FINAL YEAR PROJECT 2: DISSERTATION

# TITLE: EXPERIMENTAL STUDY OF FORMATION KINETICS OF $CO_2$ & $CH_4$ GAS HYDRATES IN PRESENCE OF POTASSIUM OXALATE MONOHYDRATE

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

MAY 2014

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# CERTIFICATION OF APPROVAL

## Experimental Study of Formation Kinetics of CO2 & CH4 Gas Hydrates in Presence of Potassium Oxalate Monohydrate

By

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Approved by,

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MAY 2014

# 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 person

AMIR AIMAN BIN ABDUL KARIM

# ACKNOWLEDGEMENT

I would like to take this opportunity to show my gratitude to several people for helping me in the journey of final year project starting from preliminary research, experimental phases and until the completion phase of this project in Universiti Teknologi PETRONAS.

First and foremost, I would like to express the highest gratitude to Allah the Almighty, for He is the One who made everything happen according to plan without any major troubles. In addition the health condition during the course of my study in this university, which allows me to gain adequate theoretical knowledge and practical skill sets as Chemical Engineer.

Deepest appreciation shall be awarded to all person I have worked together with during this project. The strong support and willingness to share knowledge and expertise have given a very delightful experience to be placed in heart. Special gratitude shall go to my supervisor, Dr Bhajan Lal who became the most important person to teach and provide guidance on the project. Not to be forgotten, all people who have helped in gaining wonderful experience along this project especially in the chemical department and friends either they work directly or indirectly in completing the job assignment. All the help and sharing of information is highly appreciated in which has enabled well performance during this period. Special thanks to my mentor, Mr. Behzad Partoon for giving me the opportunity to work together and show me the true meaning of being an engineer.

I place on record, my sincere gratitude to all the lecturers and professors, the HODs & Dean of Department of Chemical Engineering. Thank you for all the lessons and effort to arrange the final year project accordingly.

Without them, this final year program and this final report would not be completed with full satisfaction and on time.

# ABSTRACT

Gas hydrates are one of the major problems in oil and gas industry due to its tendency to cause plugging in pipelines. However as far as the industry is concerned, gas hydrates also brings benefits. Examples of this are the importance of the natural methane hydrates that are formed at the bottom of the ocean. This natural hydrate are said to have twice the number of the current world reserves which includes fossil fuel, coal and gas. In other word it is the new possible fuel energy for mankind. Another benefit of gas hydrate is its capability of storing gas for the use of transportation; this is help by the ability of gas hydrate to store large volume of gas into a smaller volume. However, due to slow formation of gas hydrate, it is difficult to implement the usage of gas hydrates for transportation vessel in the industry. The ability to understand the behavior of gas hydrates is very important as it could help and tackle the idea to improve the reaction and it is also essential to gather more data as not many works have so far been done upon the study of kinetics reaction using potassium oxalate monohydrate (POM) as promoter. In this project, a total of 8 experiments are done to study the reactivity of POM on the formation of gas hydrates. The responding variable is the induction time. The shorter the induction time, the faster a fully growth of gas hydrates are formed. Then the experiments and observations were compared with some previous works that are done using other promoter. In addition to performing and reporting on a brief literature study of the subject, a description of the equipment and related experiments in detail are provided

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# NOMENCLATURE

## Abbreviations

| | |
|---|---|
| POM | Potassium Oxalate Monohydrate |
| $CO_2$ | Carbon Dioxide |
| $CH_4$ | Methane |
| PPM | Parts Per Million |

## Symbols

| | |
|---|---|
| $^{o}C$ | Degree Celsius |
| P | Pressure |
| $M_1$ | Molarity/Concentration |
| $V_1$ | Volume, *ml* |
| $n$ | Number of Mole |
| $\omega$ | Angular Velocity, rpm |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background Study

This project is related to gas hydrates focusing on speeding up the formation kinetics of the solid ice structure in order to use gas hydrate massively in the industries. This experiment is essential as the formation of gas hydrates in nature takes about 3 days to complete which is considered very slow. Hence the method that will be used in enhancing the formation of gas hydrates for this project is by adding additive to promote the growth of the structure. Potassium Oxalate Monohydrate (POM) will be used as the additive in this experimental project as it is believed to enhance the formation in terms of the induction time and initial parameters rate. POM is a colorless crystal powder and not influenced by non-ionic or anionic surfactant properties. In (Zhang, Fan, Liang, & Guo, 2004) writing, there are 2 reasons POM is selected as additive. POM contain low concentration of salt as well as in the chemical reaction of POM, the $K^+$ and $OH^+$ ions enhance the formation of microcavities of the crystal lattice. In this experiment, a high-pressure system called the Kinetic Hydrate Batch Reactor is used as the main instrument to study the kinetics formation of gas hydrates. In this experiment, different concentration of POM solution is used as the manipulated variable. It ranges from 100 ppm up to 1500 ppm. Finally, the responding variable from this experiment would be the number of moles consumed, the induction time and the formation rate.

## 1.2 Objective

1. Effect of concentrations of POM on induction time
2. Effect of concentrations of POM on hydrate growth

## 1.3 Problem Statement

In today’s world, the depletion of fossil fuels reserves has triggered thinkers all around the world to find alternative energy to replace the hydrocarbon energy that is extracted from subsurface of earth. The current research estimate that the amount of energy stored in gas hydrates is greater by twice the number of all fossil fuels (Sloan et. all, 1999). This energy of gas hydrates can be found in the bottom of the ocean where the condition is cold and high in pressure. In terms of production, currently it is expensive to recover the gas hydrates for usage, however due to growing in energy demands, mankind are expected to tap the fuel source in nearly time in future (Sloan, 2003).

Other than as the new possible fuel energy, gas hydrates also comes with several beneficial applications for example as gas storage for transportation. With the ability to capture large volume of gas molecules and compressed it into smaller volume, the usage of gas hydrates is very suitable in terms of transferring large volume of gas from one place to another. However, the major challenge to practice of using gas hydrates in businesses is their slow formation rates (Bahman & Farshad, 2013).

The natural formation of hydrate takes about 3 days to fully growth. Therefore, in order to overcome this arising problem in the growing demand, it is required to find an alternative way to enhance the formation of gas hydrates. From literature study, using Potassium Oxalate Monohydrate as additive or promoter are suspected to be an effective way to speed up the formation of gas hydrates through minimizing the induction time.

## 1.4 Scope of Study

- Literature survey and experimental work of using Potassium Oxalate Monohydrate at various concentrations.
- Literature survey and experimental work of methane hydrate formation in POM solution at 55 bars and 273.65 K.
- Literature survey and experimental work of carbon dioxide hydrate formation in POM solution at 35 bars and 273.65 K.

## 1.5 Relevancy of the Project

The project is relevant to be conducted as it is currently lots of studies and research are done on the development of gas hydrates. This project may help to improve the understanding of the parameters involved in the formation of gas hydrates and tackle the issue in fasten up the reaction. Although there was previous study using Potassium Oxalate Monohydrate (POM) as promoter, this project is more likely act as the continuation due to the availability of more concrete parameters and specified studies. This project also could be a reference for future research that involves POM. In addition, the project can be completed in the given time frame of the Final Year Project time frame.

