$

The number of moles of liquid octane has to be calculated first before proceeding with the CO₂ loading calculation. The equation is as below.

$$\text{Density} = 0.703 \text{ g/ml} \quad V = 5\text{ml}$$

$$\text{Molecular Weight} = 114.23 \text{ g/mol}$$

$$N(\text{solvent}) = \frac{(0.703 \text{ g/ml})(5 \text{ ml})}{114.23 \text{ g/mol}} = 0.0308$$

Now, the CO₂ loading in octane is calculated as below.

$$\alpha_{CO_2} = \frac{0.0169}{0.0308} = 0.5487$$

The CO₂ loading in octane at 30 bar and at 308.15K is 0.5487. The calculation for CO₂ loading at 318.15K and 328.15K with CH₄ loading at different temperatures is calculated using the same method as above with different data input. Table 4.2 shows the overall results after calculation of the solubility experiment.

Table 4.2: CO₂ and CH₄ loading in octane from experimental data

Experiment	Temperature (K)	CO₂/CH₄ loading
CO ₂	308.15	0.5487
	318.15	0.4870
	328.15	0.4123
CH ₄	308.15	0.1818
	318.15	0.1777
	328.15	0.1613

4.1.3 Simulation Results

Table 4.3, 4.4 and 4.5 shows the results of CO₂ loading in octane at 308.15K, 318.15K and 328.15K with pressure ranges from 30 bar to 50 bar.

Table 4.3: CO₂ loading in octane at 308.15K

Temperature: 308.15 K			
Pressure (bar)	nC₈	nCO₂	CO₂ loading
30	0.6609	0.3391	0.5130
35	0.6072	0.3928	0.6470
40	0.5535	0.4465	0.8067
45	0.4989	0.5011	1.0040
50	0.4426	0.5574	1.2594

Table 4.4: CO₂ loading in octane at 318.15K

Temperature: 318.15K			
Pressure (bar)	nC₈	nCO₂	CO₂ loading
30	0.6985	0.3015	0.4316
35	0.6516	0.3484	0.5347
40	0.6054	0.3946	0.6518
45	0.5594	0.4406	0.7876
50	0.5135	0.4865	0.9470

Table 4.5: CO₂ loading in octane at 328.15K

Temperature: 328.15K			
Pressure (bar)	nC₈	nCO₂	CO₂ loading
30	0.7280	0.2720	0.3736
35	0.6861	0.3139	0.4575
40	0.6449	0.3551	0.5506
45	0.6044	0.3956	0.6545
50	0.5643	0.4357	0.7721

Table 4.6, 4.7 and 4.8 shows the results of CH₄ loading in octane at 308.15K, 318.15K and 328.15K with pressure ranges from 30 bar to 50 bar.

Table 4.6: CH₄ loading in octane at 308.15K

Temperature: 308.15K			
Pressure (bar)	nC₈	nCH₄	CH₄ loading
30	0.8667	0.1333	0.1538
35	0.8465	0.1535	0.1813
40	0.8269	0.1731	0.2093
45	0.8078	0.1922	0.2379
50	0.7892	0.2108	0.2671

Table 4.7: CH₄ loading in octane at 318.15K

Temperature: 318.15K			
Pressure (bar)	nC₈	nCH₄	CH₄ loading
30	0.8721	0.1279	0.1467
35	0.8526	0.1474	0.1729
40	0.8336	0.1664	0.1996
45	0.8151	0.1849	0.2268
50	0.7970	0.2030	0.2547

Table 4.8: CH₄ loading in octane at 328.15K

Temperature: 328.15K			
Pressure (bar)	nC₈	nCH₄	CH₄ loading
30	0.8766	0.1234	0.1408
35	0.8577	0.1423	0.1659
40	0.8392	0.1608	0.1916
45	0.8212	0.1788	0.2177
50	0.8035	0.1965	0.2446

Table 4.9 shows the comparison between the results of CO₂ and CH₄ loading from the solubility experiment using the High Pressure Gas Solubility Cell with the simulation method using Aspen HYSYS software with the same temperature and pressure.

