Phase Behaviour Measurement for High CO_2 Content Natural Gas Hydrates

by

Hwang Huongket

Dissertation submitted to the Department of Petroleum Engineering in partial fulfilment of the requirements for the Bachelor of Engineering (Hons.) (Petroleum Engineering)

SEPTEMBER 2013

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh,

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Petroleum Engineering Program

Universiti Teknologi PETRONAS

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Approved by,

_____

Dr. Khalik M. Sabil

Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER 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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Hwang HuongKet

Abstract

In this work, the effects of highly concentrated carbon dioxide (CO_2) on methane hydrate formation are investigated through measurement of phase behaviour. The experimental apparatus, called Hydreval, includes a high temperature sapphire cell (20 MPa) with standard reservoir temperature operational range between -21.15 ^{o}C and 248.85 ^{o}C, a magnetic driven stirrer and 360° fully visual cell with attached camera for recording purposes. CO_2 is a non-organic compound found in abundance within most reservoirs in Malaysia. Due to the high concentration of CO_2 content, more accurate experimental data is needed. A generalized isochoric (constant volume) with step-heating process is used for obtaining reliable gas hydrate phase diagrams. The results show that the phase behaviour of high CO_2 content natural gas hydrates is alike that of pure CO_2 natural gas hydrate. At temperatures between 5-12 ^{o}C, the pressure required for hydrate dissociation points increase slowly. However, at high temperatures above 12 ^{o}C, the shift becomes more apparent with a significant amount of pressure being required for hydrate dissociation.

ACKNOWLEDGEMENT

Firstly, the author would like to express utmost gratitude to Dr. Khalik M. Sabil, the university final year project supervisor for his patience and supervision. He has given many constructive criticisms to ensure the quality of this dissertation. Under the constant guidance of Dr. Khalik, this project was ensured to be on the right track as planned.

The author would also like to extend his gratitude to Mr. Qazi Nasir, graduate assistant for all the day-to-day guidance and support given without which this project would definitely not able to be completed in time.

Lastly, the author would like to give thanks to Universiti Teknologi PETRONAS for providing many clear key milestones which has served as useful guidelines for ensuring the project is done on time. The University is also thanked for providing access to the data collected from the instrument used in this project which is the Hydreval situated in Block 16.

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Chapter 1

Introduction

Gas hydrates are crystalline solid compounds, comprised of water molecules, which forms a rigid lattice of cages, mostly containing a molecule of natural gas, mainly methane. When the proper temperature and pressure conditions are met, water and gas with low molecular weight forms gas clathrate hydrates. In general, the formation of hydrates is occurs with high pressure and low temperatures. There are three main structures of hydrates, namely: Structure I (sI), Structure II (sII) and Structure H (sH).[1]
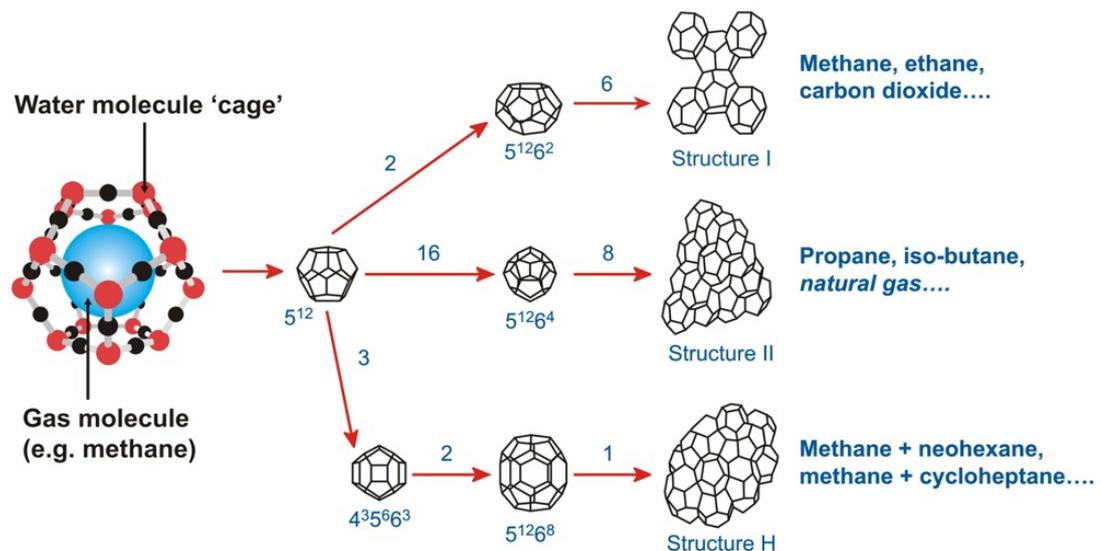
<figure>Figure 1: Diagram of Gas Hydrate Structures</figure>

sI hydrates form with guest molecules less than 6 Angstrom in diameter. (Angstrom is the equivalent of one ten-billionth of a meter or 0.1 nm). For high CO_2 content natural gas hydrate, structure I (sI) hydrate is formed. Not to be mistaken with ice, the transition to hydrate state increases the specific volume of water by $26-32\%$, while the increment of specific volume of water during freezing is just 9%. [2] Gas hydrate occurs worldwide. While there are many debates on the potential gas resources concentrated on Earth in a hydrate state, the consensus value of 21×10^{15} m^3 remains about midway between the extremes. [3] Of the global natural gas reserves, it is also estimated that a third are sour and with increasing energy demand, development of these reserves are being given new attention. For example, in Malaysia, the offshore gas fields are known to contain high percentage of CO_2.

Petronas has identified 15 of those fields, which contain an approximately 13.2 trillion cubic feet (tcf) of natural gas with CO_2 content of more than 70% in some gas fields. [4] Thus, with such significant amount of reserves containing high CO_2, the demand for accurate experimental data for high CO_2 is also high.

Chapter 2

Background Study

2.1   Definition of natural gas hydrates

There are two understandings to the term "natural" in natural gas hydrates. Firstly, "natural" indicates that the gas hydrates were formed organically on Earth and not manmade inside the laboratory or created during the transportation of hydrocarbons. Secondly, the term "natural" here is an indication of the content within the gas hydrate which is natural gas, composed of methane and more often than not, along with other hydrocarbon and non-hydrocarbon gases.

Hydrates are a subgroup of clathrates. A clathrate is a compound which is formed by the inclusion of molecules of one kind within cavities in the crystal lattice of another. The term clathrate was derived from the Latin word 'clathratus', which means 'enclosed by bars or grating'.[5] For hydrates, the 'bars' or 'gratings' are water molecules (H_2O) with the guest site occupied by gas molecules. Since water is an abundant resource on this planet, hydrates can form readily provided all conditions favour the formation requirement.

2.2   History of Gas Hydrates

While natural gas hydrate accumulation on Earth is vast, the first hydrates were discovered in a laboratory. While many researchers believed that Sir Humphrey Davy first obtained gas hydrates by cooling an aqueous solution saturated with chlorine gas [6], further research shows that the great philosopher and naturalist Joseph Priestley first discovered gas hydrates 30 years prior to Sir Humphrey Davy's discovery as reported in his work *Versuche und Beobachtungen uber vershiedene Gattungen der Luft.*[7]

However, since the discovery of hydrates showed no significant theoretical and practical value, the subject on hydrates were purely academic until the beginning of the 20th century, when oil and gas became important in the world energy balance. American chemist E.G. Hammerschmidt found out that the cause of complications for the transportation of gas through the pipelines was the presence of hydrate plugs. From there on, he also formed the main principles of hydrate plug formation

prediction and basic hydrate control methods.[8] Initial discovery of natural gas hydrate happened during the extraction of hydrate-saturated cores during the exploratory drilling at Western Siberia fields in 1967. [9] Currently, more and more gas hydrate fields are being discovered.

2.3   Objectives

The objectives of this project are:

i.   To observe and understand the phase behaviour of high CO_2 content natural gas hydrates.

ii.   To conduct experimental measurement of high CO_2 content gas hydrates over a wide range of temperature and pressure.

iii.   To compare phase behaviour of high CO_2 natural gas hydrate phase behaviour with results from commercially used software.

2.4   Scope of Study

The scope of work for this project involves mainly on laboratory experiments, whereby author carry out phase behaviour measurements using the step-heating method to obtain dissociation points of high CO_2 natural gas hydrate.

Throughout the duration of this project, author will focus on research problems, apply appropriate methodology to achieve project's objectives, analyse and produce project outcome based on experimental results and commercially used software such as CSMGem, HydraFlash and MultiFlash.

2.5   Problem Statement

Problem Identification

Through this research, the author aims to tackle the following questions:

i)   How does high CO_2 concentration natural gas affect gas hydrate formation?

    and

ii)   How good are commercially used software in predicting high CO_2 concentration systems?

