

**Enhancement of Kinetic Hydrate Inhibitor Polyvinylpyrrolidone(PVP) with
Addition of Polyethyleneoxide (PEO)**

by

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Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

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CERTIFICATION OF APPROVAL

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in partial fulfilment of the requirement for the
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UNIVERSITI TEKNOLOGI PETRONAS
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September 2012

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.

AFIQ SAFEEUDDIN BIN NORDIN

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ABSTRACT

Gas hydrates are well known problem in oil and gas industry that cost millions of dollars in production and transmission pipelines. By definition, hydrate is a solid clathrate structure, non-stoichiometric, formed due to the nucleation of polyhedral water cages which encapsulates the “guest” molecules comprises of lighter hydrocarbon such as methane and ethane at elevated pressure and low temperature. The concern on hydrate is due to its problem in blocking the pipeline, by disrupting the flow assurance capabilities in production. Hydrate is very common in a dedicated gas well which are rich in inert gases that might contribute as major constituents of hydrate structure such as carbon dioxide, sulphur dioxide and nitrogen. Basically, hydrate can be divided into 3 main clusters which are :

1. Structure 1: Very common type encases of carbon dioxide, and low hydrocarbon molecules such as methane and ethane.
2. Structure 2 :Hydrate encases of nitrogen, propane and butane
3. Structure H : hydrate encases of large mole structure such as neohexane, cyclopentane.

3 alternatives used in oil and gas industry to inhibit the hydrate formation and growth.

1. Thermodynamic Inhibitor(THI) : Earliest and most common method for controlling hydrate. THI lowers the freezing point of the aqueous solution, similar to anti-freeze agent. Example of THI is methanol or glycol.
2. Anti-Agglomerants(AA) : It allows the amount of gas hydrate but act to suppress the propagation and agglomeration by dispersing the hydrate in oil or condensate phase.
3. Kinetic Hydrate Inhibitor : Motivation of KHI development believes that this type of inhibitor delay the initial hydrate nucleation. Extensive research believes that the KHI can also lengthen the time required for succession growth of hydrate after the first nucleation.

In this project, Polyethyleneoxide (PEO) is non-ionic, water soluble, linear polymer is used as an additives added to Polyvinylpyrrolidone(PVP). PEO is actually made up into a long chain of polymer with n repeating units. PEO in water exhibits and inverse solubility temperature relationship. The objective of the work undertaken in this study is to check on the performance of PEO in adhering to existing kinetic hydrate inhibitor in lengthening the induction time. The

PEO will be added to the PVP in trace amount to see the performance of the new formulation to further lengthen the induction time for hydrate formation and growth. In particular, the existing PVP has limited efficiency in lengthening the hydrate induction time.

Since PEO exists abundantly in nature, it is feasible to use this kind of additives as catalyst in kinetic hydrate inhibitor. In this study, Micro Differential Scanning Calorimetry (DSC) will be used to experiment the heat flow that really occurs in hydrate labile cluster until its bulk phase formation. Heat flow in this structure can be either endothermic or exothermic reaction. From the trend of the graph produced, one can easily identify the induction time for hydrate formation with respective of composition of kinetic hydrate inhibitor. Besides, the result of hydrate induction time will be compared with other potential kinetic hydrate inhibitor which is the Calcium Magnesium Acetate (CMA).

Although the study of kinetic hydrate inhibitor is still new, but the expected result is believed to be promising in terms of its economic viability and environmental friendliness. KHI will beat the Thermodynamic Hydrate Inhibitor (THI) as low dosage and cost effective hydrate inhibitor.

CHAPTER 1 : INTRODUCTION

1.1 Background of Study

In the middle of 1810, first description of hydrate is made by Sir Humprey Davy. Predominantly, in his description, water encapsulates the gas molecules under suitable temperature and pressure. In precise word, the hydrate is favourable to form in an environment with low temperature at elevated pressure. Physical properties of hydrate that can be observed using the PVT analysis tools is it exists in snowy like formation, but can be start its first nucleation above the freezing point of water, 0 degree Celcius.

Foundation of gas hydrate study is provided by Hammerschmidt in 1940. By defining the favourable condition of hydrate formation, four common means are introduced to prevent hydrate formation by keeping the system outside of the hydrate stability region.

1. Remove water from the system
2. Increase the temperature to dissociate the hydrate
3. Decrease pressure until the system is out of hydrate stability region
4. Inject inhibitor such as mono ethylene glycol(MEG) to shift thermodynamic stability region so that hydrate will not form in the current temperature and pressure.

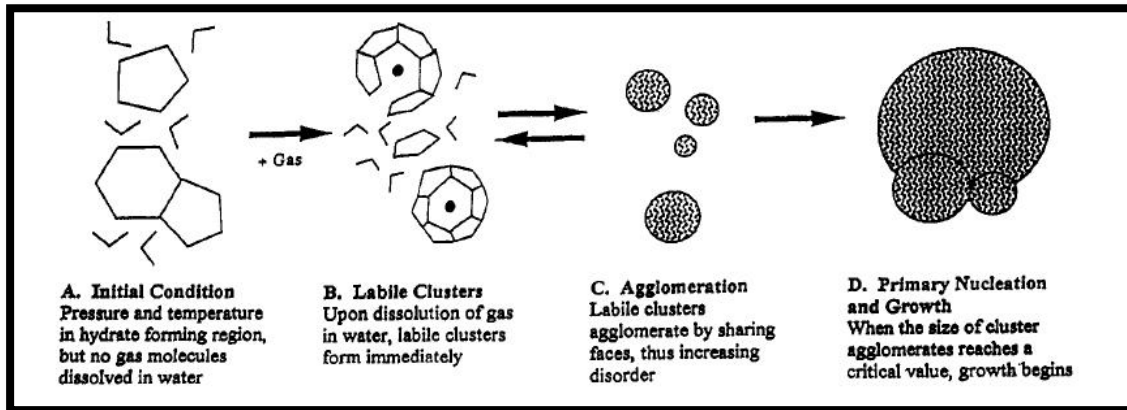


Figure 1 : Typical Stage of Hydrate Nucleation

In 1990, Sloan further discussed on the nature and type of hydrate. Through the X-ray and neutron diffraction, hydrate structure is categorized to different type, which are structure I, II and H, encases different constituent in hydrate composition.

The earliest method of hydrate prevention using THI is not economically viable due to its logistic issue and environmental pollution. THI is needed in high concentration to work effectively up to 50wt%. A huge amount of MEG is needed to be injected to reservoir to work on the hydrate inhibition. The environment will be polluted by the THI upon discharge. Motivation on the alternatives to prevent hydrate is further made. Unlike THI, KHI and AA works in different manner. KHI is needed in lower dosage rather than thermodynamic inhibitor (THI). Thus, KHI is economically viable in terms of cost optimization and utilization of logistic wise because of easy handling and less impact to pollution upon discharge.

PVP has proved to be the promising hydrate kinetic inhibitor. It consists of five member lactam rings attached to the carbon backbone. Lactam rings are characterized by the amide groups attached to the (-N-C---O-) polymer backbone (Sloan 1995). This is the place where chemical additives are attached to. In this study, PEO will be the representatives to reflect the effectiveness of KHI in further lengthening the induction time or hydrate nucleation. This polymer inhibits similar properties on hydrate formation just like lactam polymers, by interaction of the pendant alkylamides groups to the hydrate surface. The hydrate surface is made up of various open cavities where small hydrocarbon molecules (methane, ethane) would normally be placed in filled cavity in gas hydrates.

The pendant of the alkylamide group reacts to hydrate surface in two ways :-

- 1) Small alkyl group penetrate the open cavity
- 2) Amide group hydrogen bonds to the hydrate surface via carbonyl group “locking”.