Table 4.9: Comparison between experimental results and simulation method

Experiment	Temperature (K)	CO ₂ / CH ₄ loading	
		Experimental results	Simulation method
CO ₂	308.15	0.5487	0.5130
	318.15	0.4870	0.4316
	328.15	0.4123	0.3736
CH ₄	308.15	0.1818	0.1538
	318.15	0.1777	0.1467
	328.15	0.1613	0.1408

4.1.4 Henry's Constant based on simulation results

Table 4.10, 4.11, 4.12, 4.13, 4.14 and 4.15 below shows the Henry's constant of CO₂ and CH₄ in octane based on the results of HYSYS simulation.

Table 4.10: Henry's Constant of CO₂ in Octane at 35°C

Pressure (bar)	Moles of CO₂ in Octane (kmole/hr)	Volume Octane (L/hr)	Concentration of CO₂ in Octane (mol/L)	Henry's Constant (bar.L/mol)
30	10.85	4000	2.712	11.06
35	13.14	4000	3.285	10.65
40	15.63	4000	3.908	10.24
45	18.37	4000	4.593	9.80
50	21.42	4000	5.355	9.34

Table 4.11: Henry's Constant of CO₂ in Octane at 45°C

Pressure (bar)	Moles of CO₂ in Octane (kmole/hr)	Volume Octane (L/hr)	Concentration of CO₂ in Octane (mol/L)	Henry's Constant (bar.L/mol)
30	9.54	4000	2.386	12.57
35	11.52	4000	2.879	12.16
40	13.64	4000	3.410	11.73
45	15.94	4000	3.985	11.29
50	18.45	4000	4.613	10.84

Table 4.12: Henry's Constant of CO₂ in Octane at 55°C

Pressure (bar)	Moles of CO₂ in Octane (kmole/hr)	Volume Octane (L/hr)	Concentration of CO₂ in Octane (mol/L)	Henry's Constant (bar.L/mol)
30	8.50	4000	2.125	14.12
35	10.23	4000	2.556	13.69
40	12.07	4000	3.017	13.26
45	14.05	4000	3.512	12.81
50	16.18	4000	4.045	12.36

Table 4.13: Henry's Constant of CH₄ in Octane at 35°C

Pressure (bar)	Moles of CH₄ in Octane (kmole/hr)	Volume Octane (L/hr)	Concentration of CH₄ in Octane (mol/L)	Henry's Constant (bar.L/mol)
30	3.74	4000	0.934	32.13
35	4.40	4000	1.101	31.80
40	5.08	4000	1.271	31.47
45	5.78	4000	1.444	31.16
50	6.48	4000	1.621	30.84

Table 4.14: Henry's Constant of CH₄ in Octane at 45°C

Pressure (bar)	Moles of CH₄ in Octane (kmole/hr)	Volume Octane (L/hr)	Concentration of CH₄ in Octane (mol/L)	Henry's Constant (bar.L/mol)
30	3.53	4000	0.883	33.98
35	4.16	4000	1.041	33.62
40	4.81	4000	1.202	33.27
45	5.47	4000	1.367	32.93
50	6.14	4000	1.534	32.60

Table 4.15: Henry's Constant of CH₄ in Octane at 55°C

Pressure (bar)	Moles of CH₄ in Octane (kmole/hr)	Volume Octane (L/hr)	Concentration of CH₄ in Octane (mol/L)	Henry's Constant (bar.L/mol)
30	3.35	4000	0.837	35.83
35	3.95	4000	0.988	35.43
40	4.57	4000	1.142	35.04
45	5.19	4000	1.298	34.67
50	5.83	4000	1.457	34.31

4.2 Discussion

Based on the results obtained from the experiments, there are several things that could be discussed to extend the understanding of this project. With the experiments could only be conducted once a week using High Pressure Gas Solubility Cell equipment, only three experiments could be done for both CO₂ and CH₄ solubility in octane respectively at pressure of 30 bar and at three different temperature. This time limitation is due to other users of this equipment, often postgraduate students occupying the whole week for their own research and studies.

The experiments need around 4 – 5 hours to reach equilibrium state. This has to be ensured by monitoring the data logging run on the computer, determining that no large change in pressure drop occurs at a certain time. It is also crucial to let the pressure and temperature of the gas to stabilize (not keep increasing or fluctuating) when transferring the gas from the mixing vessel to the equilibrium cell as smaller changes in the value could lead to a large significant effect to the calculation of CO₂ and CH₄ loading.