The most common problem faced currently is that most literature data conducted in the past regarding CO_2 has been in low concentrations (<5%). In Malaysia, where the reservoirs have high CO_2 content, the applicability of the existing models and their uncertainties can lead to over or undersized designs. To tackle this issue, the author wishes to extend the range of CO_2 concentration in this study to over 70% to understand the effects of CO_2 concentrations over gas hydrate formation.

Significance of Project

Hydrates are solid metastable compounds whose properties and stability depend on the pressure and temperature. When hydrates are created in loosely consolidated sedimentary rocks, the hydrate will be a cementing material. [2] If the hydrate dissociates, the rock formation becomes unconsolidated and loses its strength.

During production, high CO_2 content hydrocarbon fluids are normally saturated with water. With the right temperature and pressure, this can lead to hydrate formation when the gas fluid is transported through the pipeline. Consequently, all processes with the unprocessed gas fluids are affected.

Natural gas hydrates are also a potential energy resource. With potential gas resources concentrated on Earth in a hydrate state exceeding $1.5x10^{16}m^3$, production of gas from natural hydrate deposits are of significant importance for the global growing domestic energy needs.

Using the method known as step-heating, we are able to determine the hydrate dissociation point of the gas/liquid phase in equilibrium with liquid water. The understanding of phase behaviour of gas hydrates is important as gas hydrates could form in numerous hydrocarbon production and processing operations, causing serious operational and safety concerns.

` All in all, this project allows a better understanding of the natural gas hydrate accumulations, as well as assessment of hydrate influence on engineering constructions.

Chapter 3

Literature Review

3.1 Theory

Gas hydrates are considered to be a separate solid phase consisting at least two components, despite any other solid phases apparent. It consist water, which forms the hydrate lattice, or a cage, and one (or more) enclathrated component, which is the gas molecule inside the cage. This is considered a binary system, which unlike the unary system (only a single component present), has a higher complexity of phase behaviour, and simultaneously phases diagrams representing this behaviour. (See Figure 1)
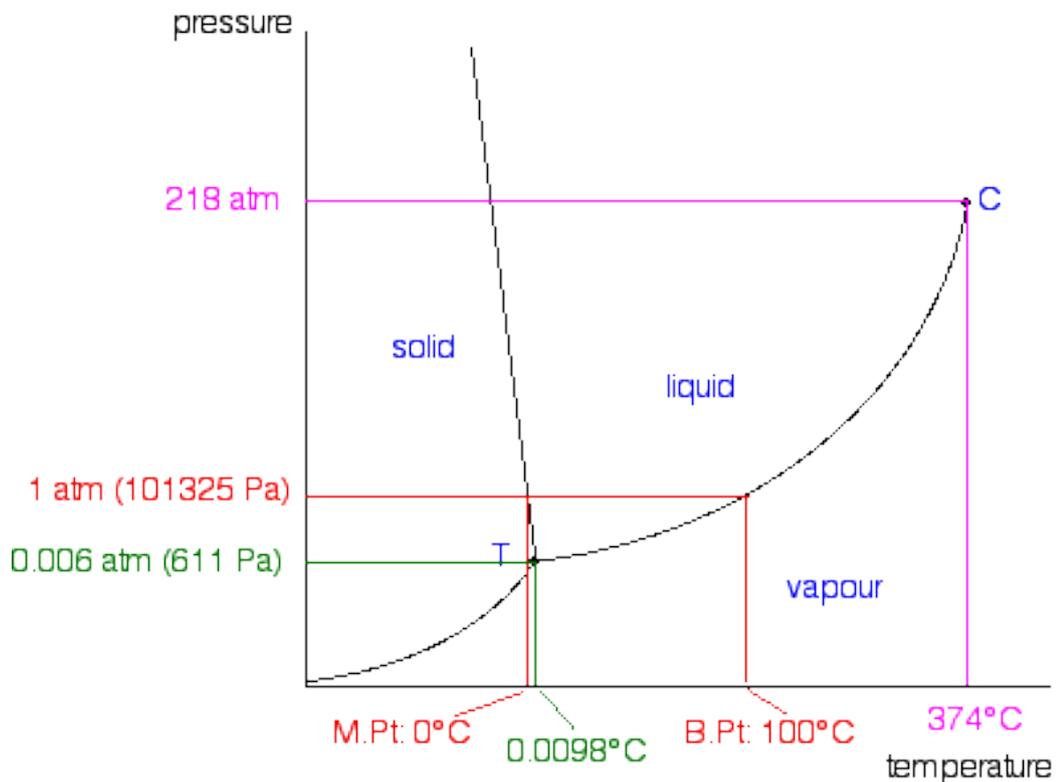
Figure 2: Phase Behaviour of Unary system (H20)

3.2 Binary Systems (with Water and Gas Molecule)

As the components increase, the number of coexisting phases increases, and so does the type of phases that can be formed. In this case, aside from the solid phase of the gas component (S), liquid phase other than L_w (L), and vapour phase (V), there is also the clathrate hydrate phase (H). [10] The main difference in the hydrate forming region of the binary systems of water and gas is the location of the gas' critical

temperature in the phase diagram. As carbon dioxide has a higher critical temperature (304.2K) than the triple point of water (273.16K), this system has a 'liquid-like' behaviour. (see Figure 2)[11]
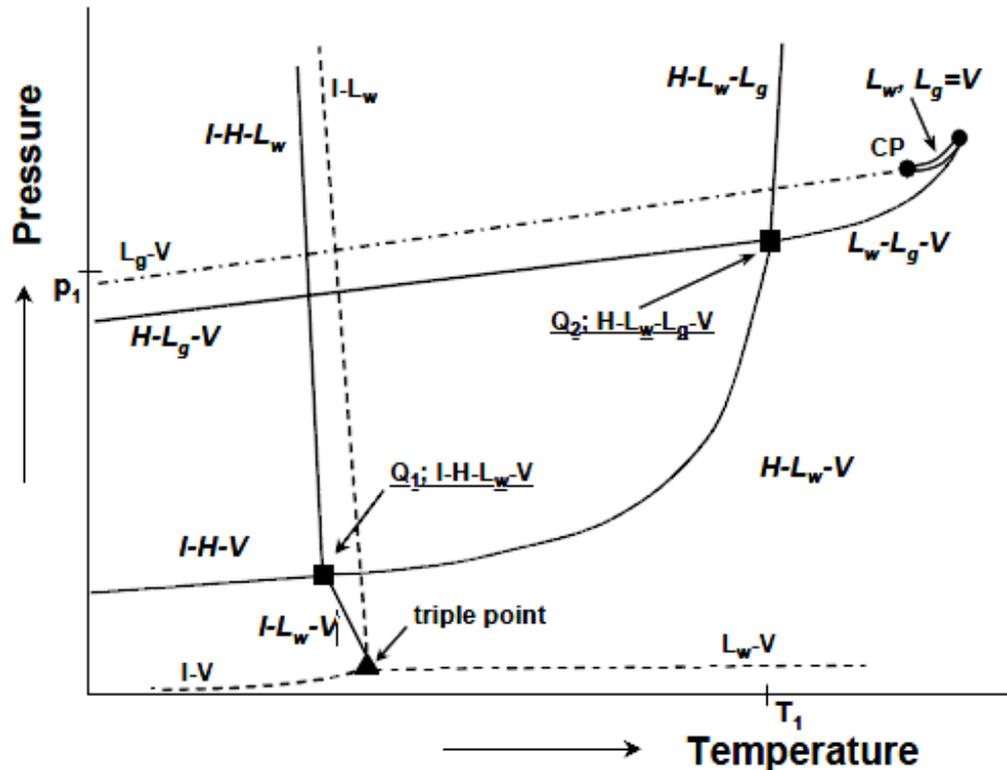
Figure 3. Schematic Diagram of the phase behaviour of Binary System H20 + Carbon Dioxide gas (---) compared to the Unary Systems H20 (- - -) and CO_2 (-.-.-.-) in a P/T projection [12]

3.3   Experimental and Modelling Studies of Gas Hydrates

The thermodynamics of gas hydrate are important in many applications, such as inhibiting the formation of hydrate in oil and gas pipelines, exploring and exploiting hydrate reservoirs, sequestrating CO_2 on the ocean floor, and analysing the salinity of fluid inclusions. Due to limitation of experimental data, studies on the development of thermodynamic model for the predicting of phase behaviour of hydrates are of great importance. A variety of thermodynamic models for the calculation of phase equilibrium properties of the hydrate system has been discussed and reviewed in literature. The basic model for phase equilibrium of gas hydrate was derived from statistical thermodynamics by van der Waals and Platteeuw [13], and generalized by Parrish and Prausnitz [14] for predicting gas hydrates dissociation pressures. The main difference among these models is the choices of different molecular potentials.

Tohidi et al [15] conducted dissociation point measurements using step-heating method, which is demonstrated as being considerably more reliable than continuous heating and/or visual techniques. The methodology done in this project is therefore based on the method recommended in the published paper.