1.2 Problem Statement

It is very obvious that the oil and gas industry is striving to find a new formulation to cope with the problem in existing hydrate inhibitor. The most former method is by injecting thermodynamic inhibitor in the pipeline to keep the system out of hydrate stability region. A very high concentration of THI is needed (25-50wt%) costly in offshore developments and onshore processing facilities. KHI usage can be an important economic factor to consider when developing the small to medium fields. As an alternatives, Kinetic Hydrate Inhibitor (KHI) has been proposed but the main drawback seems limited in efficiency. As the result is not satisfying, industry is still looking for a other classes Kinetic Hydrate Inhibitor which can yield higher degree of subcooling. One of the best proposal is by adding the Kinetic Inhibitor such as Polyvinylpyrrolidone(PVP) with additives. The most wide and commercially used in industry is called Polyvinylcaprolactam(PVCap), forming through the addition of caprolactam to PVP. In this project. PEO will be used as an additives to mix with PVP. The succession of hydrate formulation is not only to delay the process of hydrate first nucleation but also be able to lengthen the growth phase after its first nucleation. By using PEO, environmental impact can be reduced since PEO is widely used in industry and can fully utilized as a new KHI once added to PVP.

1.3 Objective and Scope of Study

The objective of this project is to :

1. Determine the feasibility of PEO addition to PVP in increasing the induction time for hydrate formation.
2. Determine the best concentration of KHI needed to give the most optimum result in lengthening hydrate formation.

The scope of the study is narrowed to the potential of chemical additives added to PVP. If the experiment yields positive feedback by lengthening the hydrate nucleation, the new formulation will be compared to another new KHI that has not been used in industry which is the Calcium Magnesium Acetate (CMA). CMA is a simple combination of dolomitic lime and acetic acid produced at Cryotech's manufacturing facility in Fort Madison, Iowa. Plus, CMA is proven to be not corrosive and safe to be used and discharged to environment like PEO. The differences of

PEO to CMA is that , PEO is not meant to be used as sole inhibitor because it is more to an additives added in trace amount to the kinetic hydrate inhibitor, PVP. To rely on the sole content in PVP is not the best solution because the hydrate formation maybe delayed during the well shut in, but not during the multiphase flow. In multiphase flow regime, turbulent flow is anticipated to present along the pipeline which will be the likelihood of rapid hydrate formation

1.4 Feasibility of Project

The project relevance towards the oil and gas industry in Malaysia is quite promising as the service company is looking for hydrate prevention during production through kinetic inhibition. The time frame for doing research and development (R&D) in new proposal is very time consuming, thus it is better to initiate the findings as soon as possible. Once the proposal is approved, in 15 years period, the kinetic hydrate inhibitor can become the primary source of hydrate inhibition program rather than using conventional type of hydrate inhibition; the THI. In the relevancy of project towards environment must be taken into consideration. One can't simply design a formulation of kinetic hydrate inhibitor which may contribute to environmental pollution upon discharge. Thus, the formulation needs to be environmental free pollution. As the kinetic hydrate inhibitor is a type of chemical, the discharging of chemical to environment won't affect ecosystem if and only if the content of chemical is low. Yet, the best way of new formulation is to design the lowest weight percent of kinetic inhibitor in yielding the optimize effect against hydrate formation in system.

How long will it take to complete the project?

According to the Gantt Chartt, the completion of project can be achieved within the time frame which is below 7 months. It is important to follow the schedule even though it's quite tight. The author already scheduled plan with colleague who are doing the same project under hydrate to take turn using the same equipment which is the Micro Differential Scanning Calorimetry. The purchase order to buy chemical in preparation of sample has been made earlier to prevent too tight in schedule.

CHAPTER 2: LITERATURE REVIEW

2.1 Sloan E. D., Jr. (1998) Clathrate hydrates of natural gases. Second edition, Marcel Dekker Inc.:New York.

Before going into details on the experiment, one must identify the important constituent of hydrate that will be used in the procedure. In this project, carbon dioxide gas will be the absolute sample for hydrate gas. To understand the condition which favors the hydrate nucleation in rich carbon dioxide well, we need to identify the temperature of hydrate first nucleation with respect to given pressure. By observing and analyzing the carbon dioxide hydrate phase diagram, we can set the parameter for starting temperature at given pressure.

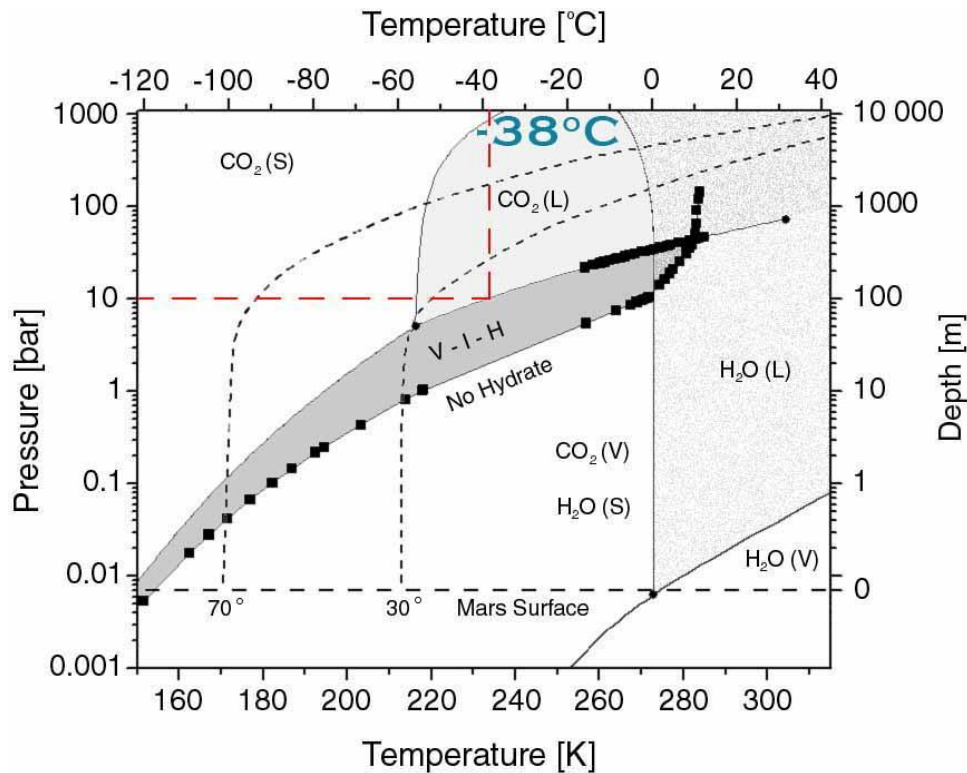


Figure 2 : Carbon dioxide phase diagram for hydrate

Based on the diagram above, if we set the apparatus at constant pressure (isobar), for instance 10 bar, we can correlate a straight line from y-axis 10 bar to the first point of hydrate formation, and propagate the straight line to top of x-axis indicating the temperature in degree Celcius. At 10 bar, the temperature for hydrate formation is at -38oC. Take note that the shaded area V-I-H is

composed of vapor, water ice , and hydrate. Looking at the trend of proposed graph, the carbon dioxide type of hydrate will form bulk of hydrate at elevated pressure and low temperature which is coherent to the initial hypothesis.

2.2 SPE 30642 Identifying Inhibitors of Hydrate Formation Rate with Viscometric Experiment by J.S. Kalbus

Firstly, the concern of this project is to find the effectiveness of adding chemical additives to PVP in order to create new formulation of KHI. According to the SPE 30642, by identifying the best chemical additives to be added to PVP via screening process, one can deduce the effect of chemical additives towards the time of hydrate first nucleation. Lists of chemical additives are used either being added to the PVP or stand-alone chemical additives without PVP. Examples of chemical additives added to PVP are:

- Mirataine CBS
- Sodium dodecyl sulfate(SDS)
- Mirawet ASC

Whereas the stand-alone chemical additives are:

- BASF F-127
- Surfonyl-465

The screening process is shown using a viscometric experiment. Based on the experiment done, PVP has shown a significant result by delaying the first nucleation of hydrate. By adding Mirawet ASC into the PVP, it is proved that the PVP delays the first nucleation and the succession on hydrate growth is inhibited by Mirawet ASC. The results also proved that the usage of KHI is needed in low dosage which is less than 1.0 weight percent. This reflects that the KHI provides less risk to environment and easy handling. In fact, Low Dosage Hydrate Inhibitor(LDHI) is lowering the chemical usage and discharge and improved the environmental profile of combined products when compared to the originally selected single application chemicals.