The additional method for this project is having simulation conducted using Aspen HYSYS software. The fluid package used for this is Peng Robinson equation of state where it is generally used in oil and gas application. The advantage of preparing simulation work is that it can be extend to a wide range of pressure, from 30 bar up to 50 bar, with different values of temperatures. Although simulation is capable in predicting the results, experimental work still need to be done for validation purposes as things might not happen the same way in reality. In essence, a best data representation is based on both experimental and simulation data.

4.2.1 Discussion based on difference of components, temperature and experimental/simulation results

The results for CO₂ and CH₄ loading in octane at 30 bar with temperature of 308.15K, 318.15K and 328.15K were presented in the figure 4.3 below comprising of both experimental and simulation data.

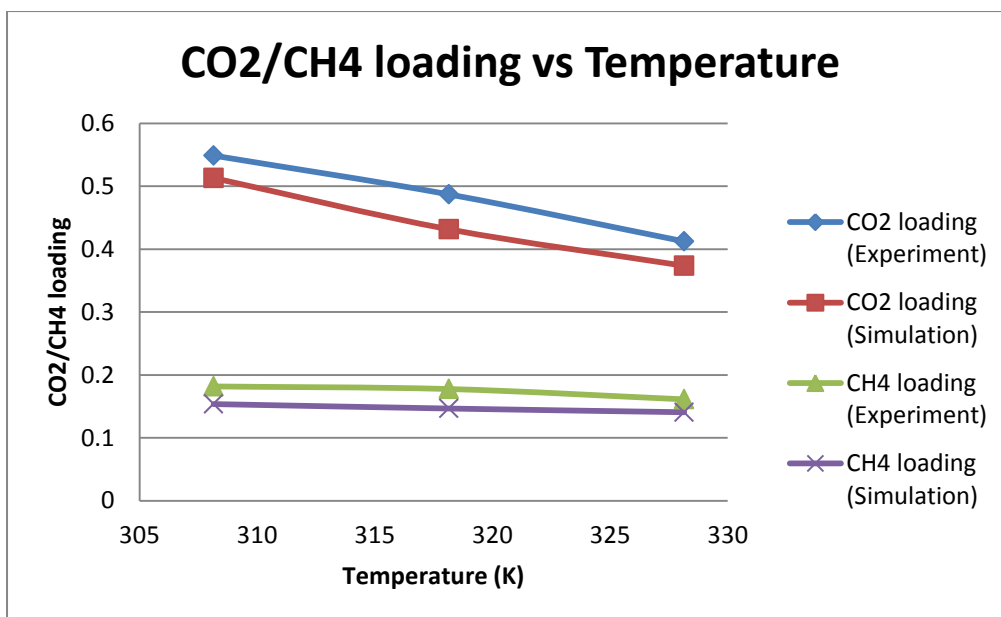


Figure 4.3: Graph of CO₂ and CH₄ loading against operating temperature of experiment and simulation at 30 bar

Based on the trending above, CO₂ and CH₄ loading values are included in the same graph to understand the solubility behaviour of these two different components and the absorption capacity of octane towards them. It is found that CO₂ have a higher loading in octane, meaning CO₂ is more soluble in octane compared to CH₄. Considering the molecular weight of CO₂ is much larger than CH₄, it has stronger intermolecular forces with the solvent that leads to CO₂ having higher solubility in octane compared to CH₄. Hypothetically, if CO₂ removal from a pure CH₄ gas stream is needed, octane could be an alternative solvent as it could absorb more CO₂ rather than CH₄. However, its efficiency still needs to be compared with other types of solvent to determine its best performance.

Referring to its solubility behaviour towards temperature, CO₂ and CH₄ loading is much higher at lower temperature compared to being operated at higher temperature. This is because at higher temperature, the molecules will gain more kinetic energy and tend to escape liquid phase entering gas phase. Other than that, it will be much more nearer to its saturation temperature as maintaining that way has been a practice in the industry to avoid acid gases to become soluble and contaminate solvent especially water. Therefore, CO₂ and CH₄ will be more soluble at low operating temperature.

As observed in the graph, the experimental data is not 100% accurate with the simulation value. There is a slight difference where both CO₂ and CH₄ loading of experimental work has a larger value compared to the simulation work. This could be justified through a few reasons. The fluid package set in Aspen HYSYS to run the simulation is Peng Robinson as there are other equations of state as well such as PRSV and SRK that is commonly used by various researchers towards their experiments. From this, it will give a different value that might be close in agreeing with the experimental data or even further differ from the actual value. Based on PRSV and SRK values, it will give a much lower value than the Peng Robinson which could result in bigger deviation between experimental and simulation. Furthermore, the experiment conducted using the High Pressure Gas Solubility Cell should be free from any leakage as it may affect the results. Time as well should be given freely for the operating pressure and temperature to stabilize as small change in the values affect the solubility calculation.