Rui Sun and Zhendao Duan[16] presented an improved model for prediction of phase equilibria and cage occupancy for methane and CO_2 hydrate in aqueous state over a wide temperature-pressure range from angle-dependent ab initio intermolecular potentials. The model was able to accurately predict the equilibrium pressure of methane and CO_2 hydrate in binary systems with and absolute average deviation of less than 3%.

M.M. Mooijer-van den Heuval [12] did a study on the gas hydrate phase behaviour of ternary systems water + carbon dioxide and also compared the phase behaviour and pressure reducing effects of organic additives such as tetrahydropyran, cyclobutanone, cyclohexane and methylcyclohexane with the previous system. The experiment was conducted using Cailletet equipment. The author conducted the experiment using step-heating method, by fixing the pressure with a dead weight pressure gauge, and after hydrates are formed, changed the temperature stepwise until the last hydrate has disappeared. The results obtained from the experiment were then compared with data from literature and is depicted in Figure 3.
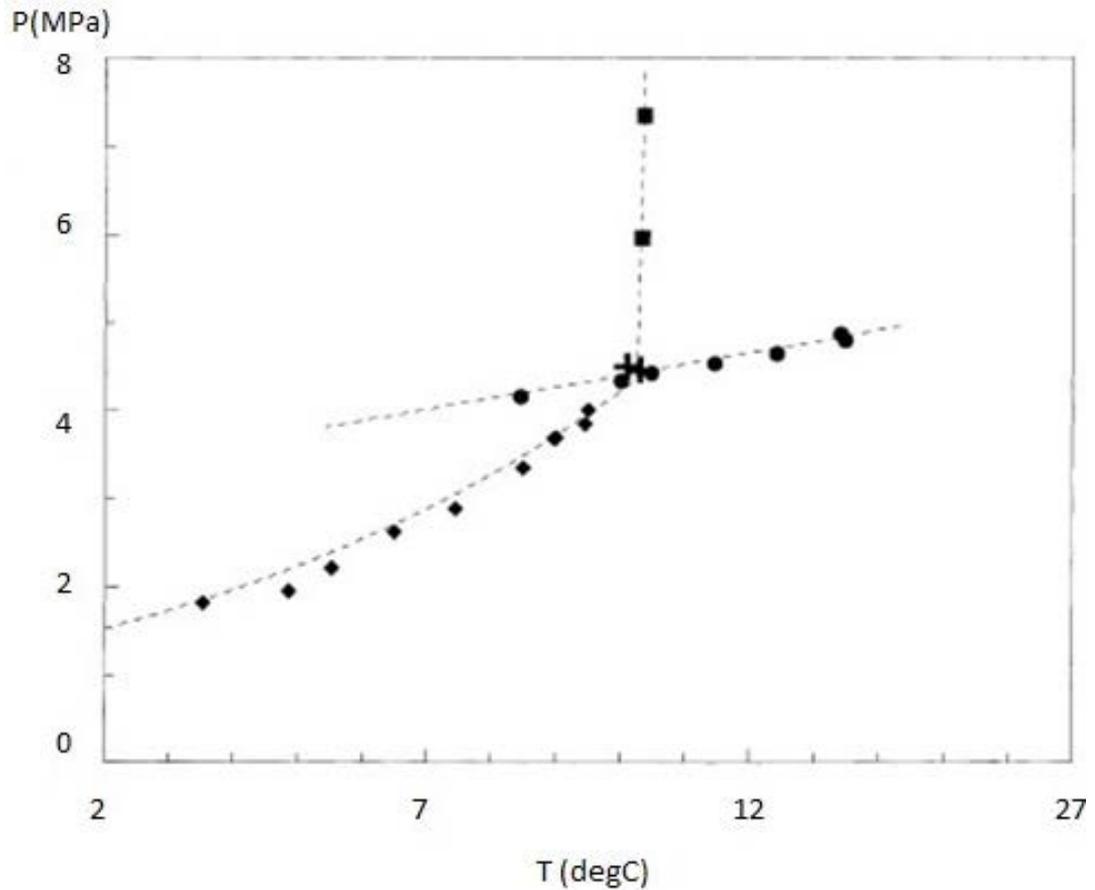
Figure 4: P/T diagram for hydrate equilibria of system H20 +CO₂ (Square Marker) compared to literature data (---)

In another research to study carbon dioxide mitigation and CO_2 enhanced hydrocarbon recovery, Ruffine L. [17] also conducted measurements for hydrate equilibrium curves in aqueous solutions for the system ($CO_2 + H_2O$). The experiment was conducted in a high-pressure cell coupled with sapphire windows and a thermostatic bath with glass walls for visual observation. To form hydrates, the bath temperature was initially set at T = 23 $^\circ$C and filled with gas at pre-determined pressure, and then lowered to T = -1 $^\circ$C when most hydrates form rapidly. Once hydrate formation is completed, the bath temperature is increased in steps of 0.3 $^\circ$C with 1 hr intervening periods.

For modelling studies, the authors computed a curve based on the Krichevsky-Kasarnovsky (KK) equation. The KK equation is based on the simplification of the exact conditions of phase equilibrium in which the activity coefficients of solvent and solute are taken to be unity leading to the following expression:

$$\ln\frac{f_2}{x_2} = \ln H_{21} + V_2[(p - p_1^\sigma)/RT]$$

Whereby f_2 is partial fugacity of solute, H_{21} is Henry's constant recommended by Carroll et al., V_2 is partial molar volume of the solute, determined by Moore et al. and p_1^σ is the vapour pressure of pure solvent.

The results from experimental measurements and the predicted curve shows good agreement, and is then compared with literature data to obtain Figure 4:
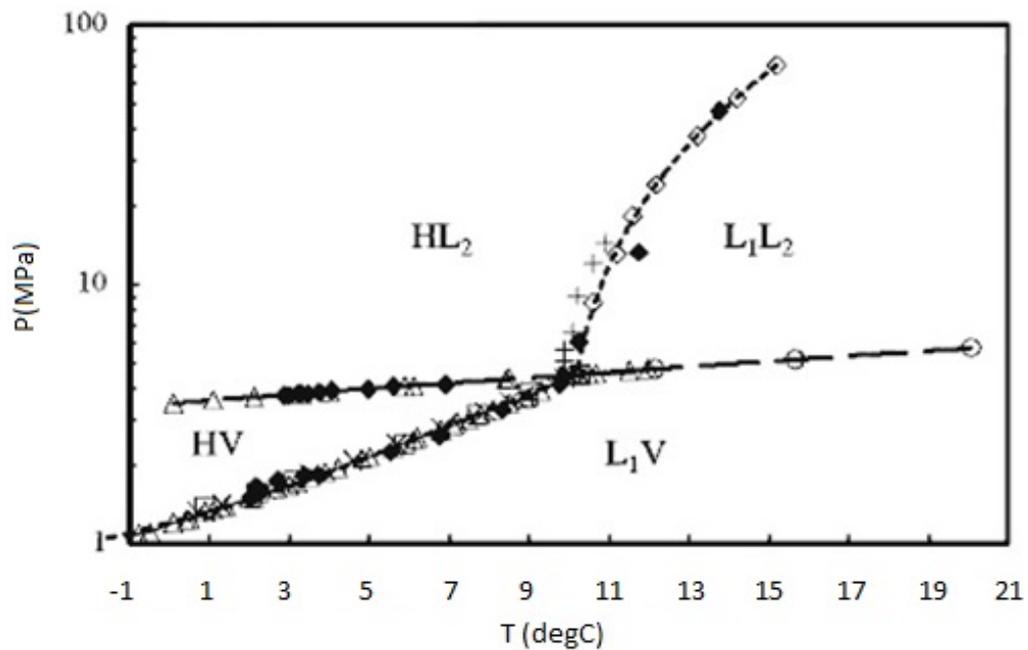

Figure 5: P/T diagram of hydrate phase for binary system (CO_2 + H2O); Experimental results (diamond marker) and literature data comparison. [17]

Chapter 4

Methodology

4.1   Materials

Pure deionised and degassed water is used throughout the duration of all tests. Gas components include a variety of mixture of carbon dioxide, nitrogen, methane and ethane. List of components and respective suppliers are as below:

Table 1. Materials and respective suppliers

No.	Material	Supplier
1	Carbon Dioxide (99.995%)	Gas Walkers Sdn Bhd
2	Methane (99.95%)	
3	Deionised Water	Block 5 Laboratory