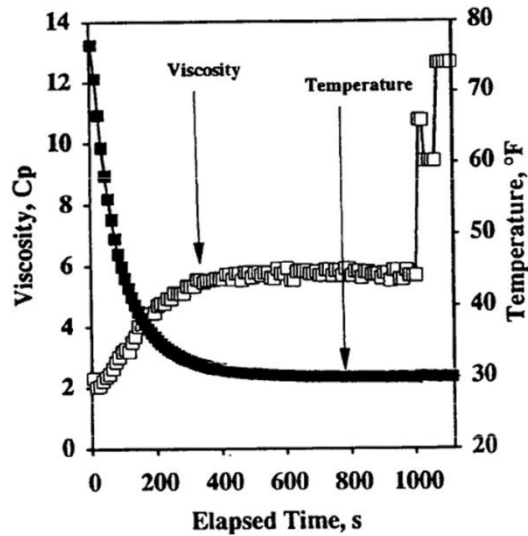


Figure 3 : Typical Viscosity and Temperature Response 20wt% THF and 80wt.% Filtered ASTM Sea Water at 34.0°F (without inhibitor only sample)

- From Figure 3, we can see that only the sample is tested without any inhibitor. A sharp increase in viscosity at 1000 seconds indicates the formation of hydrate. The hydrate formation is very fast due to the absence of any inhibitors in the sample to delay the nucleation of hydrate. Nevertheless, this sample is served to a standard only.

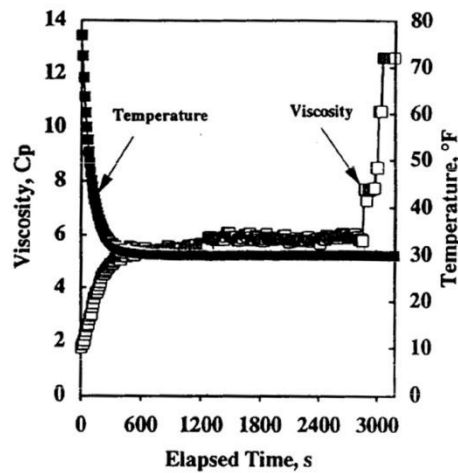


Figure 4 : Typical Viscosity and Temperature Response for 0.1wt% PVP in 20wt% THF and 80wt.% Filtered ASTM Sea Water at 34.0°F (PVP only)

- From Figure 4, 0.1 wt% of PVP is added into the THF and ASTM Sea Water. The result of first hydrate can be seen at 3000 seconds where the viscosity increases sharply. Thus,

the addition of PVP will lengthen the time for hydrate first nucleation in a factor of 3. The induction time for hydrate first nucleation compared to the sample without the inhibitor three times faster than the sample added with PVP.

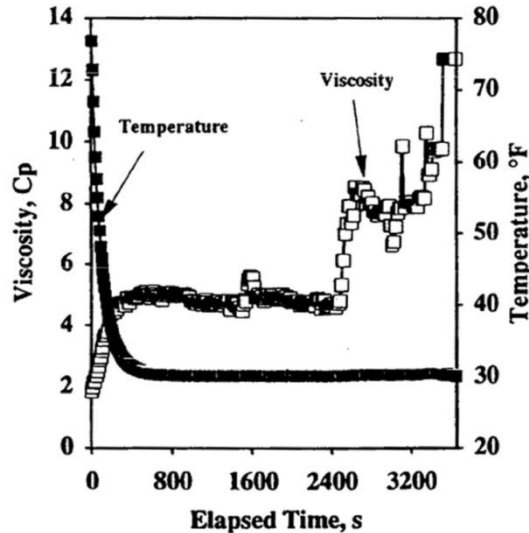


Figure 5: Typical Viscosity and Temperature Response for 0.1wt% PVP and 0.1wt% Mirawet ASC in 20wt% THF and 80wt.% Filtered ASTM Sea Water at 34.0°F(PVP and Mirawet ASC)

- From Figure 5, 0.1wt% of Mirawet ASC is mixed with 0.1wt% PVP then is put in the THF and ASTM Sea Water. We can see that the first hydrate nucleation can be seen at 2600 seconds. By then, after the hydrate formed, the growth phase is lengthen into almost steady rate of low viscosity increment. At 3600 seconds, the hydrate crystals growth continues. Based on the result of the experiment, we can deduce that the addition of Kinetic inhibitor such as PVP will delay the hydrate first nucleation
- The successive growth of hydrate is further inhibited by the Mirawet ASC for some period of time. Thus, addition of chemical additives will enhance the ability of PVP to delay first hydrate nucleation and also inhibit successive growth on hydrate crystals.

2.3 SPE 99388, Combined Kinetic Hydrate and Corrosion Inhibitor in Southern North Sea

KHI will not change the thermodynamic properties of hydrate formation by lowering the freezing point, but it promotes in delaying the first nucleation of hydrate and retard the hydrate growth overtime. In SPE 50683, it is proven that the KHI is more efficient in inhibiting structure I type hydrate. Structure I mostly comprises of inert gases such as carbon dioxide. According to this paper too, the Kinetic Inhibitor is best to move in the liquid phase. Since the KHI is a water soluble chemicals, it will saturate the gas to avoid vaporization of water contained in the additive formulation and to transport chemical in multiphase conditions. The KHI is used in lower concentration compared to methanol(THI) and also considered not harmful towards the environment.

2.4 Enhancement of Performance of Kinetic Inhibitors with Polyethylene Oxide (PEO)

Fourth literature review is from an excellent paper by Ju Dong Lee & Peter Englezos.

Kinetic inhibitors		
Product	Alias	Supplier
GHI 101	INH1	ISP Technologies (Wayne, NJ, US)
Inhibex 501	INH2	ISP Technologies
Luvicap EG	INH3	BASF Corporation (Charlotte, NC, US)
Luvitec K90	INH4	BASF Corporation
Luvitec VPC 55	INH5	BASF Corporation
K65 W		
Gaffix	INH6	ISP Technologies
VC-713		
PVP	INH7	ALFA AESAR (Ward Hill, MA, USA)
NEL-411-31	INH8	ISP Technologies

Figure 6 : Kinetic Inhibitors used in the experiment with respective Alias

Methane hydrate experiments				
No.	System	P_{exp} (kPa)	T_{exp} (K)	Induction time (min)
1	No inhibitor	6000	273.7	0.5
4	INH1	6000	273.7	1253
5	INH1 + P	6000	273.7	9006
6	INH2	6000	273.7	40
7	INH2 + P	6000	273.7	27
8	INH3	6000	273.7	86
9	INH3 + P	6000	273.7	148
10	INH4	6000	273.7	8.6
11	INH4 + P	6000	273.7	15.6
12	INH5	6000	273.7	6.5
13	INH5 + P	6000	273.7	82.3
14	INH6	6000	273.7	1.3
15	INH6 + P	6000	273.7	16.6
16	INH7	6000	273.7	6.6
17	INH7 + P	6000	273.7	7.3
19	INH8	6000	273.7	30
20	INH8 + P	6000	273.7	21.3

Figure 7 : Result for Induction Time (min) for hydrate crystallization and according to different sample.

Polyethylene oxide also is proved not to be a kinetic inhibitor by itself. Thus, PEO needs to have an initiator to be mixed in order to be an efficient kinetic hydrate inhibitor. As an example, polyvinylpyrrolidone(PVP) semi batch is added to the PEO to enhance the effectiveness of PEO as hydrate inhibitor. In an article in Chemical Engineering Science, “enhancement of performance of kinetic inhibitors polyethylene oxide”, the researchers said that the previous work has shown that PEO exhibits weak thermodynamic inhibition by itself. Therefore, several samples of Kinetic Inhibitor is proposed in the experiment to show the effect of kinetic inhibitor to the induction time for hydrate crystallization and rate of hydrate growth thru gas uptake measurement. One of the listed kinetic inhibitor used to prove the sample is PVP. The experiment is done with kinetic inhibitor alone(INH) and a mixture of aqueous solution 0.5wt% of KI and 0.025wt% of PEO (INH+P solution) . The experiment is also conducted isothermally and isobarically at which the temperature is maintained at absolute temperature 273.7K, and 2770kPa respectively. Table 1 shows the Kinetic Inhibitor sample used in the experiment

whereas Table 2 below shows the result of hydrate induction time from addition of KI and KI plus PEO solution.