## 1.6 Feasibility of Project

With the guidance and supervision from the supervisor, research assistant and the coordinator, the project has become within capability of a final year student to be accomplished. The time frame given is adequate and the project can be completed within the time allocated as the materials can be gathered easily and the experiment is easy to be conducted. In addition, the previous research projects with the same general foundation can be used as a reference. This would help and ease to achieve the final conclusion.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Gas Hydrates

### 2.1.1 What is Gas Hydrates?

Gas hydrate is a compact slush that is formed in the hydrogen bonded in water that stores gas molecules in its capsule. The void spaces formed by water molecules are called the “host” and the gas molecules are termed as “guests”. In the presence of water and gas molecule such as methane, ethane, propane, etc., the gas hydrates can be formed at high pressure and low temperature (Arvind, Jason, Sloan Jr, & Koh, 2008). Basically there are three types of crystal structures which differ in size and shape; there are I (sI), II (sII) and H (sH) (Zhang et al., 2004). These gas hydrates can be found vastly in the ocean seabed or popularly in gas pipelines where the condition is favorable for gas hydrates to form. Today, the energy utilization by human societies is gradually involved with hydrates. These include many technological aspects, for example the anticipation and prevention of plugging of oil pipelines for transporting natural gas the formation, the storage of clathrate hydrates as cool storage media for home air conditioning and the disposal of liquefied carbon dioxide at the ocean (Sugaya & Mori, 1996). Below displays the types of structure of gas hydrate taken from an article (Sloan, 2003).

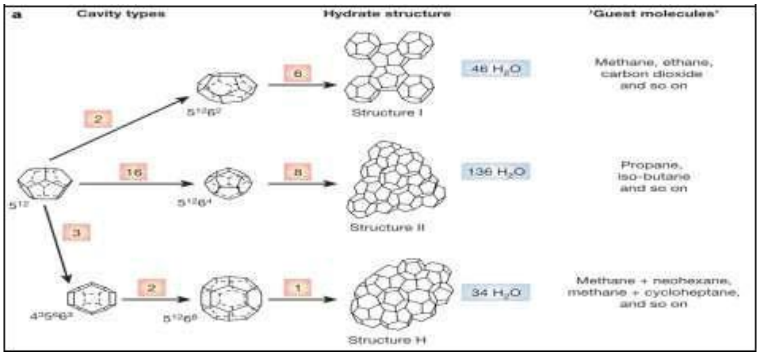


*Figure 2.1: Gas Hydrate Structure*

### 2.1.2 Fundamentals of Hydrates

Gas hydrates are mainly made up from water. Due to this factor, the surface phases of gas hydrates are likely to be hydrophilic. Every guest molecules that are capsulated in the hollow created by the water molecules is not chemically bonded. All three type structures (figure 2.0) will carry similar concentrations of water (85% mol) and guest (15% mol) after all the cavities are occupied (Mohammed, 2006). The gas hydrates formation includes variety of processes such as physical, chemical and physicochemical. When both of the gas and liquid water are merged soluble in each other, they are limited to macroscopic interface between the two fluid phases. The hydrate that once formed may constantly decompose if the liquid water and the gas species are not saturated. Hydrates that decompose will release the molecules of the guest species which will dissolve in water and eventually causing mass transfer process. To maintain the mutual contact, the further growth of the hydrate is depending on the penetration of water and guest species across the very hydrate phase (Sugaya & Mori, 1996).

### 2.1.3 Formation of Gas Hydrates

The formation of gas hydrate is closely associated to crystallization process. There are many studies done on the hydrate formation kinetics, which can be separated into two categories: Primary nucleation and the crystal growth process. The limelight is given to the hydrate growth and the diameter distribution of hydrate pellets. Meanwhile, less research are done on the nucleation rate where hydrate formed on the free surface of gas-water contact (Khalik, Vicente, Geert-Jan, & Cor, 2010). The process of hydrate formation is just like any other crystallization process. They are not under the principle of thermodynamic, but stochastic (random variable). The key parameters to enlightening the nucleation and the growth process are induction time, the driving force and the memory effect. The meaning of induction time is the elapsed time for the hydrate nuclei to reach a critical size for commencing the hydrate growth.

Figure 2.1 shows the induction time is calculated by $t_{ind}$ - $t_{sol}$ ($t_{sol}$ is the time required for pressure to stabilize after small pressure drop due to solubility).

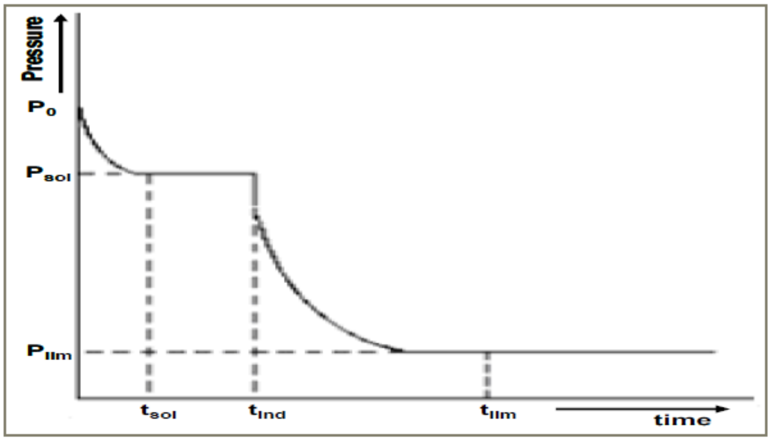


Figure 2.2: 'Pressure vs. Time' Graph

After that it is associated with the thermodynamics driving force. The common driving force is Subcooling and Supersaturation. Besides the two parameters, in kinetics formation of hydrate, the history of the water involved in the formation is also important, though some researches claimed that there is evidence of non-existence of this memory effect (Olivia & Livio, 2014). Since the kinetics of hydrate formation is still a current research and not fully understood, a few numbers of theories has been brought up to explain the mechanism of kinetics hydrate. Another example suggested that gas hydrates form in an autocatalytic reaction mechanism (Lederhos, Long, Sum, Christiansen, & Sloan Jr, 1996).

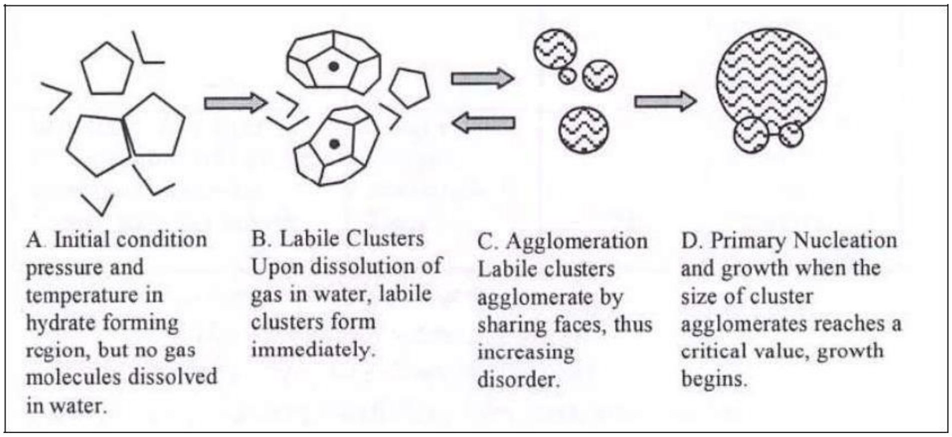


Figure 2.3: Autocatalytic reaction mechanisms for hydrate creation

## 2.2 Potassium Oxalate Monohydrate (POM)

### 2.2.1 Why we need additives?

The appealing uses of gas hydrates in industry are stalled down by some of the problems it carries such as the slow formation rate. As the natural gas solubility in water is potentially low, this has resulted only a thin layer of gas hydrates are formed at the interface between the water and gas. Accordingly, there are two methods to overcome this problem using chemical and mechanical means. By mechanical perspective, the method comprises of stirring technique, spraying and bubbling of gas in the continuous phase (O Iwasaki, Katoh, Nagamori, & Takahashi, 2005). In term of chemical point of view, this problem can be overcome by adding low dose of surfactant to alter the properties of reactant system. The function of surfactants are to reduce the gas and liquid interfacial tension as well as to enhance the solubility of gas in liquid water. Surfactant such as Sodium Dodecyl Sulfate (SDS) is proven to decrease the formation time and enhance the gas storage efficiency. Other than that, this surfactant aid in minimizing the mass transfer and difficulties in movement during the formation phase. Besides SDS and POM, there are many previous surfactants are used to study their effectiveness in enhancing the formation, such as calcium hypochlorite, linear alkyl benzene sulfonic acid etc. (Sun et al., 2011).