4.2.2 Discussion based on difference of pressure

Figure 4.4, 4.5 and 4.6 below shows the simulation data of CO₂ and CH₄ loading at 308.15K, 318.15K and 328.15K temperature respectively against a range of pressure from 30 bar to 50 bar.

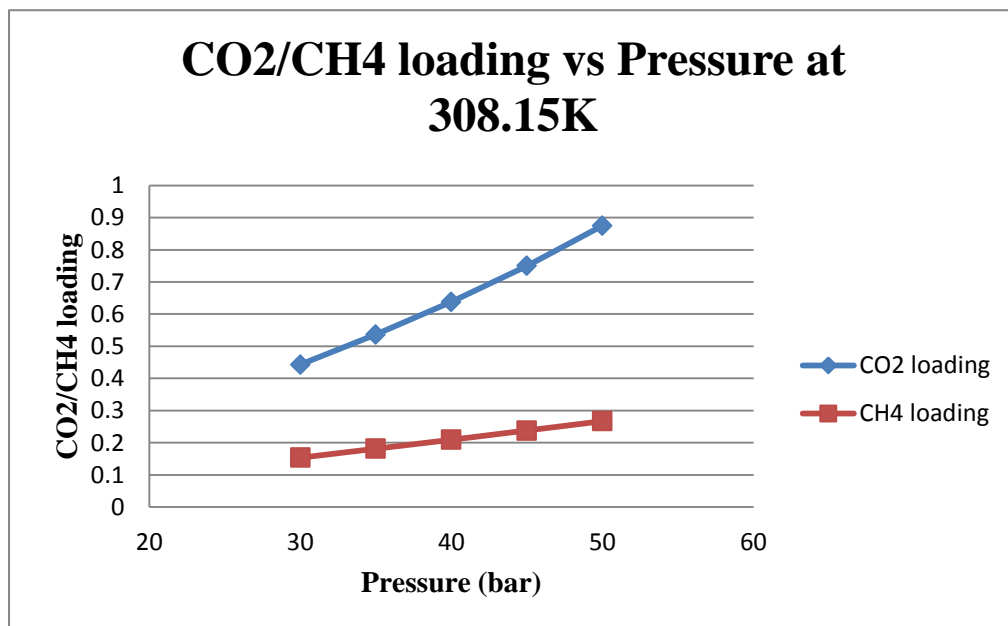


Figure 4.4: Graph of CO₂ and CH₄ loading against pressure at 308.15K

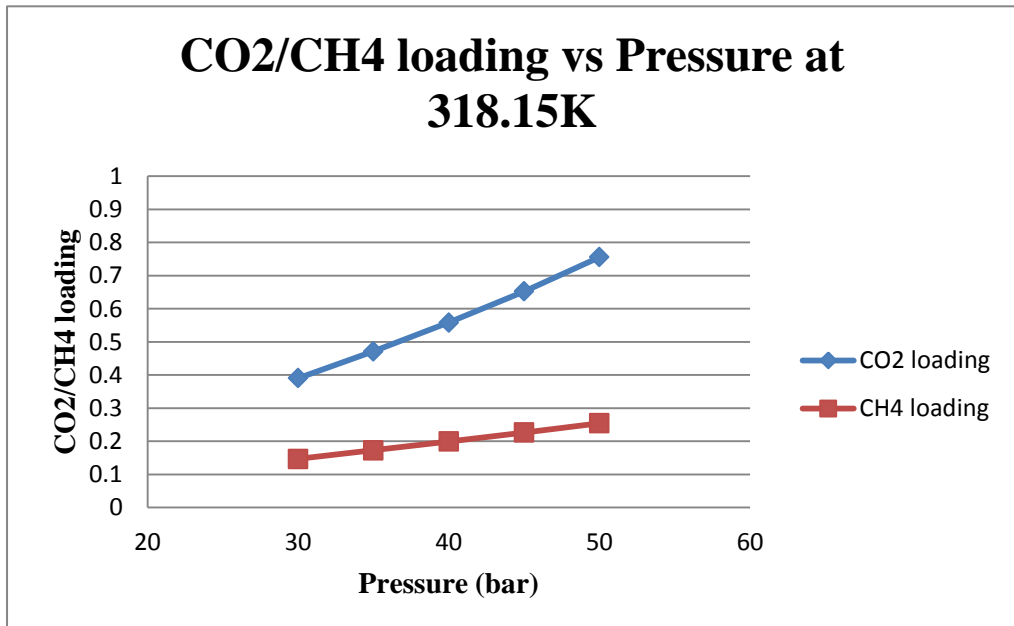


Figure 4.5: Graph of CO₂ and CH₄ loading against pressure at 318.15K

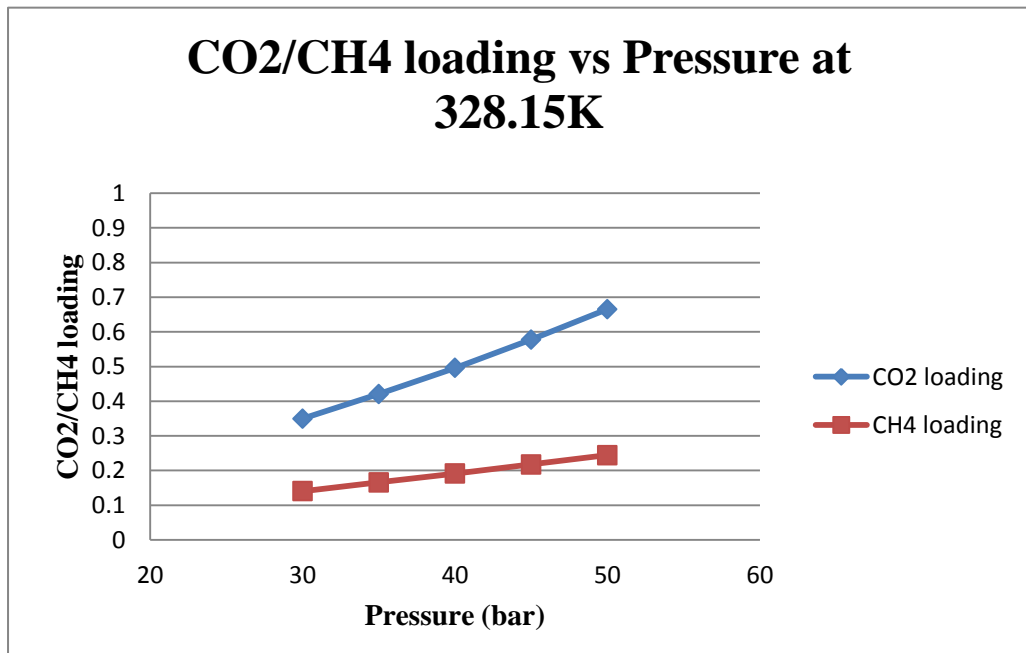


Figure 4.6: Graph of CO₂ and CH₄ loading against pressure at 328.15K

From the graphs above, it fulfils the theory that the CO₂ and CH₄ solubility in octane increases with an increase in pressure. Hence, it means that the absorption capacity of octane is more effective with increasing pressure. As observed from the three graphs, the trend for the CO₂ and CH₄ loading against pressure are similar; proportional towards each other. The difference is only the value of CO₂/CH₄ loading that is affected by the temperature as lower solubility and loading occurs at high temperature condition. Due to the gases compressed at a higher pressure, it forces the molecules to interact more with the solvent strengthening the intermolecular forces between each other, thus, becomes more soluble. With that, high pressure condition provides more absorption of gases as it is more soluble.

4.2.3 Discussion based on Henry's constant

Figure 4.7 and 4.8 below shows the trending of Henry's law constant calculated against CO₂ and CH₄ loading respectively at 308.15K, 318.15K and 328.15K.