In the absence of inhibitor, the time for hydrate to form in the system is approximately 30 seconds. From the table above, we can infer that the addition of 0.025wt% of PEO to any of these kinetic inhibitor will give positive feedback to hydrate inhibition by lengthening the induction time for first hydrate nucleation except for INH 2 and INH 8. The PVP kinetic inhibitor is represented with INH 7 sample. The additional PEO solution to INH 7 yield longer induction time for hydrate formation compared to PVP alone by 0.7 minutes.

2.5 The Effect of PVCap On Methane Hydrate Nucleation & Growth by Hailu K. Abay, Jonas Hovland & Thor.

In this paper, the study is conducted using methane as hydrate formers. A different concentration of PVCap is used to determine whether increasing the concentration of the KHI will yield positive feedback to the induction time of hydrate. Basically, the stimulation of KHI selection proves that the presence of active molecule such as the double oxide, nitrogen and oxyle on the PV Cap molecular structure makes it enable to attach to the surface of hydrate by means of adsorption. When it adsorb to the bulk surface of hydrate, hydrate will be unable to agglomerate further. Another study also conducted proves that the PVCap can reduce the diffusion of hydrate formers (gases) from the bulk phase where the hydrate growth prefers to proceed.

PVCap, dry powder with molecular weight 6000, was dissolved in deionized water at concentrations of 0, 20, 50, 100, 500, 1000, and 2000 ppm. The result for the hydrate is showing that the effectiveness of the PVCap is not the function of concentration.

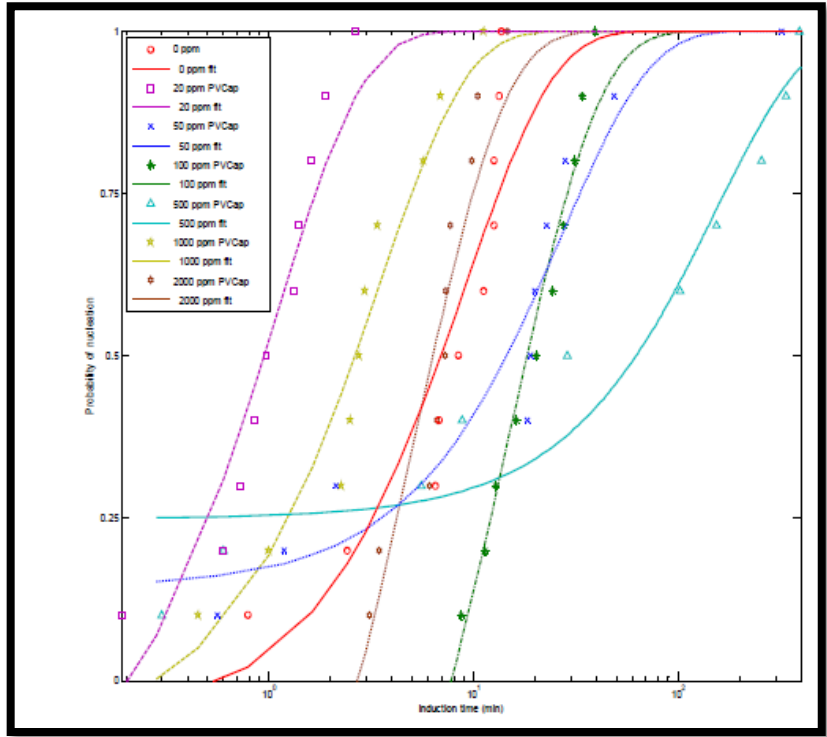
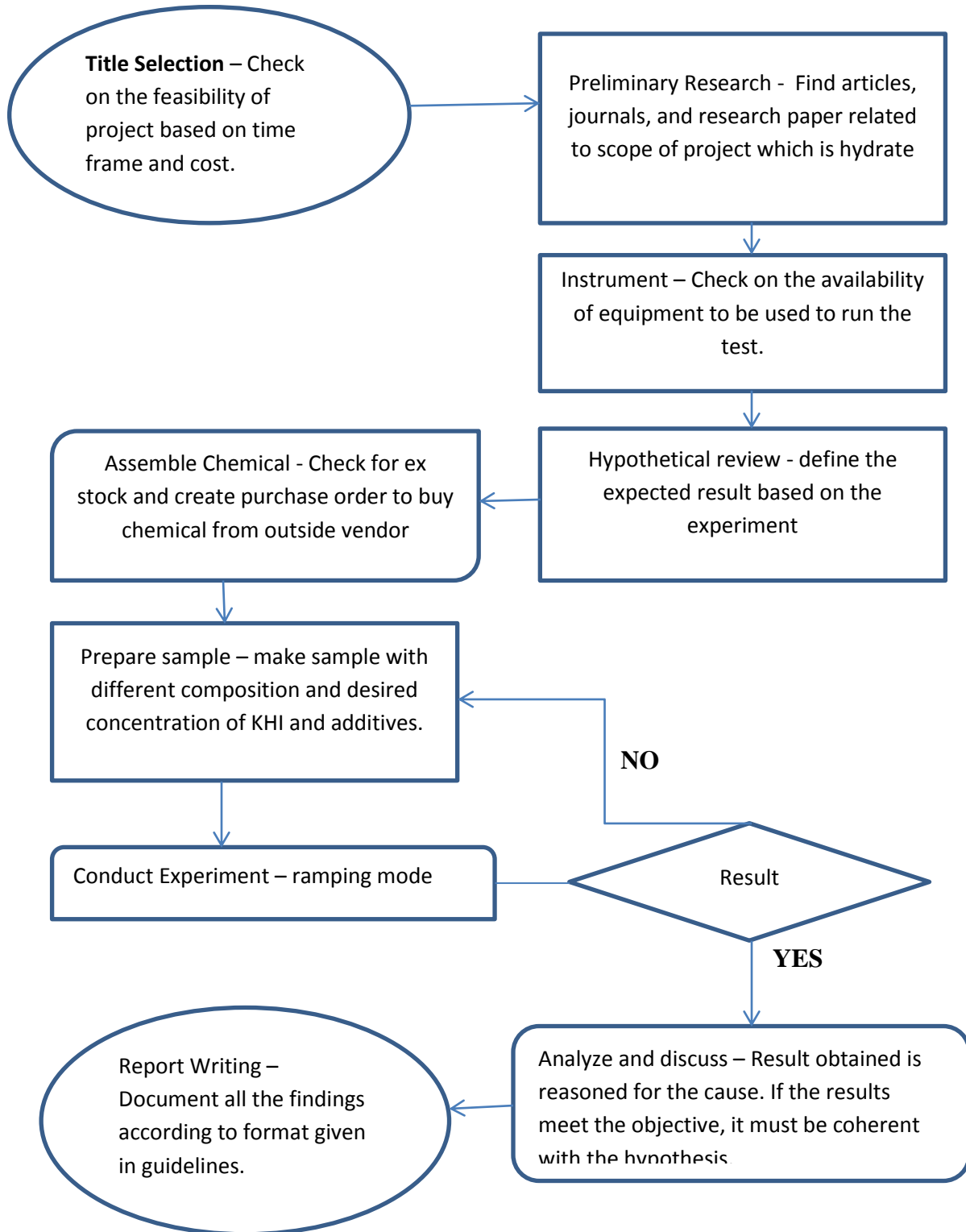


Figure 8 : Probability of Hydrate Nucleation from different concentration of PVCap.

From the graph, the most promising result using different concentration of PVCap is the best for 50 and 500ppm of PVCap. It yields longer induction time for hydrate to first form. From here, we can deduce that the proper selection of concentration of KHI is needed to ensure optimum result.

CHAPTER 3: METHODOLOGY

3.1 Project Activities



3.2 Procedure using Hardware/Software

3.2.1 Setaram Instrumentation- Micro Differential Scanning Calorimetry (MicroDSC) Evolution 7

This instrument is used to transfer heat flux to a sample that is measured versus time or temperature while the temperature of sample is programmed, in a controlled atmosphere. By following the differential in calorimetric in between the crucible sample and reference sample, the exothermic value can be validate.

For the case of this project, the samples (will be explained later) tested in 60 mg array of cell, with thermocouples totally surrounds the reference chamber. The diagram below depicting the experimental set up to simulate the ramp mode.