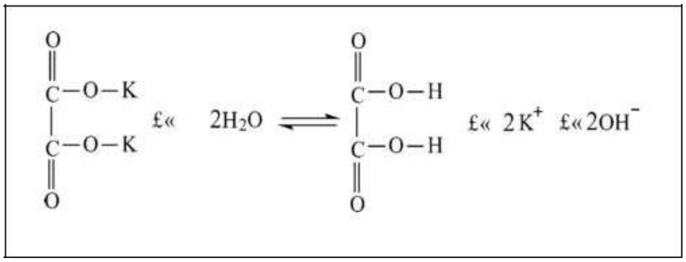
### 2.2.2 Background of Potassium Oxalate Monohydrate

Potassium oxalate monohydrate is also known as Oxalic Acid which belongs to the group of dicarboxylic acids. This compound is colorless and miscible in alcohol, ether and water. POM's molecular weight is 184.21 g moles and it is the only probable compound with two carboxyl groups joined together. This is the factor which contributes oxalic acid to be one the strongest acids in organic compounds. It is also promptly oxidized and can merge together with potassium to form less soluble salts named oxalates. Oxalates are useful as reducing agents for various uses such as precipitation of rare-earth metals in processing operations, bleaching agent in textile, and as a reagent in analytical chemistry (Chemicalland21, 2013).

### 2.2.3 History of Potassium Oxalate Monohydrate on Gas Hydrates

POM is an ionic surfactant. This additive is colorless crystal powder and severally tested on previous research to study the effect on the formation growth of gas hydrates. It is proposed that POM could develop the template of gas hydrates formation and termed as 'templating agent' which will provide the suitable setting for the formation. Basically, there are two reasons why it is selected as additive (Zhang et al., 2004).

- Contain low concentration of salt that may promote the hydrate formation
- In chemical reaction of POM, the [$K^+$] and [$OH^+$] enchanced the formation microcavities of a crystal lattice as well as help the hydrate formation. Below is the chemical reaction formula in POM aqueous solution:



$$(\text{COOK})_2 \;\text{£«}\; 2H_2O \rightleftharpoons (\text{COOH})_2 \;\text{£«}\; 2K^+ \;\text{£«}\; 2OH^-$$

Figure 2.4: Chemical Reaction Formula in POM aqueous solution

# CHAPTER 3

# METHODOLOGY

## 3.1 Project Activities

Figure 3.1 shows the project activities for the project throughout the research work period

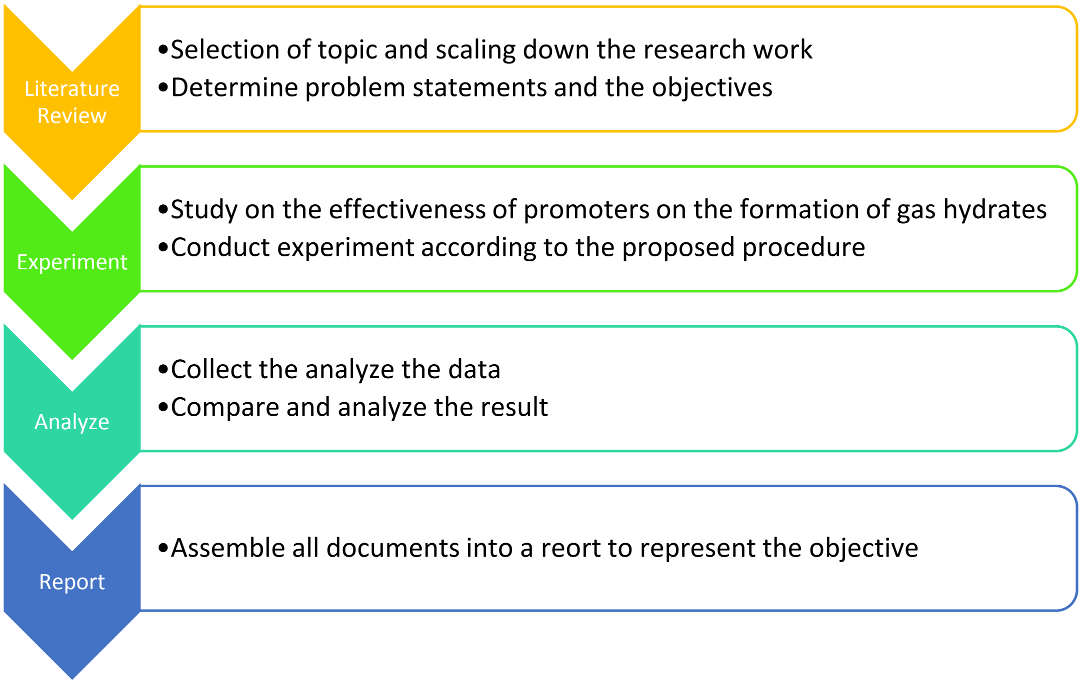


*Figure 3.1: Project activities*

## 3.2 Experiment Procedure

### 3.2.1 Solution Preparation

1. In this project, four concentrations were used which 100 ppm, 375 ppm, 750 ppm and 1500 ppm
2. A 100ml of 6000 ppm of POM solution was generated/ready in the lab
3. This concentrated solution (6000ppm) is use to create the four concentrations by dilution method
4. Pour approximately 20 ml of 6000 ppm POM solution into a beaker
5. By using special device, eVol® XR hand-held automated analytical syringe, a specific volume is taken out from the beaker and dispensed to a conical flask
6. This specific volume is calculated by using $M_1V_1 = M_2V_2$ formula. Example are as below for all concentrations

*Figure 3.2: eVol XR hand-held automated syringe*

Example for 100 ppm:

$$M_1V_1 = M_2V_2$$

$$(6000)(x) = (100)\ (100)$$

$$X = 1.6667\ ml$$

Example for 375 ppm:

$$M_1V_1 = M_2V_2$$

$$(6000)(x) = (375)\ (100)$$

$$X = 6.25\ ml$$

Example for 750 ppm:

$$M_1V_1 = M_2V_2$$

$$(6000)(x) = (750)\ (100)$$

$$X = 12.5\ ml$$

Example for 1500 ppm:

$$M_1V_1 = M_2V_2$$

$$(6000)(x) = (1500)\ (100)$$

$$X = 25\ \mathrm{ml}$$

7. After that, the conical flask is fill with distilled water till the 100 ml line
8. Shake the conical flask thoroughly to mix the solution

### 3.2.2 Experiment set-up

1. The water bath system was remove from the reactor
2. The high pressure vessel was unlocked using Hex Key
3. The reactor was opened and clean inside it using deionized water
4. After that, the steel reactor was dried using a special oven at temperature of $100^{O}C$ for about 15 minutes
5. The reactor was taken out from the oven after it was completely dried and let it cool in standard temperature for about 30 minutes.
6. Solution was poured into the reactor, followed by the stirrer. For example 100ml of 100 ppm POM
7. Reactor was sealed tightly using Hex key
8. The liquid bath system was installed on the reactor
9. Reactor was prepared for vacuum process