4.2   Experimental Equipment

The main experimental apparatus used here is Hydreval, a motor driven PVT cell. Developed by Vinci Technologies, the Hydreval (Figure 5) is designed for the determination of hydrates formation and dissociation conditions as well as the evaluation of hydrates inhibitor. The set-up is comprised of a sapphire chamber with a piston at one end and the other by a titanium alloy cell head. The cell volume is approximately $80cm^3$ and has a maximum operating pressure of 20MPa. The temperature for Hydreval operations ranges between -21.15 ^{o}C and 248.85 ^{o}C. The stirring mechanism for the equipment is magnetic driven. Measurements of volume, pressure and temperature are recorded in computer software linked to the machine every 2 seconds with an accuracy of $\pm 0.001cm^3$, ± 0.01 MPa and ± 0.1C respectively. The apparatus also features a recording camera attached to the fully visual cell for constant observation purposes. The apparatus is linked to an external pump that separates gas and liquid injection into the cell.
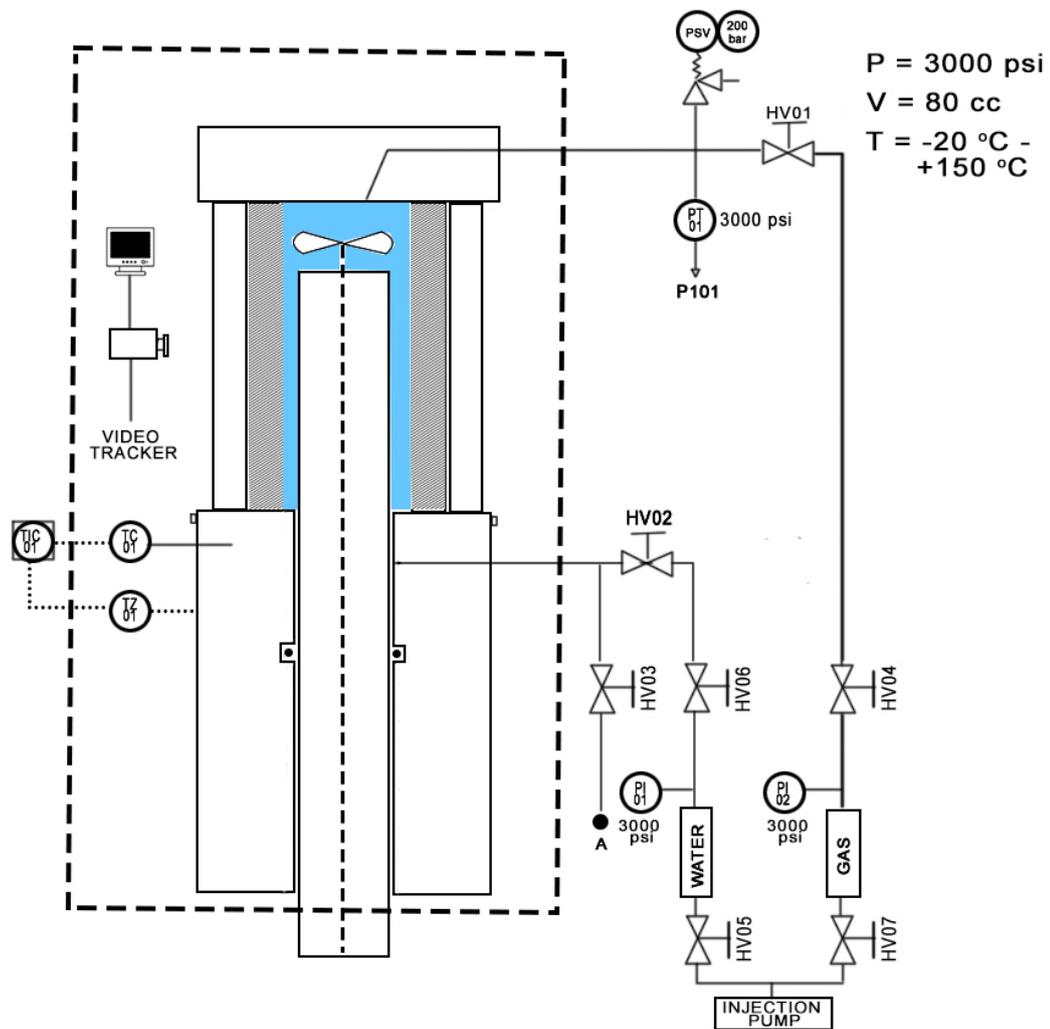
Figure 6. Schematic Diagram of Hydreval

4.3 Preparation of Apparatus

Before initiating the experiment, the apparatus has to be thoroughly prepared to avoid contamination, which may cause erroneous results. The sapphire cell is initially washed and vacuumed to remove residual from previous experiment. The cell is then flushed with predetermined gas mixture to ensure the cell content is air-free. The aqueous solution is then injected into the cell using an external pump. The cell is cooled to temperature above hydrate equilibrium temperature to ensure hydrate formation does not occur before the start of experiment. The gas is then supplied into the cell at a pre-determined pressure.

4.4   Experimental Procedure

Clathrate dissociation points are measured by standard constant volume cell isochoric equilibrium step-heating techniques. This method has been proven to be more reliable and repeatable than conventional continuous heating and/or visual techniques. [15] The procedure to conduct the experiment starts by lowering the temperature of the cell already containing the gas-aqueous solution mixture (A to B). Growth of hydrates is detected by means of visual observation, accompanied by an associated pressure drop (B to E). Once hydrates are fully formed, the cell temperature is then raised step-wise (at 0.5 / 1 Celsius intervals), allowing enough time at each step for equilibrium to be reached. In this phase, cell dissociation begins (C to E). Once the cell temperature passed the final dissociation point, any increase in temperature will yield only small amount of pressure rise (E to A). This process results in two very different slopes on the P/T diagram. (See Figure 6) The intersection point between the two (Point E) is then taken as the dissociation point.
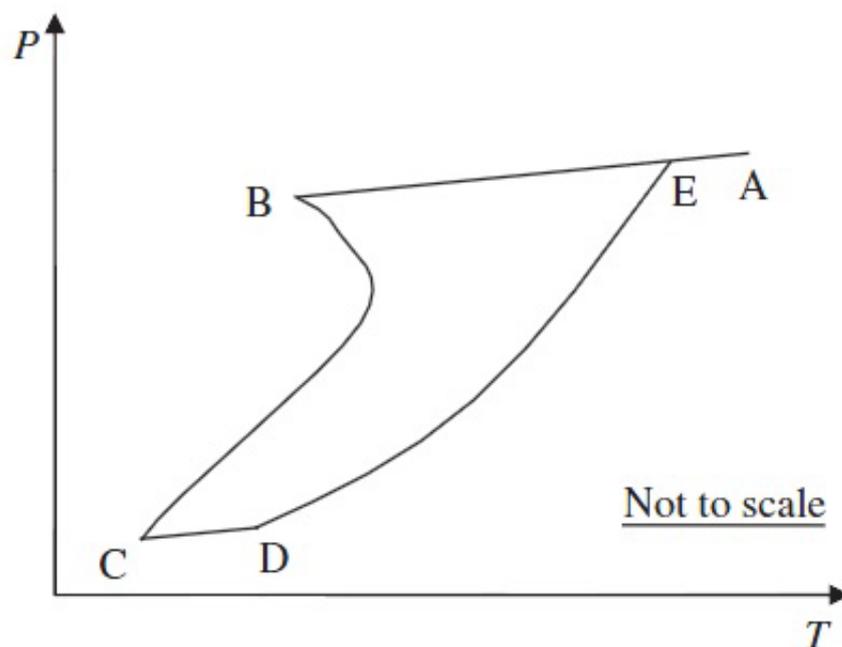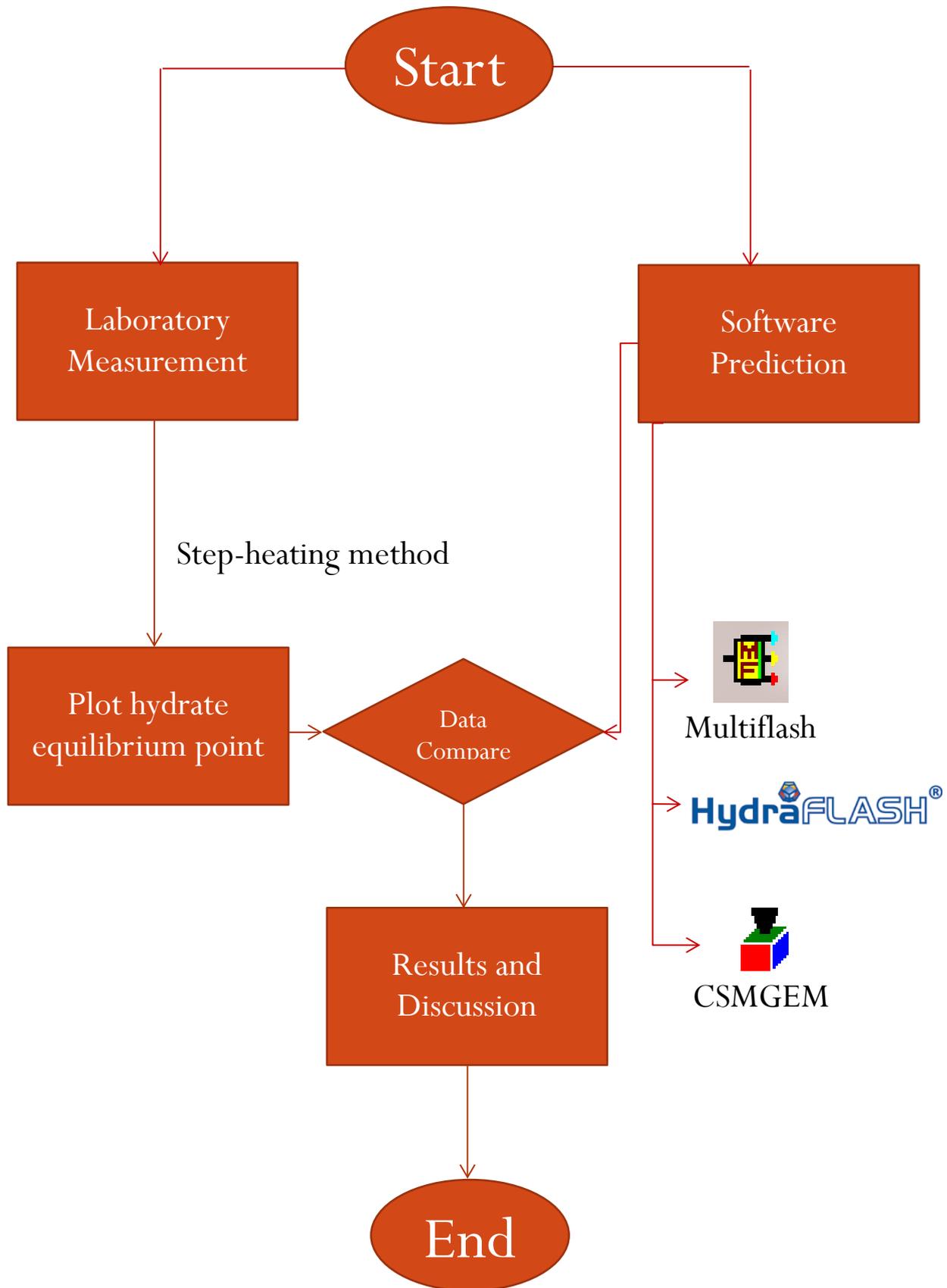