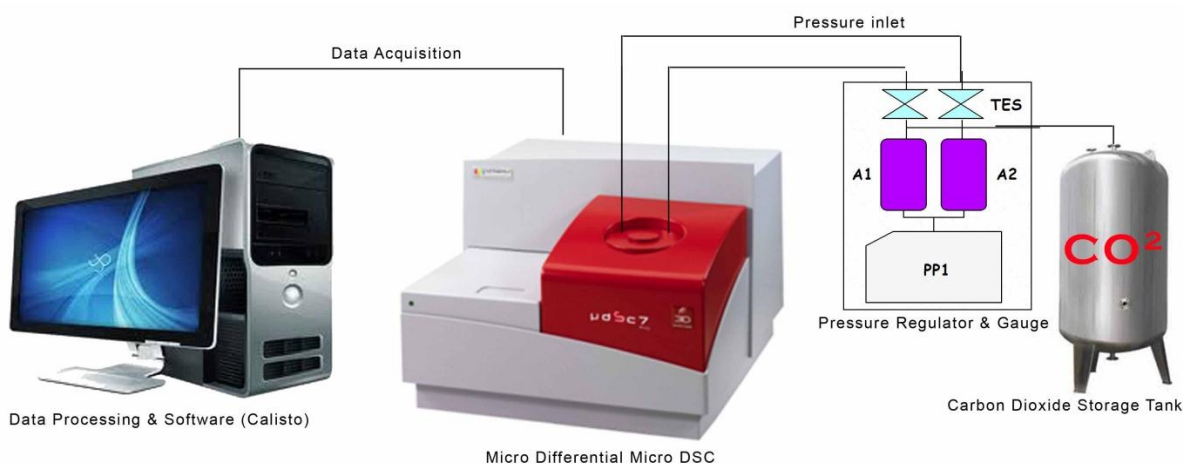


Figure 9 : Experimental Setup using Micro DSC

The carbon dioxide is used as hydrate formers, serve as a guest molecules in the condensate sample. Carbon dioxide is belongs to the hydrate structure I hydrate. Carbon dioxide is not potentially hazard, inflammable towards heat source compared to other hydrate gas formers such as methane and ethane.

3.2.2 Kinetic Inhibitors (Polyvinylpyrrolidone)

Polyvinylpyrrolidone(PVP) is one a KHI which already been used in oil and gas hydrate mitigation industries. It delays the offset for hydrate first nucleation. It belongs to acrylamide group. It consists of 5 members of lactam rings bonded together with active molecules known as the oxyle group, double oxide and nitrogen.

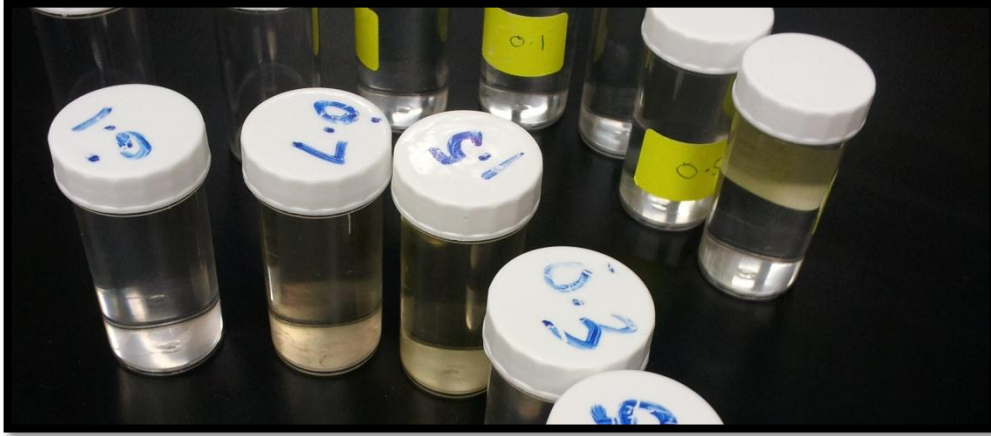


Figure 10 : Samples tested with different composition and concentration

Unlike PVP, PVCap comes with 7 members of lactam rings and have similar active molecules at carbon branch. As has been mentioned before, the lactam rings active molecules may adsorb to the bulk phase of hydrate formers to prevent further agglomeration of hydrate, thus time for hydrate first nucleation is lengthen.

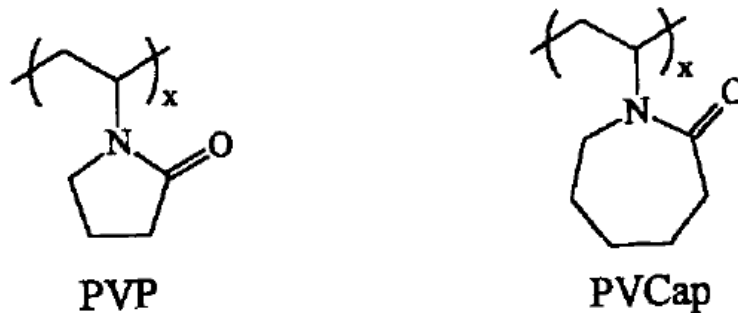


Figure 11: The molecular structure of acrylamide group PVP and PVCap.

3.2.3 Polyethylene oxide (PEO)

PEO is a water soluble, non-toxic long chain polymers. It is usually used in plastic products. The special properties that make it as promising additives to be added to KHI is that it is flexible and provide thickening and lubrication. Since it exhibit non-ionic properties, the end structure of PEO can combine with water to form a different concentration of solution.

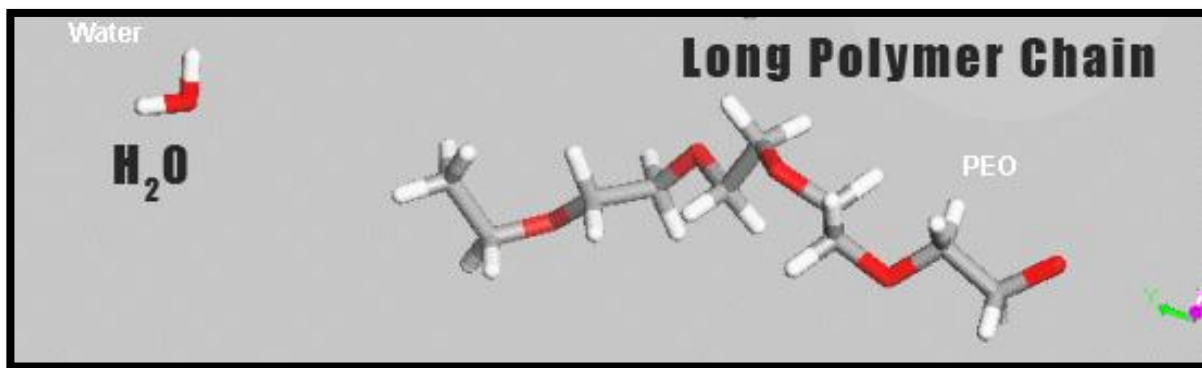


Figure 12: Long polymer chain of PEO can react with deionized water to form different concentration.

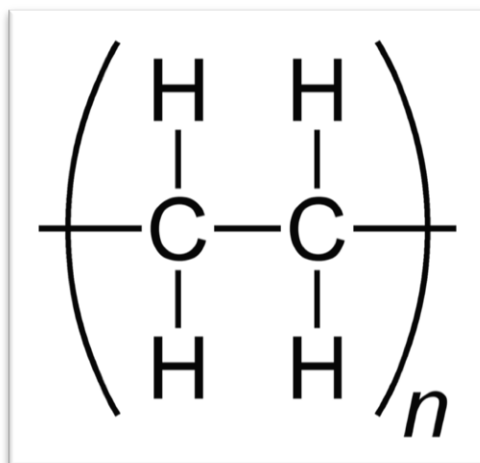


Figure 13: Single polymeric structure of PEO

The list of concentration to be used in the experiment is stated below :

- Deionized water (Blank Sample)
- 0.1wt% Polyvinylpyrrolidone
- 1.0wt% Polyvinylpyrrolidone
- 0.07wt% PVP + 0.03wt% PEO
- 0.7wt% PVP + 0.3wt% PEO

3.2.4 Procedure: Preparation of Sample

- 1) The solute is weighed on the electronic beam
- 2) 100ml of distilled water is poured into the beaker
- 3) The solute mass is poured little by little into the distilled water with constant stirring rate

$$\text{Mass percent of solution} : \frac{\text{Mass of solute or powder (g)}}{\text{Volume of 100 ml distilled water}} \times 100\%$$

- 4) The aqueous solution is kept in a container rated for chemical storage.