### 3.2.3 Reactor vacuum

1. At the reactor system, the inlet and outlet valve was opened to allow circulation.
2. Switched on the vacuum pump at the vacuum section system
3. The feed switch was set to open, while the outlet switch was set to close
4. At the pressure controller system, the power was switched on
5. Select the external for the feed selection and open for the output switch
6. The compressor gas pipeline valves was opened
7. Wait till the pressure become 0 bar (indication of vacuum process is complete)

### 3.2.4 Gas Purging

1. At the reactor system, close the inlet and outlet valve to stop circulation of any gas
2. Switch off the vacuum pump at the vacuum section system
3. The feed switch is set to close, while the outlet switch is remain close
4. At the pressure controller system, select external for the feed selection and open for the output switch
5. Close the compressor gas pipeline valves
6. Open the valve for the desired gas to be purged in the reactor
7. At the pressure controller system, set the pressure at 55 bars for methane gas and 35 bars for carbon dioxide gas
8. Open the inlet valve of the reactor to allow gas to be purged
9. Raise the temperature to 22$^{o}$C to aid the purging process

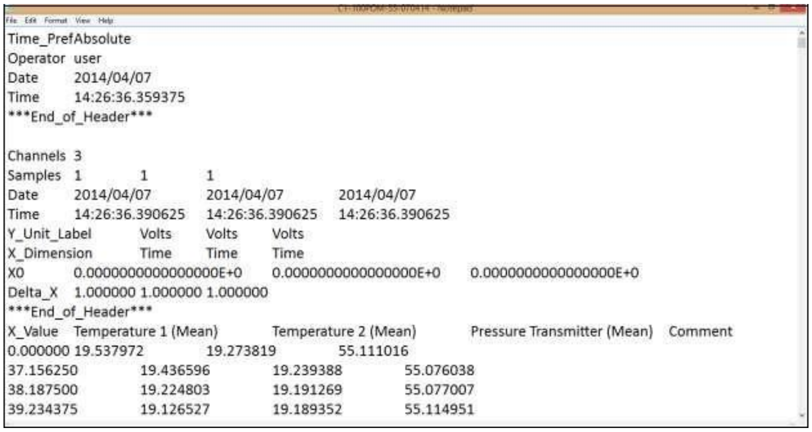
### 3.2.5 Running the experiment

1. Wait for the pressure to stabilize at 55 bars or 35 bars
2. While waiting, set the magnetic stirrer at optimum stirring rate which is at 300 rpm
3. When pressure has stabilized, set the temperature at 15$^{o}$C and wait till it stabilizes
4. Once the temperature has stabilized, press the record button on the computer and again set the temperature to 0$^{o}$C.
5. After the temperature reach and stabilize, set the temperature up to 15$^{o}$C
6. Stop the recording when the temperature stabilize at 15$^{o}$C.

## 3.3 Data Calculation

In order to estimate the formation kinetics of gas hydrates, several parameters need to be analyzed first. The data that was produced from the experiment such as time, temperature and pressure were then being used to calculate for latter results. These results which, the degree of subcooling, induction time, formation rate and mole consumed were essential for estimating and predicting the effectiveness of addictive (POM) on the formation kinetic of gas hydrates.

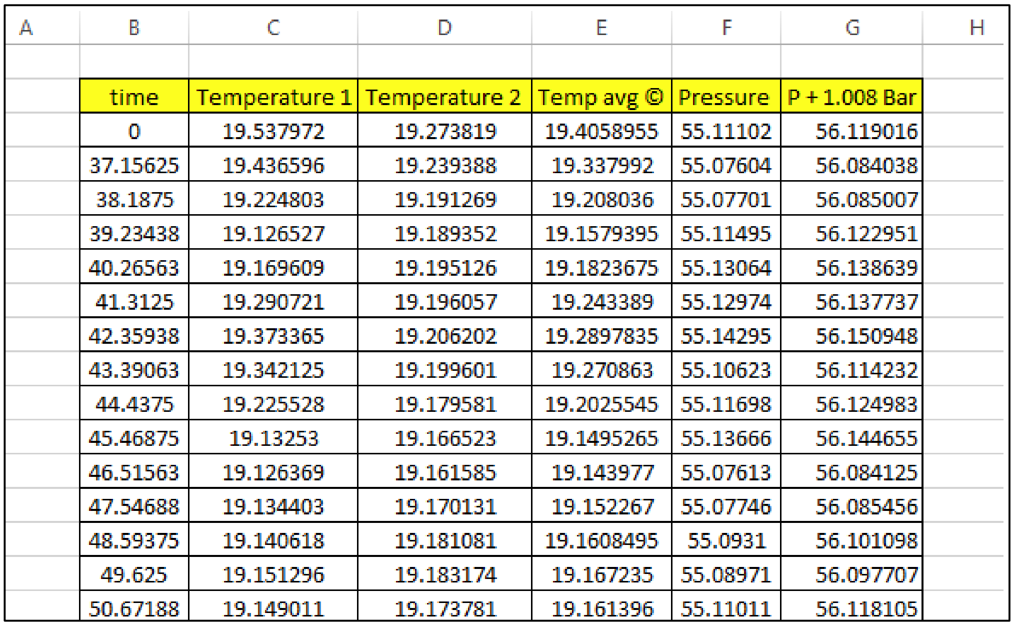
Basically, a single run of experiment is specifically for a single concentration, for example using 100 ppm of POM in methane or carbon dioxide gas. This experiment normally took about one day to be completed and done before continuing to next concentration. The raw data that was taken from the lab is in LabView format, it is then converted to a viewable format such as notepad. These values was then transferred to Excel for analysis and manipulation to other figures.



```
Time_PrefAbsolute
Operator  user
Date      2014/04/07
Time      14:26:36.359375
***End_of_Header***

Channels  3
Samples   1               1               1
Date      2014/04/07      2014/04/07      2014/04/07
Time      14:26:36.390625 14:26:36.390625 14:26:36.390625
Y_Unit_Label      Volts   Volts   Volts
X_Dimension       Time    Time    Time
X0        0.0000000000000000E+0   0.0000000000000000E+0   0.0000000000000000E+0
Delta_X   1.000000 1.000000 1.000000
***End_of_Header***
X_Value   Temperature 1 (Mean)    Temperature 2 (Mean)    Pressure Transmitter (Mean)   Comment
0.000000 19.537972        19.273819       55.111016
37.156250         19.436596       19.239388       55.076038
38.187500         19.224803       19.191269       55.077007
39.234375         19.126527       19.189352       55.114951
```