Figure 7: Achieving hydrate equilibrium point through isochoric method

4.5   Modelling Studies

From the dissociation points obtained through experimental work, the data is then compared with predicted results obtained from software-generated models to assess the applicability of the current model. The results are then tabulated.

4.6   Flow Chart

4.7   Gantt Chart and Key Milestones

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Sem Break	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Work	■	■																											
2	Understanding of Natural Gas Hydrates			■																										
3	Background studies, objectives, problem statements			■	■																									
4	Literature review: Experimental study						■	■																						
5	Literature review: Modelling study							■	■																					
6	Methodology: Laboratory familiarization									■	■																			
7	Methodology: Simulation familiarization											■	■																	
8	Laboratory Experiment													■	■		■	■												
9	Software Prediction																		■	■										
10	Results and Discussion																				■	■								
11	Submission of Progress Report																						■							
12	Conclusion and Recommendation																							■	■					
13	Pre-SEDEX																									■				
14	Submission of Technical Paper and Dissertation																										■	■		
15	Oral Presentation & Hardbound Copy Submission																												■	■

■ Key Milestone

Table 2:Gantt Chart for FYP I / FYP II

Chapter 5

Results and Discussion

5.1 Relationship of natural gas hydrates with high CO_2 content

The objectives of this project were to conduct experiments for natural gas hydrates with high CO_2 content over a wide range of temperature and pressure. To achieve this, literature data has been compiled from numerous sources to obtain a plot of methane, water and CO_2 gas mixture and to compare it with another plot of methane, water and CO_2 of high concentration.

Experiments conducted based on the methodology stated in the previous chapter. Data of dissociation points are collected to form a plot of pressure (MPa) given temperature (deg C) shown in Figure 7.
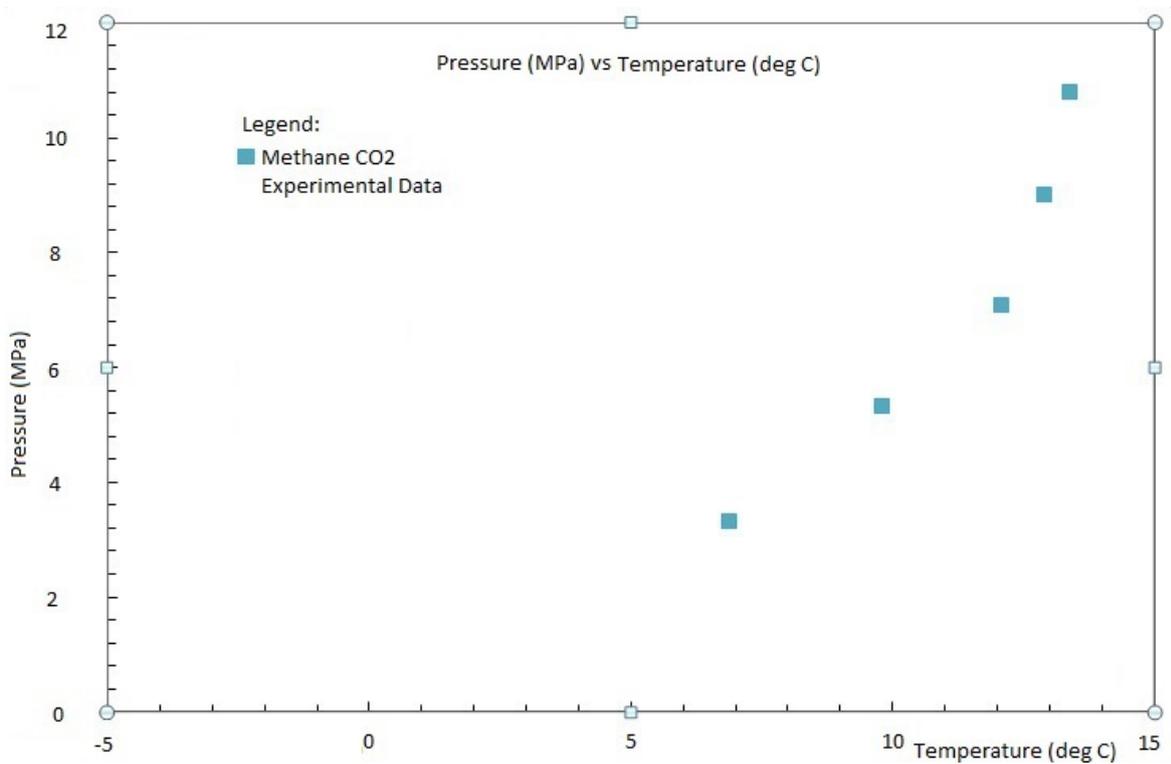

Figure 8: Hydrate dissociation points of methane + CO_2 binary gas system

For this experiment, a high amount of CO_2 is used to simulate the effect of high CO_2 concentration found within natural gas hydrates. More accurately, the composition of CO_2 used in this experiment is approximately 72.5%.