3.2.5 Procedure: Experiment Setup

- 1) The cell must be cleaned with distilled water and rinsed with dry air
- 2) Using disposable pipette, 60 mg of sample is dropped in the cell carefully using electronic beam balance.
- 3) The cell is brought and attached to the chamber
- 4) The cell is closed with the cap rated for medium pressure thread connection type Swagelok.
- 5) The valve for carbon dioxide supply is opened to the pressure regulator
- 6) Pressure regulator is controlled until reaching 30 bar (Isobar) and wait for the pressure to stabilize. It is important to make sure the connection has no leaking by checking on the digital pressure gauge.
- 7) Once the pressure is maintained, software Calisto is used to set the scanning rate and furnace temperature.
- 8) Scanning rate is set at 0.5°C per minute.

- 9) Temperature is set up at initial value of 25°C and the end value for the temperature is set at -25°C to check on hydrate formation curve(exothermic). See table below for more details.
- 10) The cell is reheated to 25°C to check on the hydrate dissociation curve.(endothermic)
- 11) The result is processed in Calisto, in the form of Graph Heat Flow (mW) versus Time(min) for all sample.

No.	Start Temp (°C)	End temp (°C)	Scanning Rate (°C/min)	Duration (min)	Gas intake	Process
1	25	25	-	10	CO ₂	stabilization
2	25	-25	0.5	60	CO ₂	cooling
3	-25	-25	-	10	CO ₂	stabilization
4	-25	25	0.5	60	CO ₂	heating
5	25	25	-	10	CO ₂	stabilization

Figure 14 : Table for Design of Experiment

No	Activities	Date
1	Project Work Continuation	Progress
2	Submission of Progress Report Prelim)	7/October/2012
3	Project Work Continuation	8/Oct/2012 – 25/Oct/2012
4	Pre-SEDEX	26/October/2012
5	Submission of Draft Report	2/November/2012
6	Submission of Dissertation (soft bound)	9/November/2012
7	Submission of Technical Paper	9/November/2012
8	Oral Presentation	16/November/2012
9	Submission of Project Dissertation (hard bound)	30/November/2012

Figure 15: Key Milestone

Activities	Baseline Start	Baseline End	2012			
			Sept	Oct	Nov	Dec
Project Work Continuation	Sept-12	07/10/2012				
Submission of Progress Report Prelim)	07/10/2012	07/10/2012				
Project Work Continuation	08/10/2012	25/10/2012				
Pre-SEDEX	26/10/2012	26/10/2012				
Submission of Draft Report	02/11/2012	02/11/2012				
Submission of Dissertation (soft bound)	09/11/2012	09/11/2012				
Submission of Technical Paper	09/11/2012	09/11/2012				
Oral Presentation	16/11/2012	16/11/2012				
Submission of Project Dissertation (hard bound)	30/11/2012	30/11/2012				

Figure 16: Gantt Chart

CHAPTER 4 : RESULT & DISCUSSION

The data acquisition is processed in Calisto software in ramping mode. Once the experiment is finished, the data is processed, tabulated and formed in graph of Heat Flow (mW) versus Time(min). The purpose of this plotted graph is to take a look at the trend of heat flow during the hydrate dissociation and formation.

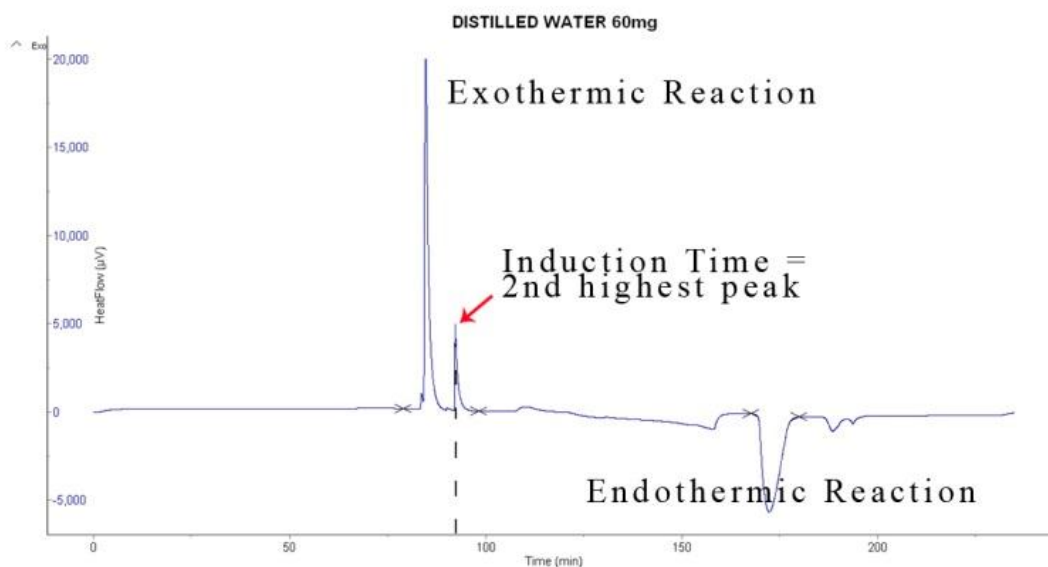


Figure 17 : Graph of Heat Flow (mW) versus Induction Time(min) for blank sample (deionized water)

The graph above is showing the trend of heat flow for sample with 60 milligram of deionized water. The deionized water serves as the blank sample (without addition of any inhibitors). Since the concern of kinetic hydrate inhibitor is to check on the induction time, one must know how to verify the precise timing from the graph. In a book written by Kalbus 1998, "Viscometric Experiment of Gas Hydrate", the induction time is defined as the time at which hydrate finish forming its bulk phase. If a system consists on gas hydrate such as carbon dioxide, the induction time for hydrate is calculated using the gas uptake measurement.

In this case using micro DSC, the induction time for hydrate formation is verified by looking at the second peak of heat flow (Fig. 17). The heat flow that is increasing sharply indicates the

exothermic reaction. In fact, when hydrate nucleation starts to cease, most of heat from the system is released to surrounding to allow the bond of labile cluster in orderly form. Usually, the first peak indicates the ice formation. Before labile cluster is form, ice will take precedent in forming hydrate because polyhedral water cages are formed first before gas molecules enter the entrapment.

The endothermic reaction is found from the tremendous decrease in heat flow. The heat energy is needed to break the bond of hydrate bulk phase. Thus, heat energy will be absorbed from the surrounding into the hydrate structure, initiating the breakthrough of labile cluster.

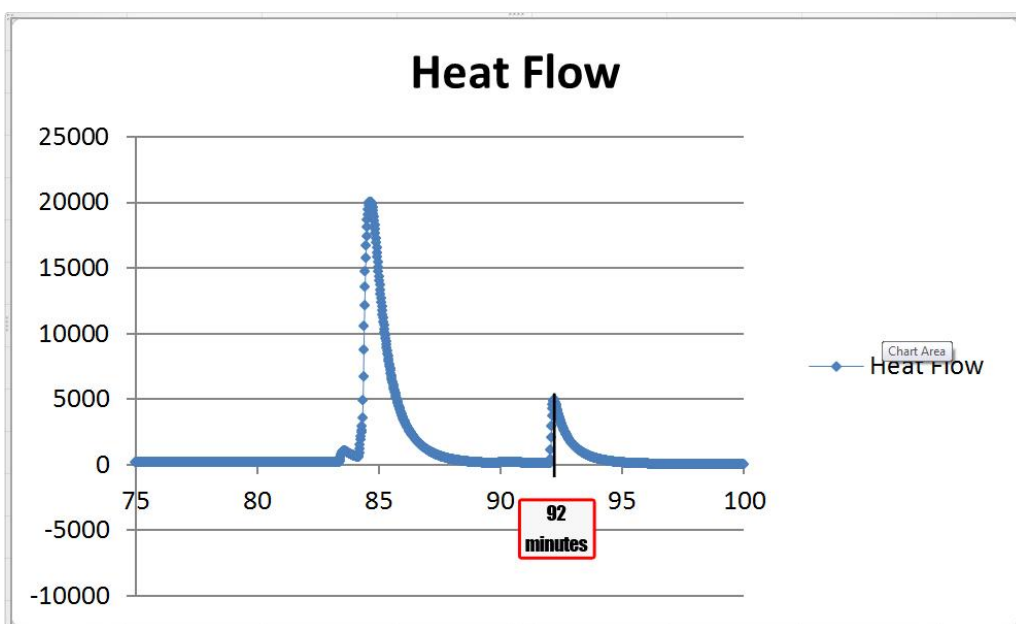


Figure 18: Graph of Heat Flow (mW) versus Time(min) for blank sample – MS Excel

From the graph of deionized water that has been zoomed in above, it can be deduced that the induction time for hydrate is 92 minutes when the inhibitors are absent. The result found served as the reference sample to check on the effectiveness of PVP alone and PVP added with PEO in terms of lengthening the induction time.