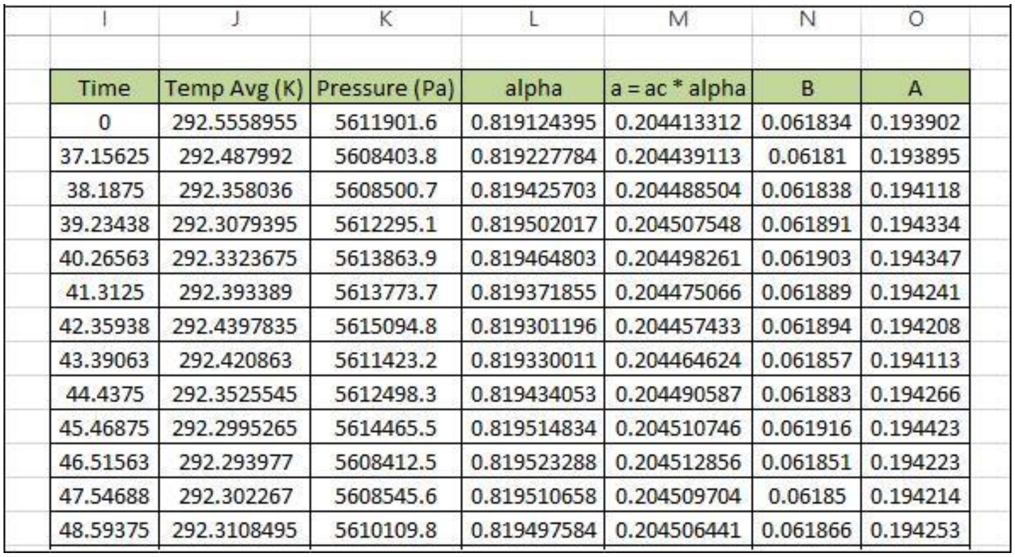
*Figure 3.3: Screenshot of raw data*



| time | Temperature 1 | Temperature 2 | Temp avg © | Pressure | P + 1.008 Bar |
|---|---|---|---|---|---|
| 0 | 19.537972 | 19.273819 | 19.4058955 | 55.11102 | 56.119016 |
| 37.15625 | 19.436596 | 19.239388 | 19.337992 | 55.07604 | 56.084038 |
| 38.1875 | 19.224803 | 19.191269 | 19.208036 | 55.07701 | 56.085007 |
| 39.23438 | 19.126527 | 19.189352 | 19.1579395 | 55.11495 | 56.122951 |
| 40.26563 | 19.169609 | 19.195126 | 19.1823675 | 55.13064 | 56.138639 |
| 41.3125 | 19.290721 | 19.196057 | 19.243389 | 55.12974 | 56.137737 |
| 42.35938 | 19.373365 | 19.206202 | 19.2897835 | 55.14295 | 56.150948 |
| 43.39063 | 19.342125 | 19.199601 | 19.270863 | 55.10623 | 56.114232 |
| 44.4375 | 19.225528 | 19.179581 | 19.2025545 | 55.11698 | 56.124983 |
| 45.46875 | 19.13253 | 19.166523 | 19.1495265 | 55.13666 | 56.144655 |
| 46.51563 | 19.126369 | 19.161585 | 19.143977 | 55.07613 | 56.084125 |
| 47.54688 | 19.134403 | 19.170131 | 19.152267 | 55.07746 | 56.085456 |
| 48.59375 | 19.140618 | 19.181081 | 19.1608495 | 55.0931 | 56.101098 |
| 49.625 | 19.151296 | 19.183174 | 19.167235 | 55.08971 | 56.097707 |
| 50.67188 | 19.149011 | 19.173781 | 19.161396 | 55.11011 | 56.118105 |

*Table 3.1: Data in Excel spreadsheets*

The unit for temperature and pressure was converted to SI unit from Celsius to Kelvin and Psi to Pascal in order to calculate the number of mole using PV=znRT.



| Time | Temp Avg (K) | Pressure (Pa) | alpha | a = ac * alpha | B | A |
|---|---|---|---|---|---|---|
| 0 | 292.5558955 | 5611901.6 | 0.819124395 | 0.204413312 | 0.061834 | 0.193902 |
| 37.15625 | 292.487992 | 5608403.8 | 0.819227784 | 0.204439113 | 0.06181 | 0.193895 |
| 38.1875 | 292.358036 | 5608500.7 | 0.819425703 | 0.204488504 | 0.061838 | 0.194118 |
| 39.23438 | 292.3079395 | 5612295.1 | 0.819502017 | 0.204507548 | 0.061891 | 0.194334 |
| 40.26563 | 292.3323675 | 5613863.9 | 0.819464803 | 0.204498261 | 0.061903 | 0.194347 |
| 41.3125 | 292.393389 | 5613773.7 | 0.819371855 | 0.204475066 | 0.061889 | 0.194241 |
| 42.35938 | 292.4397835 | 5615094.8 | 0.819301196 | 0.204457433 | 0.061894 | 0.194208 |
| 43.39063 | 292.420863 | 5611423.2 | 0.819330011 | 0.204464624 | 0.061857 | 0.194113 |
| 44.4375 | 292.3525545 | 5612498.3 | 0.819434053 | 0.204490587 | 0.061883 | 0.194266 |
| 45.46875 | 292.2995265 | 5614465.5 | 0.819514834 | 0.204510746 | 0.061916 | 0.194423 |
| 46.51563 | 292.293977 | 5608412.5 | 0.819523288 | 0.204512856 | 0.061851 | 0.194223 |
| 47.54688 | 292.302267 | 5608545.6 | 0.819510658 | 0.204509704 | 0.06185 | 0.194214 |
| 48.59375 | 292.3108495 | 5610109.8 | 0.819497584 | 0.204506441 | 0.061866 | 0.194253 |

*Table 3.2: Data in Excel spreadsheet*

### 3.3.1 Calculation Results

Most of the calculations involve in this project was spent on finding the mole at every interval of time. After the calculation of mole is complete, the data were manipulated against time to find the formation rate and mole consumed. Peng Robinson equation of state was used to find the number of mole at every interval of time. Below are the procedure, formulas used and as well as an example of calculation using **100 PPM of POM (Methane gas)**, at a single interval time.

$$Z^3 - (1 - B)\,Z^2 + (A - 3B^2 - 2B) - (AB - B^2 - B^3) = 0 \quad \text{——} \quad \textit{equation (1)}$$

- $b = 0.077726\,\frac{RT_c}{P_c}$, where Tc and Pc are critical temperature and pressure.