To study the relationship of gas hydrates with high CO_2 content, a few control experiments were also conducted, using pure methane with water and also pure CO_2 with water. The results obtained are then plotted.
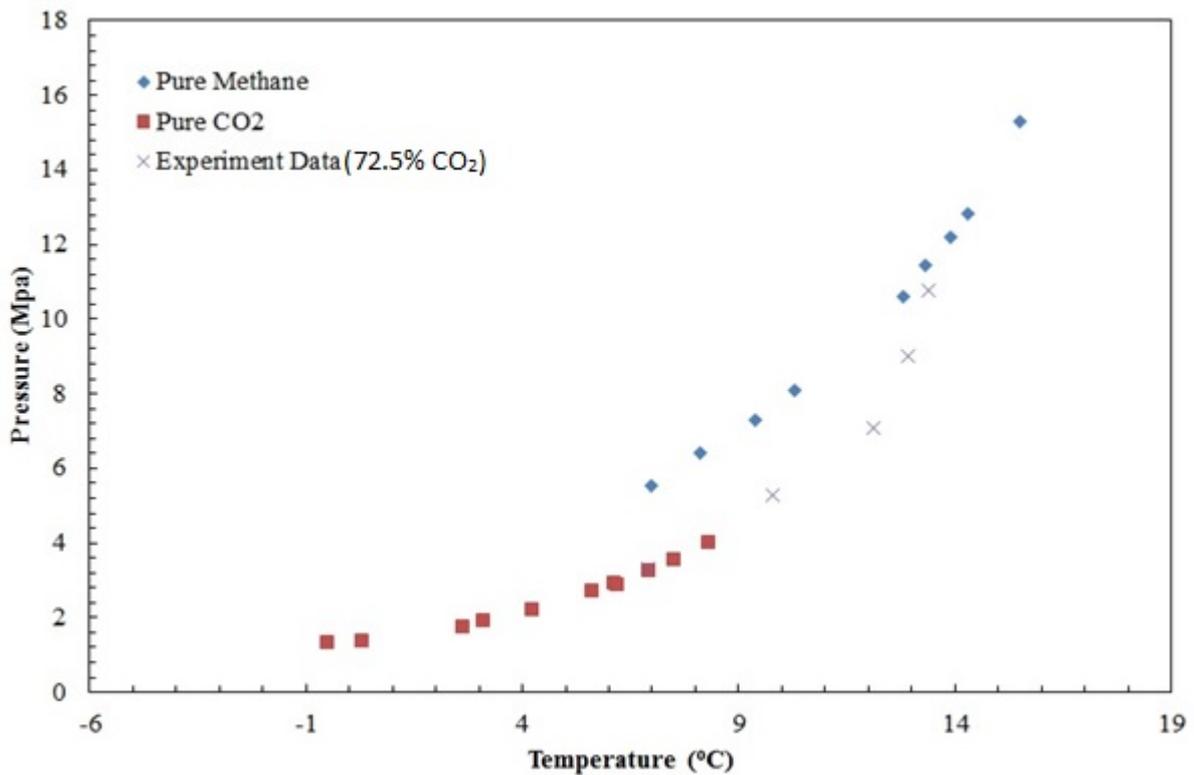
From Figure 8, it can be observed that the equilibrium line of high CO_2 content natural gas hydrate is almost identical to the pure CO_2 gas hydrate equilibrium line, since the gas mainly consists of carbon dioxide. At a higher temperature, a higher pressure is observed to achieve hydrate stabilization. This can be explained by understanding the properties of CO_2 which changes upon temperatures higher than Q2, a four phase equilibrium point $L_w - H - L_{CO2} - V$ into $L_w - H - L_{CO2}$, where the CO_2 vapour would convert to liquid phase.
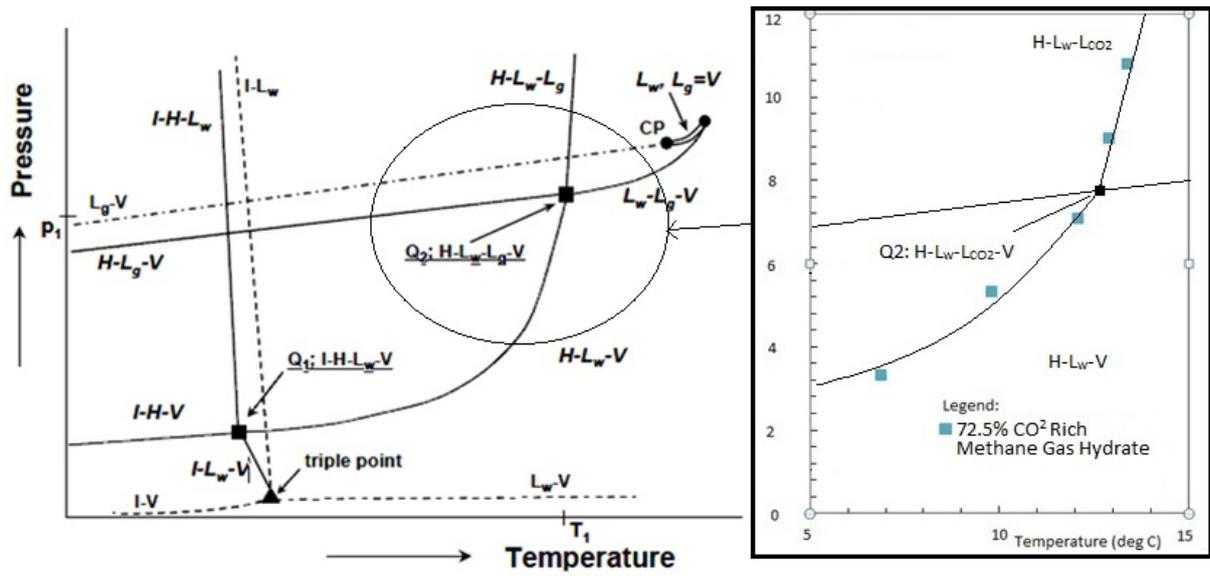
Figure 10: Hydrate Equilibrium Curve above the Quadruple point

5.2   Comparison with Literature Data

From various literatures obtained, a general plot of pressure (MPa) given temperature (deg C) for each dissociation point is also formed. The literature data collected has various CO_2 concentrations, ranging from 10% to 90%.
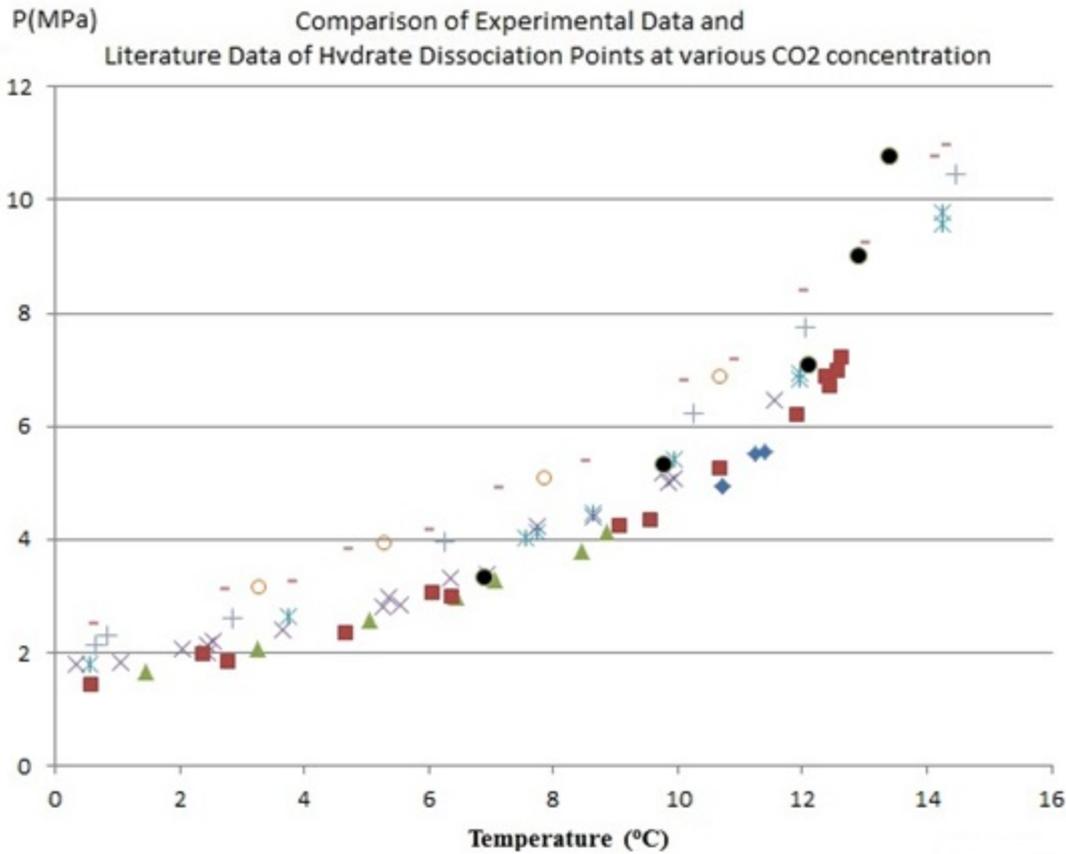
P(MPa)　　　Comparison of Experimental Data and
Literature Data of Hvdrate Dissociation Points at various CO2 concentration

Figure 11: Hydrate dissociation points of Methane + CO$_2$ binary gas system.[18-22]

−　　　10% CO$_2$ Concentration [18, 19]

+　　　20% CO$_2$ Concentration [18, 19]

○　　　30% CO$_2$ Concentration [20]

*　　　40% CO$_2$ Concentration [18]

×　　　50% CO$_2$ Concentration [18, 20, 21]

▲　　　70% CO$_2$ Concentration [18]

■　　　80% CO$_2$ Concentration [18, 20-22]

♦　　　90% CO$_2$ Concentration [21, 22]

●　　　Experiment Data (from this work)