4.1 PVP 0.1 wt% 60mg)

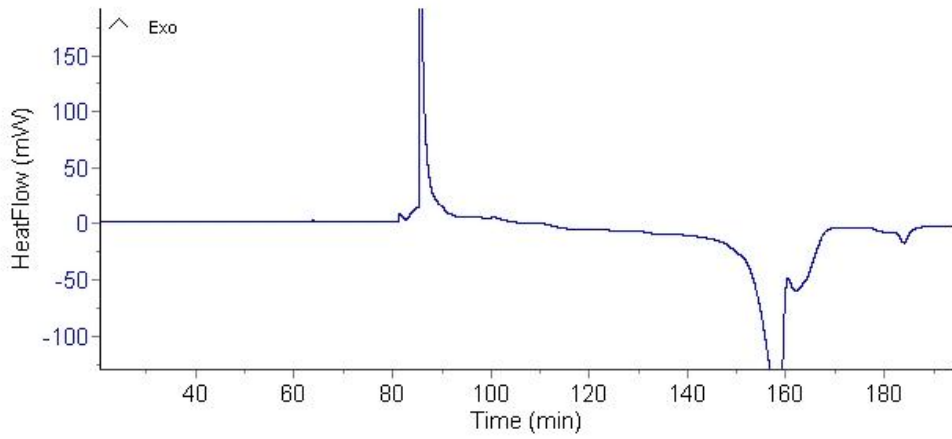


Figure 19 : Graph of Heat Flow (mW) versus Induction Time(min) for PVP 0.1 wt%.-**Calisto**

Heat Flow PVP 0.1wt%

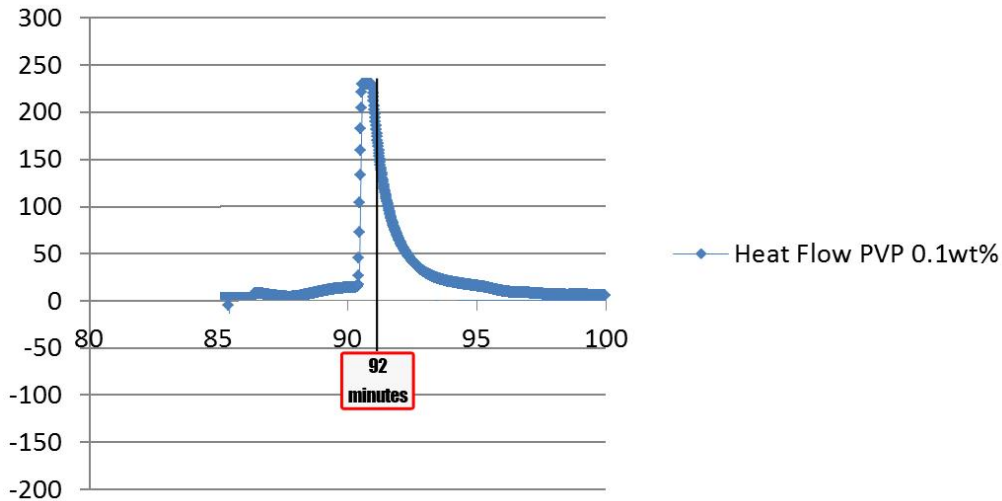


Figure 20 : Graph of Heat Flow (mW) versus Time(min) for PVP 0.1 wt%.-**MS Excel**

The graph above showing the heat flow versus time for 0.1.wt% PVP. The induction time for hydrate formation is 92 minutes. The value of induction time for PVP 0.1wt% and blank sample is the same. It can be deduced that 0.1wt% of PVP is not sufficient to lengthen the induction time.

4.2 PVP 1.0 wt% (60mg)

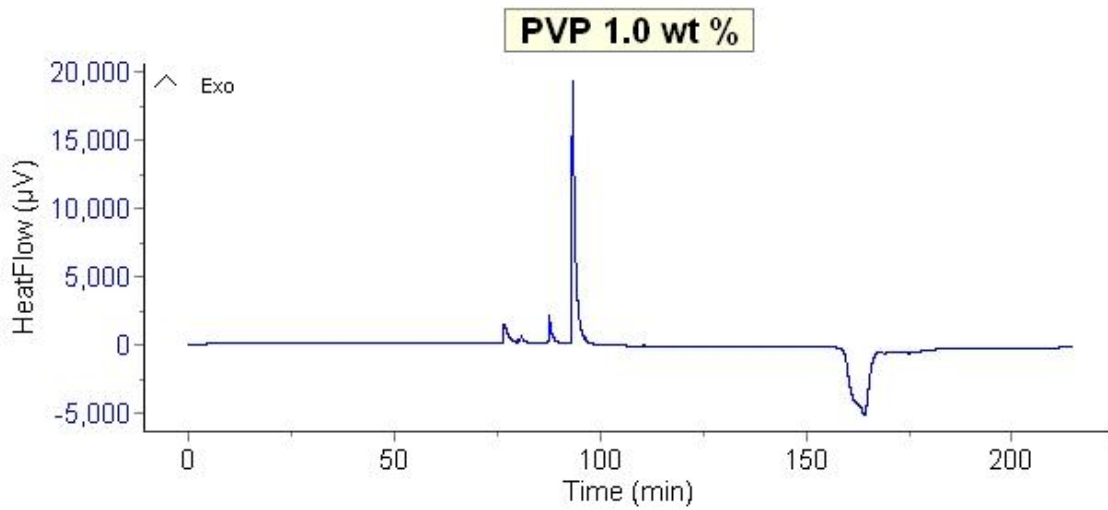


Figure 21 : Graph of Heat Flow (mW) versus Induction Time(min) for PVP 1.0 wt%-**Calisto**

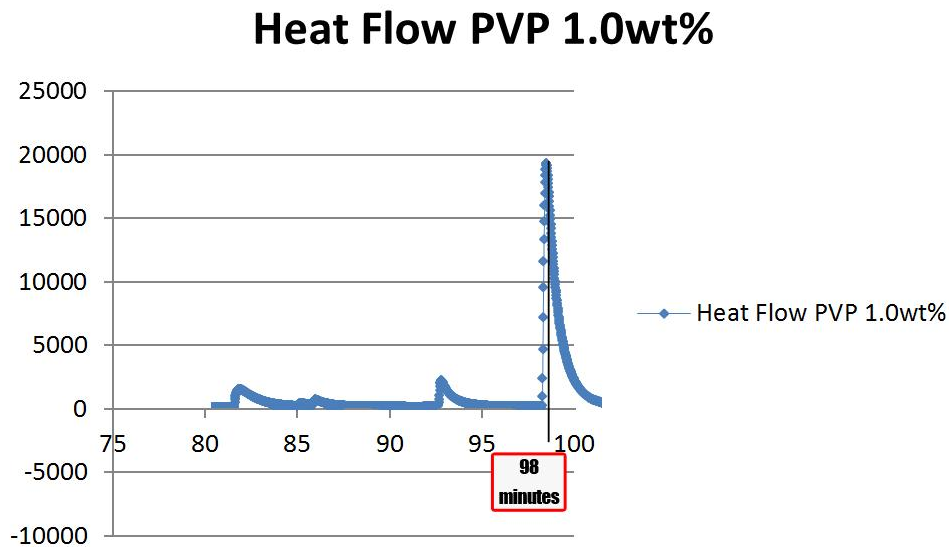


Figure 22 : Graph of Heat Flow (mW) versus Time(min) for PVP 1.0 wt%-**MS Excel**

The graph above is the result for sample using 1.0 wt% PVP. It can be observed that the exothermic reaction occur at several timing. Thus, the induction time is at the second highest peak of heat flow. The first peak is not too high, but it is significant for hydrate formation because it indicates the formation of ice before the successive bonding to bulk phase hydrate.