  *Calculation example:*

$$b = 0.077726\,\frac{(8.314)(190.56)}{4599000}$$

$$b = 0.0000268$$

- $a_c = 0.457235\,\frac{R^2 T_c{}^2}{P_c}$

  *Calculation example:*

$$a_c = 0.457235\,\frac{(8.314^2)(190.56^2)}{4599000}$$

$$a_c = 0.249551$$

- $m = 0.37564 + 1.542226w - 0.26992\,w^2$

  *Calculation example:*

$$m = 0.37564 + 1.542226(0.014) - 0.26992\,(0.014)^2$$

$$m = 0.397178$$

- $\alpha = (1 + m\left(1 - T_r{}^{0.5}\right))^2$, where Tr = T/Tc

  *Calculation example:*

$$\alpha = (1 + (0.397178)\left(1 - (\frac{292.55}{190.56})^{0.5}\right))^2$$

$$\alpha = 0.81912$$

- $a = a_c \, x \, \alpha$

  *Calculation example:*

$$a = 0.249551 \, x \, 0.81912$$

$$a = 0.2044$$

- $B = \frac{bP}{RT}$

  *Calculation example:*

$$B = \frac{(0.0000268)(5611901)}{(8.314)(292.55)}$$

$$B = 0.061834$$

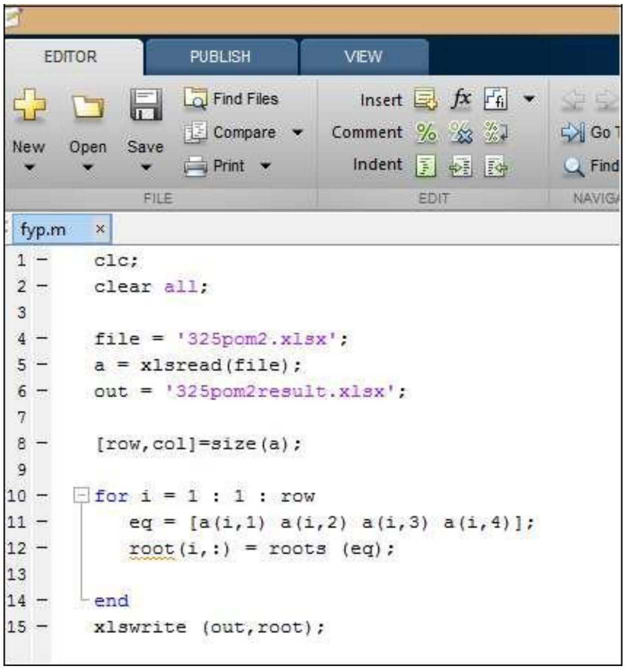
- $A = \frac{aP}{(RT)^2}$

  *Calculation example:*

$$A = \frac{(0.244)(5611901)}{((8.314)(292.55))^2}$$

$$A = 0.193902$$

The value of A and B was then substituted into equation (1). From this, a cubic equation was formed. After that, the roots of this equation was calculated. The highest value and ranging from 0.7 to 0.9 was selected. This root fundamentally represent the z-correlation which will be used in the equation of state to find number of mole. Due to excessively large number of data (at least more than 40000 data) and the impossibility of solving one by one using Excel, Matlab software was used to overcome this problem. A simple coding using the function of ‘For’ and ‘Roots’ was built to solve all the equations. Below is the snapshot of the coding.



```
clc;
clear all;

file = '325pom2.xlsx';
a = xlsread(file);
out = '325pom2result.xlsx';

[row,col]=size(a);

for i = 1 : 1 : row
    eq = [a(i,1) a(i,2) a(i,3) a(i,4)];
    root(i,:) = roots (eq);

end
xlswrite (out,root);
```

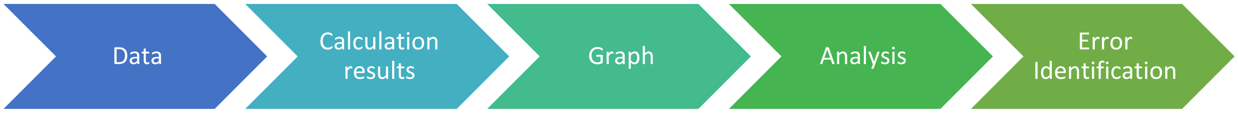
*Figure 3.4: Coding to find roots of equation*

After obtaining the root of the equation or Z-value, the number of mole is calculated in Excel using the formula n = (PV)/(ZRT). This procedure was repeated for other concentration. All of the data, for example the pressure, temperature, time and number of mole are used to find the degree subcooling, induction time, mole consumed and formation rate.

# CHAPTER 4

# RESULT AND DISCUSSION

In every several steps, there were results to be presented before proceed to further step until final result is acquired. Below is the illustration of the results analogy throughout the project.



## 4.1 Data Results

### 4.1.1 Induction Time

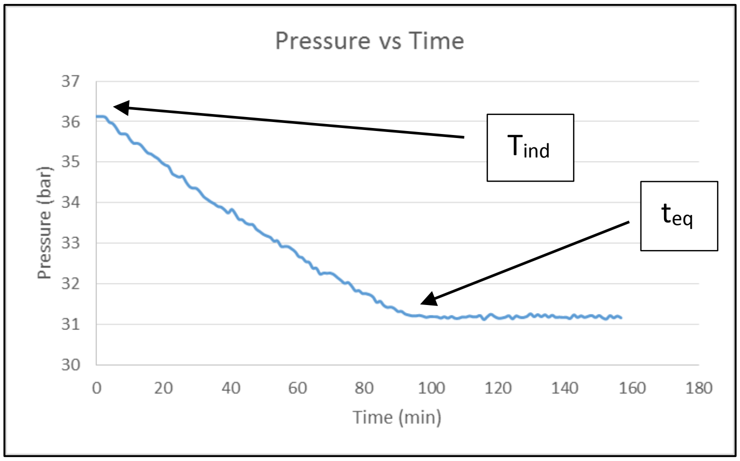


*Figure 4.1: Pressure vs. Time graph, ex: 100ppm using CO2*

Induction time is the time elapsed during the nucleation processes which include formation of gas-water clusters and their growth to stable nuclei with a critical size. From pressure-time graph, the induction time can be obtained by finding the time difference between time at equilibrium and time hold. Time equilibrium is the time taken when system start to stabilize at $0^{o}$C, meanwhile time hold is the time taken when a sudden pressure drop is observed.

$$\Delta t = t_{eq} - t_{ind}$$

### 4.1.2 Degree of Subcooling

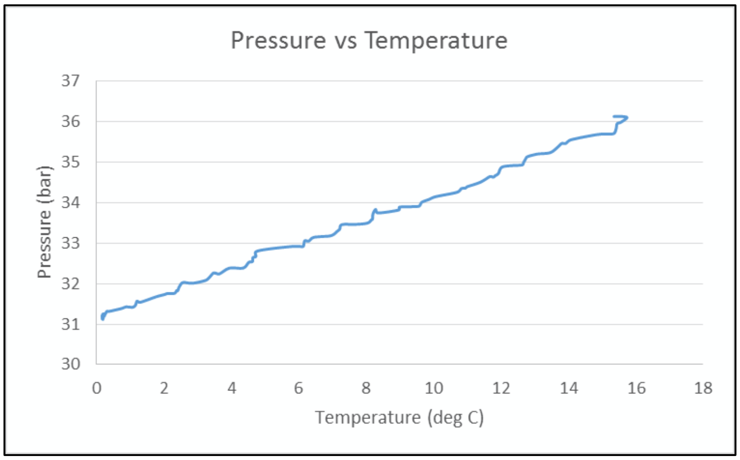


*Figure 4.2: Pressure vs. Temperature graph, ex: 100ppm using Co2*

From the above Pressure vs Tempperature graph, it can be observed that pressure is directly proportional to temperature based on pressure law when the temperature is set to 0°C from 15°C.

$$\frac{Pressure}{Temperature} = constant$$

From pressure-temperature relationship, the degree of subcooling can be gained by calculating the temperature span between T equilibrium and T induction. Normally, in this project the degree of subcooling are slightly around 13°C to 16°C for all concentrations regardless of gas surrounding.

### 4.1.3 Mole Consumed

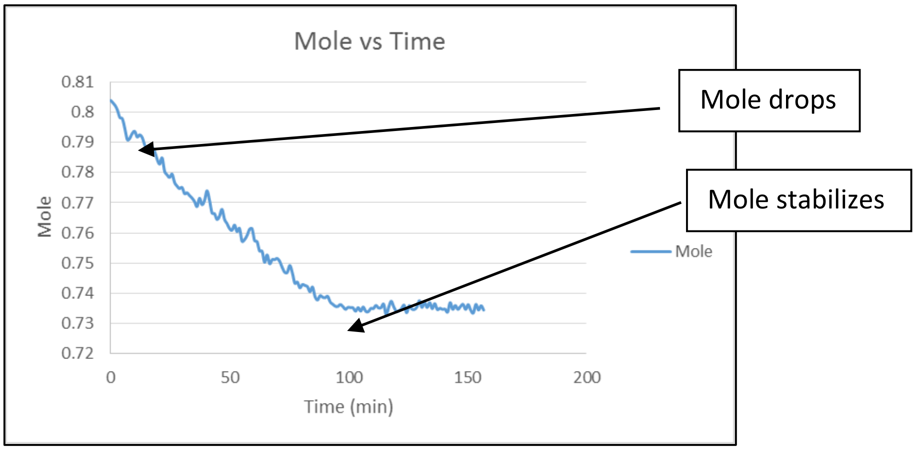


*Figure 4.3: Mole vs. Time graph, ex: 100ppm using CO2*

The mole-time graph is created to find two parameters which are the mole consumed and the formation rate. The mole consumed can be found in the graph by calculating the height of Y-axis from the point where mole starts to drop till it stabilizes. Mole consumed means the amount of gas has been taken and stored in hydrate from the gas surrounding in the reactor. Meanwhile, the formation rate means how fast the gas hydrates are formed in term of time. This can be simply achieved by divide the mole consumed with time in minute.