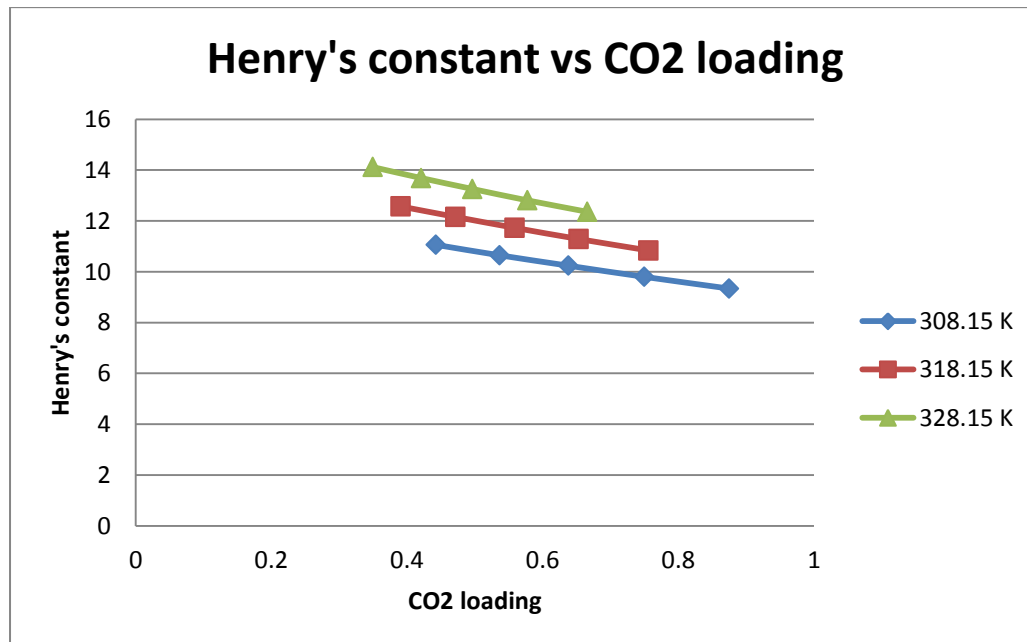


Figure 4.7: Graph of Henry's constant against CO₂ loading at 308.15K, 318.15K and 328.15K

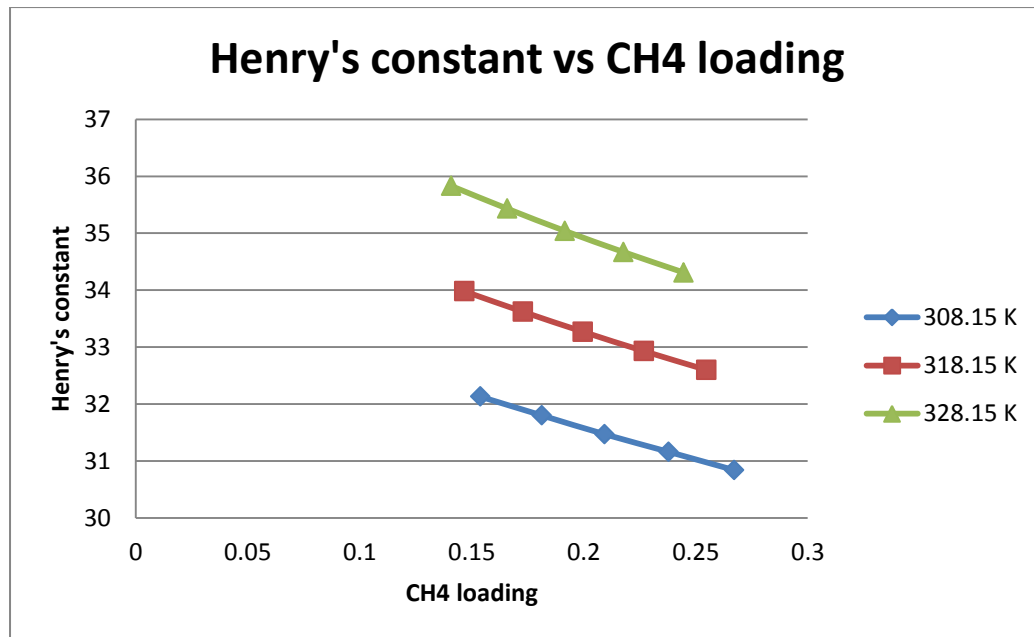


Figure 4.8: Graph of Henry's constant against CH₄ loading at 308.15K, 318.15K and 328.15K

Physical absorption should be represented in Henry's constant as well as it plays a role in stating that solubility of gas in a liquid is directly proportional to the partial pressure of gas above the liquid. In mathematical terms, Henry's constant can be calculated through the equation given.

$$P = K_h C$$

Based on the equation, P is the partial pressure of the solute in gas above the solution, C is the concentration of the solute and K_h is the Henry's constant.