It can be observed that the experimental value does not differ much from the literature data. CO$_2$-rich gas hydrates form easily under low temperature and low pressure. At high temperatures, the pressure value of hydrate equilibrium point for CO$_2$-rich gas hydrates exponential increment. Gas mixtures with low CO$_2$-content gas hydrates shows a hydrate

equilibrium curve almost identical to pure methane gas hydrate equilibrium curve, because it mainly consists of methane gas.
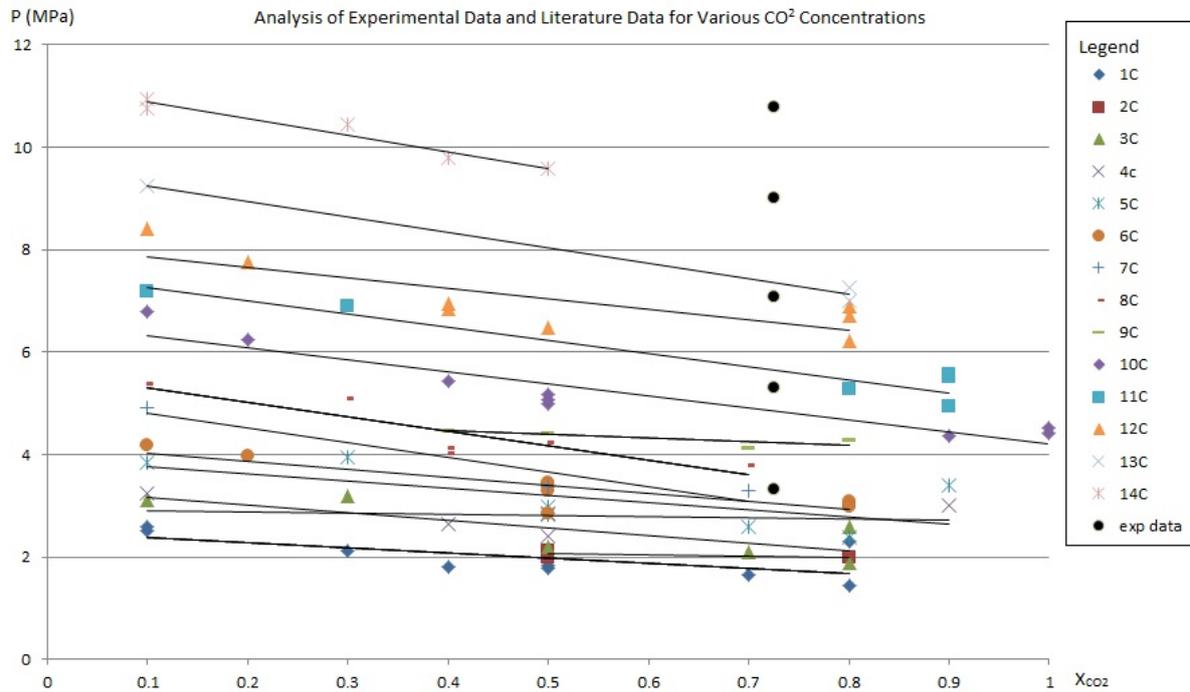

Figure 12: Isotherms for literature and experimental data for various concentrations of CO$_2$ + methane gas hydrates

Figure 11 shows the isotherms for various concentrations of the binary system CO$_2$ and methane gas hydrate obtained from literature data and the experimental data. From this figure, we can see that most experimental data for the 72.5% gas mixture does not deviate from the isotherm except for two points which were the hydrate equilibrium points from above the Q2 quadruple point. This isotherm analysis further proves that these two equilibrium points are in the L$_w$ – H – L$_{CO2}$ region, therefore requiring more pressure to stabilize due to the high CO$_2$ content in the gas mixture.

5.3   Comparison of Prediction Data with Experimental Data

Aside from that, another objective was to compare phase behaviour of high CO$_2$ natural gas hydrate with results from commercially used software. In this study, a few software, both freeware and licensed software, were used, including CSMGem, MultiFlash and HydraFlash. With the available software provided, the following data was obtained.
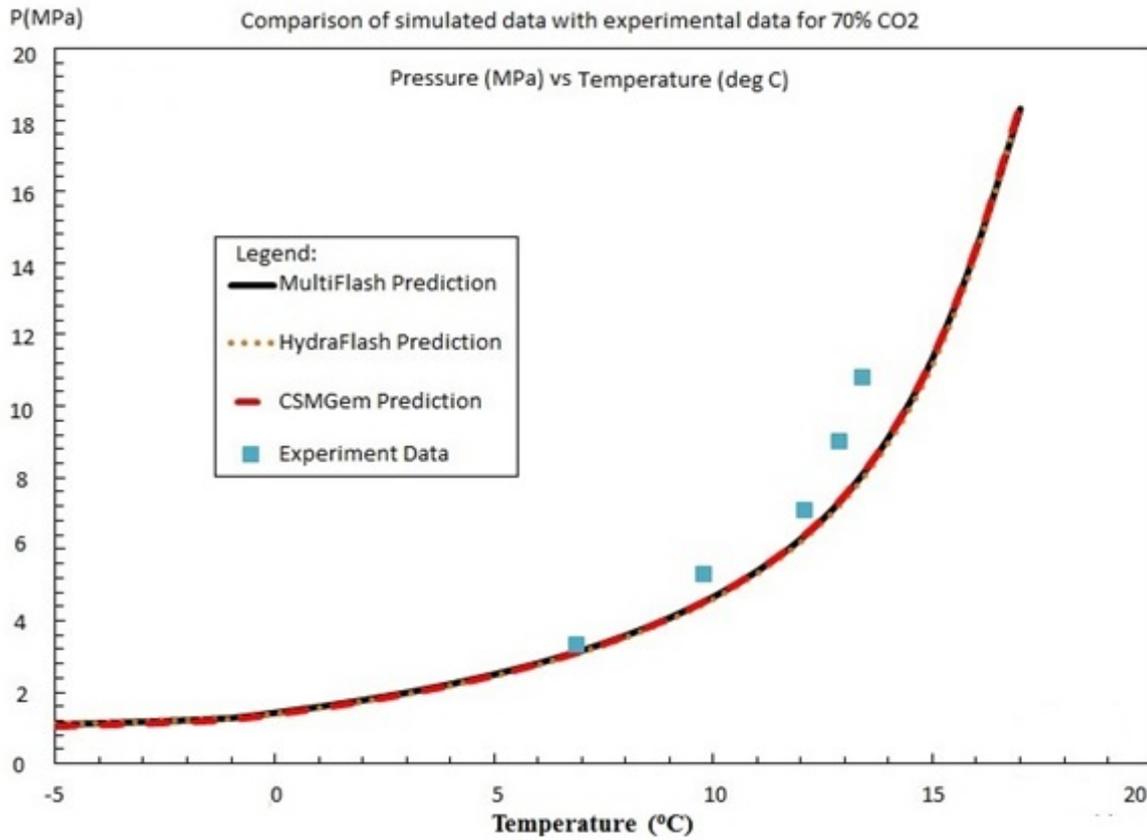
Figure 13: Simulated data and Experimental Data (70% CO_2)

The function simulating the data using software is to predict the outcome from experiment. In this study, the forecasted data from each software are almost the same. A comparison is made with the experimental data in order to evaluate the accuracy of the prediction. To do this, the Average Absolute Error (AAE) is calculated. Based on Nasrifar and Moshfeghian's [4] definition, the average value of error is calculated by:

$$AAE = \left(\frac{1}{np}\right) \sum_{i}^{np} (P_{cal,i} - P_{exp,i})$$

Calculation of the AAE shows is tabulated in Table 3:

Table 3: AAE of 70% CO_2 concentration simulated data

Software	$\sum P_{calculated}$(MPa)	$\sum P_{experiment}$(MPa)	AAE
MultiFlash	29.52	37.80	1.66
HydraFlash	29.13	37.80	1.74
CSMGem	29.59	37.80	1.64

The Average Absolute Error is used to calculate the deviation of the mixture with the prediction. The same equation can also be used to calculate the average value of error for single gas component.
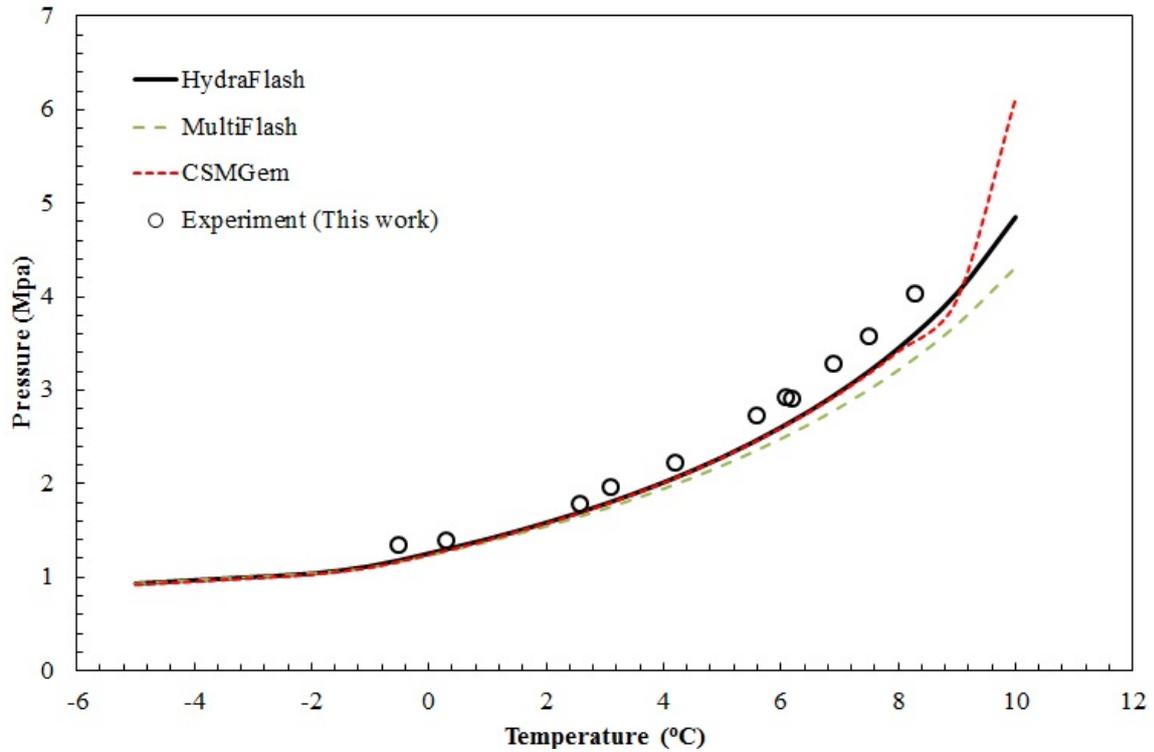