## 4.2 Result and discussion using Methane gas

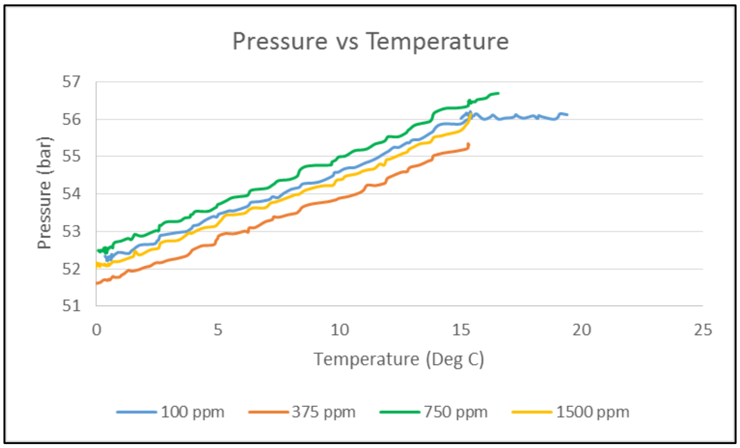


*Figure 4.4: Degree of Subcooling graph for all concentrations (methane)*

Based on the experimental using methane gas, the result shows that the degree of subcooling for all concentrations are nearly the same at about 14$^{o}$C to 16$^{o}$C due to the experiment procedure where it is required to use initial temperature at 15$^{o}$C and cool down to 0$^{o}$C. However, the difference between 375 ppm and 750 ppm in terms of pressure height is may be because to the random error or the disability of the reactor to sustain pressure in the vessel at certain value.

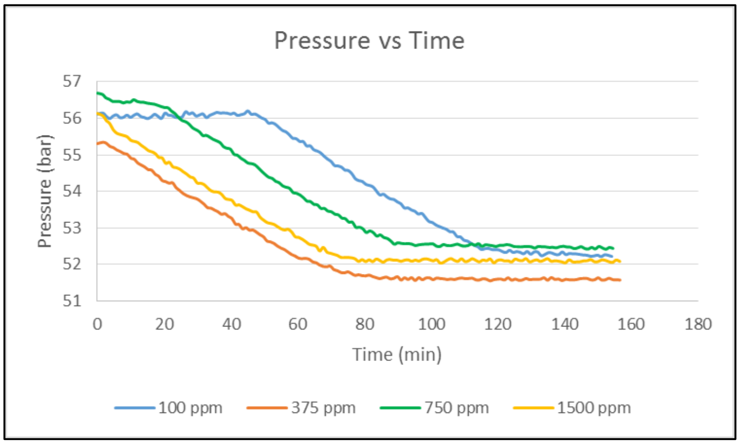


*Figure 4.5: The Induction Time graph for all concentrations (methane)*

| Concentration | Time equilibrium (min) | Time hold (min) | Time Induction (min) |
|---|---|---|---|
| 100 ppm | 115 | 50 | 65 |
| 375 ppm | 75 | 0 | 75 |
| 750 ppm | 90 | 24 | 66 |
| 1500 ppm | 80 | 0 | 80 |

*Table 4.1: Induction Time table for methane gas*

The graph above summarize the pressure-time relationship for all the concentrations involved in this project which is 100ppm, 375ppm, 750ppm and 1500ppm. In this graph, the curves went down due to temperature decreased as it will obey the pressure law. According to table 2, we can conclude that by using 100ppm concentration, the induction time is the least by 65 minutes. In other word, it takes 65 minutes for the temperature to drop to zero meanwhile for other concentrations take slightly longer time by additional 15 minutes. However, this could not be accept as a precise answer as there are maybe some random error or human error during this project.

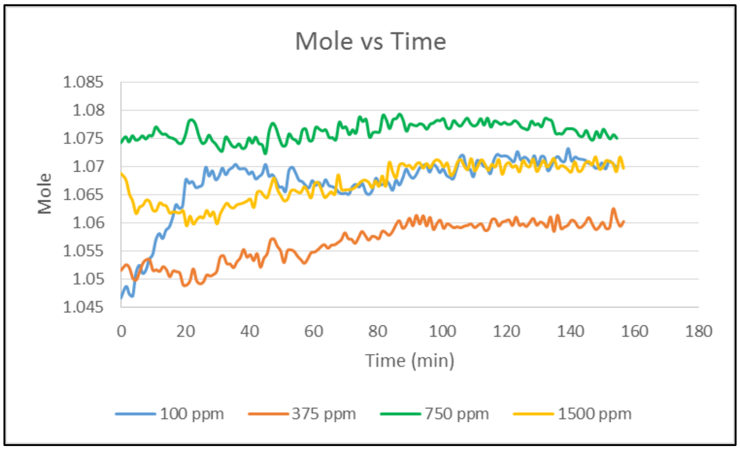


*Figure 4.6: The Formation Rate graph for all concentrations (methane)*

The graph above illustrates the trend of mole-time relationship for experiment using methane gas. In the literature review, it was anticipated the trend of the curve should go downward instead of constant or increasing. This is because the mole that was calculated is the mole for gas that was purged inside the reactor, instead of mole of hydrate. Hence, through period of time, when the hydrates are able to store the gases inside the cages, the mole of gas should get lesser. This graph was build up utill time 160 minutes where the temperature has stabilized at $0^{o}$C.

## 4.3 Result and discussion using Carbon dioxide gas

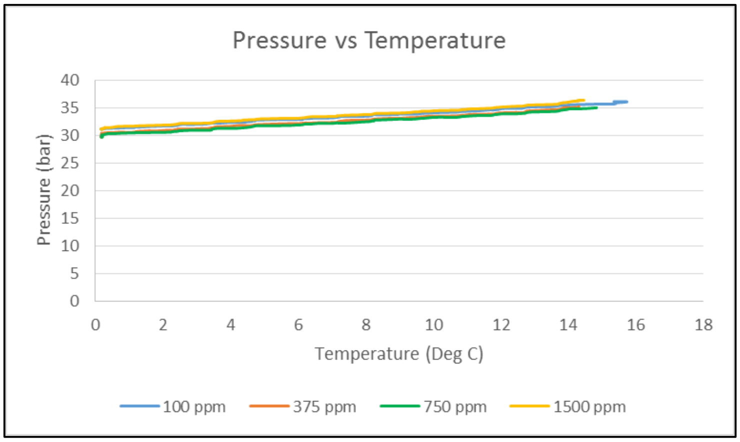


*Figure 4.7: Degree of Subcooling for all concentrations (Carbon Dioxide)*

Based on the experimental using carbon dioxide gas, the graph displays the degree of subcooling for all concentrations are approximately similar at about 14°C to 16°C due to the experiment procedure where it required to use initial temperature at 15°C and cool down the system to 0°C. In this run using Carbon Dioxide gas, it is observed that the line are nearly the same for all concentrations. This shows that no error occurred in data recording process for this part of test.