A pressurized condition of the gas will lead to a more concentrated mixture of solution as molecules will be forced to interact with each other. Hypothetically, it results in a lower value of K_h with increasing pressure and concentration. After calculations were done and as discussed earlier that CO₂ and CH₄ loading increases with increasing pressure, it leads to a decreasing trending with the increasing of both of the loading.

K_h is also defined as the escaping tendency of a compound existing as a vapour as opposed to the fugacity of being dissolved in the solvent. As observed per figure 4.7 and 4.8 above, a low value of K_h gives a more soluble CO_2 and CH_4 in the solvent. This indicates that molecules will tend to remain dissolved in solvent having low value of Henry's constant that is commonly refer to molecules with low activity coefficient in solvents and high fugacity in air. High fugacity in air shows a tendency to condense from gas to liquid phase with low activity coefficient tends to stay soluble in solvents.

As per differences in temperature, it is justified earlier that lower temperature gives more solubility in the solvent. Thus, it is supported as per figures above by having low value of K_h that favours solubility. Between components of CO_2 and CH_4 , CO_2 is much more soluble in the solvent compared to CH_4 . Henry's law constant agrees with it by having a value of around 9 – 14 (bar.L/mol) for CO_2 solubility which is much lower than CH_4 solubility with K_h value of around 30 – 35 (bar.L/mol).

Therefore, from this representation of Henry's law constant against the solubility of both CO_2 & CH_4 , it can be concluded that low value of Henry's law constant provides more soluble product at a lower temperature and higher pressure.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

In overall, this project has managed to achieve its main objective of evaluating the equilibrium performance of CO₂/CH₄ solubility in liquid octane which acts as a physical solvent for absorption based on difference in pressure and temperature. The solubility of CO₂ and CH₄ is determined through CO₂/CH₄ loading per mole of octane used. Based on the results, the highest solubility achieved is at 308.15K and 50 bar for CO₂ which follows the principal theory of absorption where it is favourable at high pressure and low temperature; more soluble.

All in all, solubility is affected with operating temperature and pressure. It is proven that lowering the temperature and increasing the pressure will result in higher solubility for both of the gases. Apart from that, it can be concluded that CO₂ is more soluble than CH₄ in octane indicating that it could be applicable in the real situation as it absorb more CO₂ for the purpose of separation; an alternative solution. CH₄ solubility is relatively small, just below 0.3 making octane a potential solvent for CO₂ capture processes. In terms of Henry's law constant, it proves that lower value of the constant results in higher solubility with lower temperature and higher pressure.

In conclusion, implementation of octane as physical solvent is applicable and feasible for CO₂ separation from natural gas based on the findings and discussion above.

5.2 Recommendations

There are some recommendations that can be made for the project to enhance the quality performance of the solvent with the objective of capturing CO₂. Firstly, since the experiments were only done separately for both CO₂ and CH₄ component, it is really important to test the solubility of CO₂ and CH₄ in a composition mixture, resembling the realistic condition of natural gas stream before implemented in the industry. In this way, the results will be more accurate comparing between researches – wise based with practical – life situation where natural gas stream will exist in a composition of main components and side components or impurities.

Secondly, based on literature review that has been discussed earlier, higher chain alkanes will enhance CO₂ absorption while lower chain alkanes ensures the solvent remains in liquid form throughout the process. With this, it is a suggestion to commit to this theory by having a mixture of solvent for the same purpose of CO₂ capture. Octane (C₈) can be mixed with other range of alkanes such as (C₁₂ – C₁₄) that might produce better performance and a more effective and efficient process.

Thirdly, one of the wayforward for this project is having simulated the process flow diagram of the separation units before having implemented in the industry to evaluate the feasibility of the operations. This can be done through simulation software such as Aspen HYSYS or iCON simulation. Through this, several process flow could be developed and being compared with each other to get the best performance economically and operationally. This might include using different arrangement of equipment that will also affect the process efficiency in producing a more pure natural gas stream. The main units for this purpose are basically the use of absorber column or the addition of flash drum to actually improve the separation process. In essence, it is the matter of designing the equipment (size, operating conditions, solvents, number of units), putting it in a flow to visualize the process, and optimize the process in terms of cost estimation as well as product purity.

6. REFERENCES

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