Figure 14: Comparison of Prediction and Experiment Data for Pure CO_2 Clathrate

For single component pure CO_2 gas hydrate, the AAE is tabulated in the table below:

Table 4: AAE of pure CO_2 gas hydrate simulated data

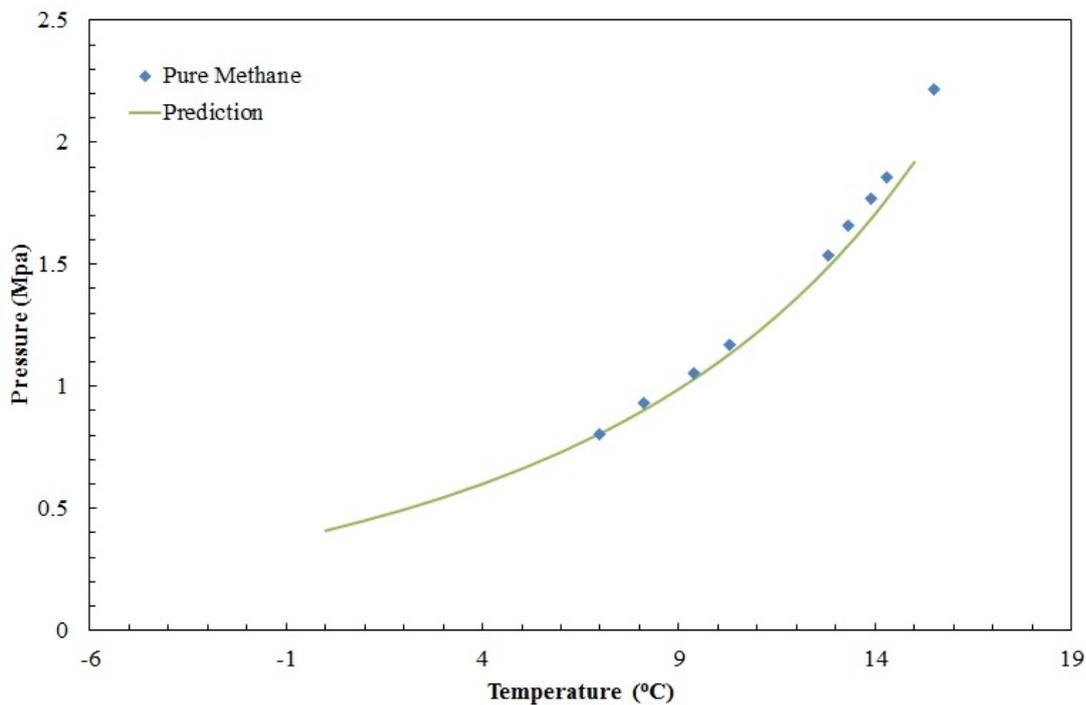| Software	$\sum P_{calculated}$(MPa)	$\sum P_{experiment}$(MPa)	AAE
MultiFlash	24.85	28.08	0.29
HydraFlash	25.72	28.08	0.21
CSMGem	25.72	28.08	0.21

Figure 15: Comparison of Prediction and Experiment Data for Pure Methane Clathrate

For single component pure Methane gas hydrate, the AAE is tabulated as such:

Table 5: AAE for pure methane simulated data

$\sum P_{calculated}$(MPa)	$\sum P_{experiment}$(MPa)	AAE
84.98	89.62	0.52

The AAE for pure components are very low, ranging from 0.21 to 0.52. Unlike that, the AAE for CO_2-rich natural gas hydrate shows a higher AAE value, ranging from 1.64 to 1.74. Even though the prediction from each software is consistent, the accuracy of the values are slightly lower than that of pure components.
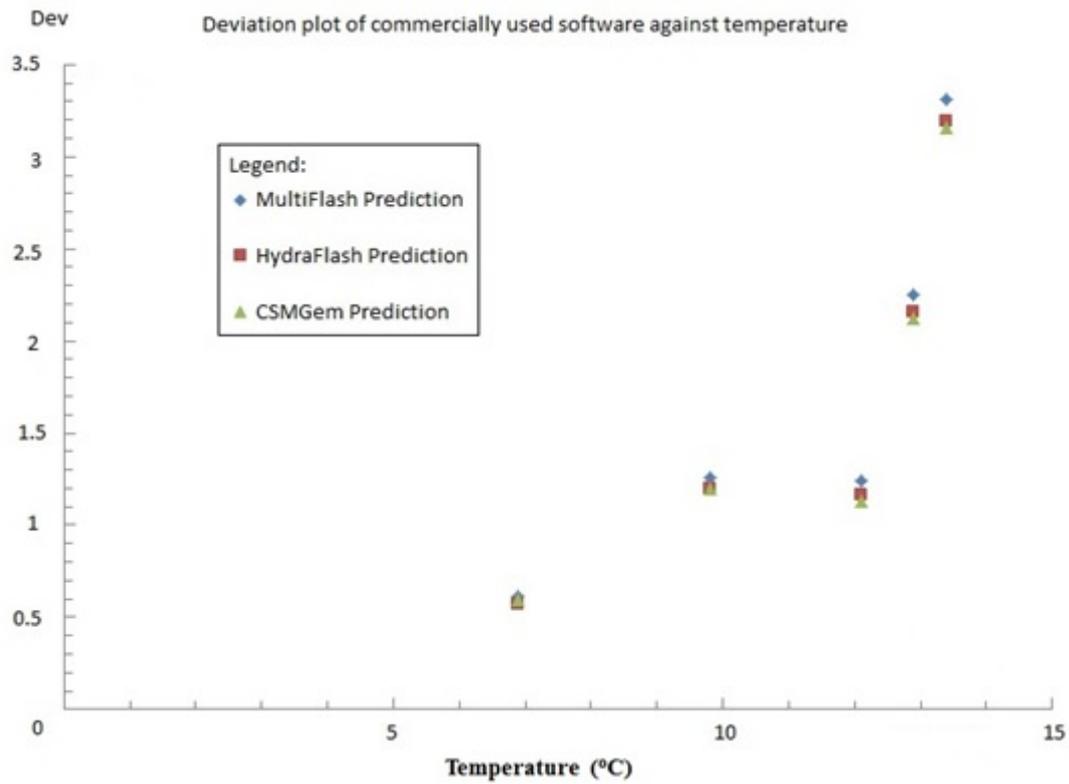
Figure 16: Deviation of each prediction compared to experimental data

In Figure 15, we can see that above 10 ^{o}C, the prediction data from commercially used software deviate a lot from the actual experimental data. The current software available in the market fare well in predicting the hydrate equilibrium curve between Q1 and Q2 quadruple points, but may not be adequate to conduct prediction for CO_2-rich natural gas hydrates at the $L_w – H – L_{CO2}$ phase region.

Chapter 6

Conclusion

The principal objective of this work was to investigate natural gas hydrate with high CO_2 content through experimental measurement of gas hydrates across a wide range of temperature and pressures. The experiments were conducted successfully with each step taken done meticulously to reduce the risk of uncertainty and error. To achieve optimum result, the experiment was conducted using isochoric equilibrium step-heating techniques.

Predictions from commercially available software were compared with the experimental data for a wide range of temperature and pressure. A good agreement between predictions and experimental data was observed, showing the reliability of the experimental data obtained.

Knowledge of phase behaviour and properties of CO_2-rich natural gas systems is of great value to the oil and gas industry. Therefore, it is hoped that this work could provide an extension to a wider range of temperature/pressure of data available and further enhance the reliability of available literature data.

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