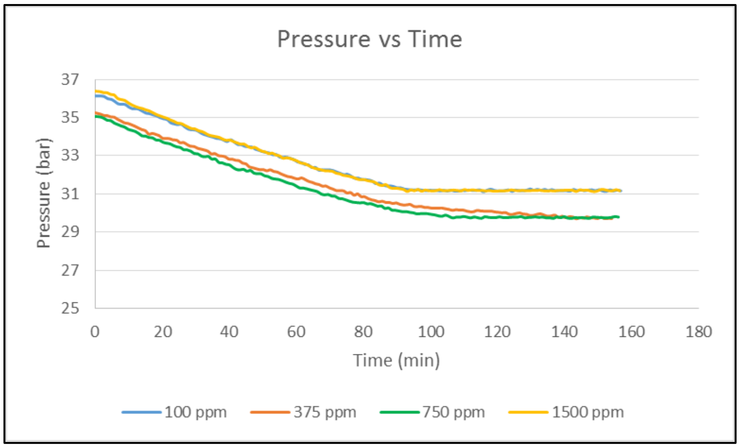


*Figure 4.8: The Induction Time graph for all concentration (Carbon Dioxide)*

| Concentration | Time equilibrium (min) | Time hold (min) | Time Induction (min) |
|---|---|---|---|
| 100 ppm | 92 | 5 | 87 |
| 375 ppm | 110 | 2 | 108 |
| 750 ppm | 106 | 2 | 104 |
| 1500 ppm | 93 | 6 | 87 |

*Table 4.2: Induction Time table for Carbon Dioxide gas*

Table 3 summarizes the comparison of the pressure-time relationship for all four concentrations. In this run using carbon dioxide gas, it is observed that the curve for all 4 parameters are closely identical compared to the test using methane gas. Both 100 ppm and 1500 ppm solution recorded the same induction time around 87 minutes. Meanwhile, it was recorded more than 100 minutes for both 375 ppm and 750 ppm. It was checked on both 375 and 750 ppm that these both run starts with pressure at 35 bars meanwhile for 100 and 1500 ppm at 36 bars.

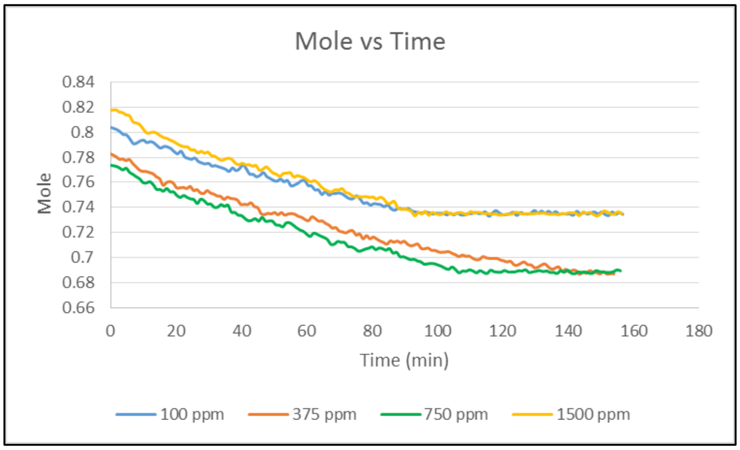


*Figure 4.9: The Formation Rate graph for all concentrations (Carbon Dioxide*

The graph above demonstrates the trend of mole-time relationship for experiment using carbon dioxide gas. For this experiment, the trend followed the suggested curve as describe in the literature review where the number of mole will decrease with time as the gases are trapped inside the cages of liquid molecule. In addition, in this experiment, it is easier to determine the mole consumed and formation rate compare to the previous experiment using methane gas where the graph shows numerous fluctuations. Table below summarizes the rate of formation and the mole consumed.

| Concentration | Mole Consumed (mol) | Time to stabilize (min) | Formation rate (mol/min) |
|---|---|---|---|
| 100 ppm | 0.069 | 97.36 | 0.000708 |
| 375 ppm | 0.09 | 141.22 | 0.000637 |
| 750 ppm | 0.09 | 106.67 | 0.000843 |
| 1500 ppm | 0.08 | 94.17 | 0.000849 |

*Table 4.3: Summarize of mole-time relationship*

## 4.4 Overall discussion on result

In order to choose the best and optimum concentration for both experiments using methane and carbon dioxide gas, the screening process have been made. The value of time induction must be as low as possible. If the time induction is reduced, it means the hydrates formed faster. Hence, based on the result using methane gas, 100 ppm concentration generated the least time induction compare to other 3 concentrations. Meanwhile for test using carbon dioxide, it was discovered that using 100 ppm and 1500 ppm produced similar induction time. As noted, the mechanism of the additive concentration affects the induction time of hydrate formation required further thorough study.

For the formation rate and mole consumed selection, the graph (figure 15) shows a constant mole consumed and even negative trend which are likely different from the literature review and the result anticipated for mole-time relationship graph. Unlike using carbon dioxide gas as the guest molecules (figure 18), it shows downward curves which what as expected. Through this, the mole consumed and formation rate can be found. In overall statistic for run using $CO_2$ gas, it shows using 1500ppm of POM solution will generate a good mole consumed at around 0.08 mol within 94.17 minute compare to its nearly competitive result, which is using 750 ppm solution which produces 0.01 mol higher but with a slower time to stabilize. The overall shows 1500 ppm produces 0.000849 mol per minute (mol/min). As noted, the more the gas molecules are in the liquid phase, the more chances they have to collide and trap inside the cages made by hydrate bonded water molecules which also helps the formation of hydrate nuclei.

Hence, in methane gas surrounding, 100 ppm was selected as the best concentration because it produces the shortest time induction, however due to the fluctuation on the mole-time graph, the result for formation rates could not be achieved as it is treated as error in machine. For the test using $CO_2$ gas, the best concentration is by using 1500 ppm POM solution as it yields the shortest time induction as well as decent formation rate compared to other concentrations.

# CHAPTER 5

# CONCLUSION AND RECOMENDATION

## 5.1 Conclusion

The experimental run using methane gas and carbon dioxide gas using different concentrations were successfully done by utilizing the high pressure kinetic vessel. No major accident had occur. As for screening result, it shows that concentration of 100ppm for methane gas and 1500ppm for carbon dioxide gas are the best for both of the surrounding gas. However, this is also depends on the water solubility of the gas in order to get in contact with the water cages. Other than that, the effect of pressure, temperature and the stirrer rate also plays important role in determining the results. In overall, this experimental study of formation kinetics of $CO_2$ and $CH_4$ gas hydrates in presence of additive, Potassium Oxalate Monohydrate, has showed a result that improved the formation rate however they are **not significant**. In other word, using POM would not largely affect the formation rate nor the induction time in terms of potentially utilizing it in industry as there are other additives would produce better result.

## 5.2 Future Work

The experiment only conducted at one pressure for each gas surrounding which is 35 bars for carbon dioxide and 55 bars for methane gas. Pressure can be reflected as one of the parameters that need to be given more attention especially when purging the gas in the reactor as it would determine the concentration of gas in the reactor. Hence directly contribute to the variety of mole consumed data. Other than that, the recommendation would be to consider more time frame for completing the project and adding the experimental set-up for future works as the understanding of gas hydrates is important to industry and more rapid research need to be done. This will also help in term of saving time as other student also use the same experiment set up for his project.

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