The ice can be observed at 75th minutes. Whereas, the induction time for hydrate formation is at 98th minutes. Comparing the result for this sample to the previous(0.1wt% PVP) , it can be concluded that increasing the concentration of PVP to 1.0 wt% will further prolong the induction time for hydrate by 6 minutes.

Increment (%)PVP 1.0wt% to blank sample

$$= \frac{\text{Ind. time PVP 1.0wt\%} - \text{Ind. time blank sample}}{\text{Ind. time blank sample}} \times 100\%$$

$$= (98 - 92) / 92 \times 100\%$$

$$= 6.52\%$$

4.3 PVP 0.07 wt% + PEO 0.03 wt% (60mg)

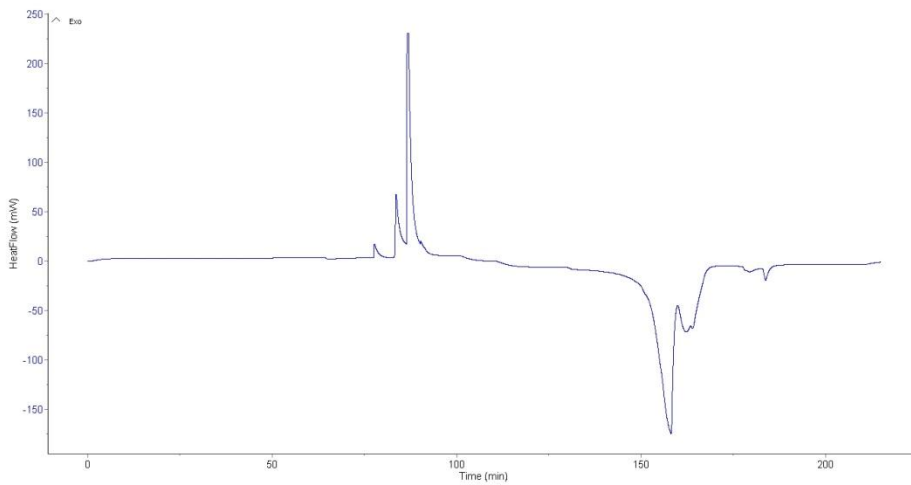


Figure 21 :

Figure 23 :Graph of Heat Flow (mW) versus Induction Time(min) for PVP added with PEO 0.1wt%-Calisto

Heat Flow PVP +'PVP+PEO 0.1wt%

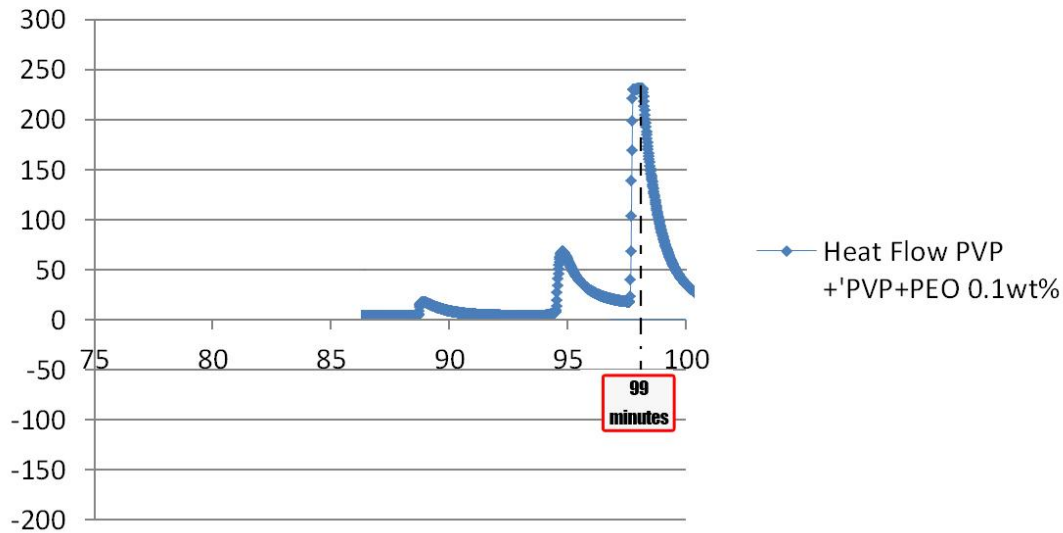


Figure 24 : Graph of Heat Flow (mW) versus Time(min) for PVP added with PEO 0.1wt%-MS

Excel

The graph above showing the result for sample using 0.07wt% PVP with addition of 0.03 wt% Polyethylene oxide(PEO) Merck 4000. PEO is an additives used to enhance the ability of PVP to further lengthen the induction time for hydrate formation. Based on the graph obtained from MS Excel, it can be seen that the induction time for hydrate formation is at 99th minute The induction time gave almost the same value like using PVP 1.0 wt % but the ice formation is delayed. By referring at the first peak of exothermic reaction, the ice started to occur at 75th minute. It can be deduced that the addition of small concentration of additives will delay the nucleation of ice as well as hydrate.

Increment (%)PVP + PEO 0.1 wt% to blank sample

$$= \frac{\text{Ind. time PVP + PEO 0.1wt\%} - \text{Ind. time blank sample}}{\text{Ind. time blank sample}} \times 100\%$$

$$= (99 - 92) / 92 \times 100\%$$

$$= 7.61\%$$

4.4 PVP 0.7 wt% + PEO 0.3 wt% (60 mg)

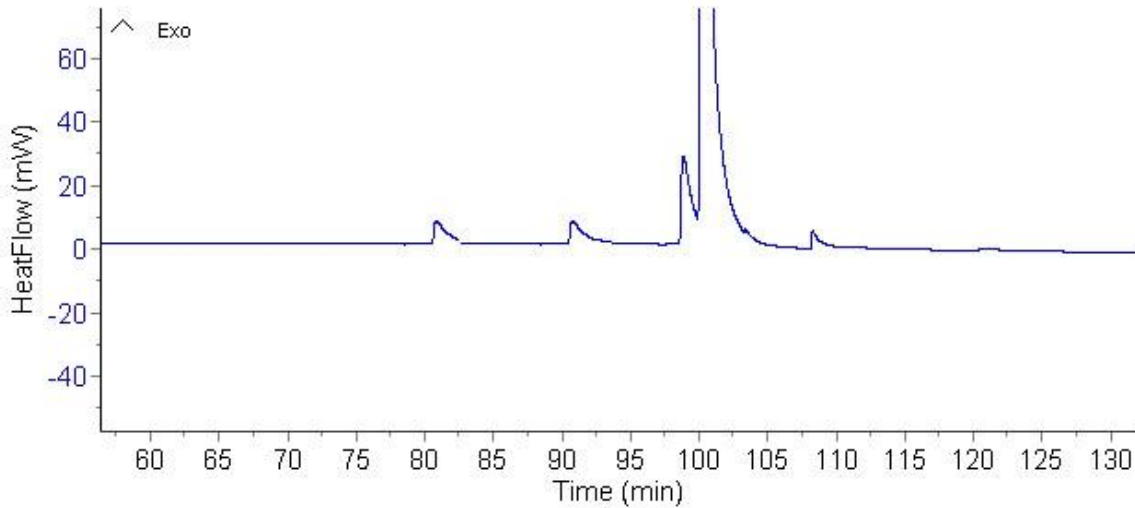


Figure 25 : Graph of Heat Flow (mW) versus Induction Time(min) for PVP added with PEO 1.0wt%-**Calisto**

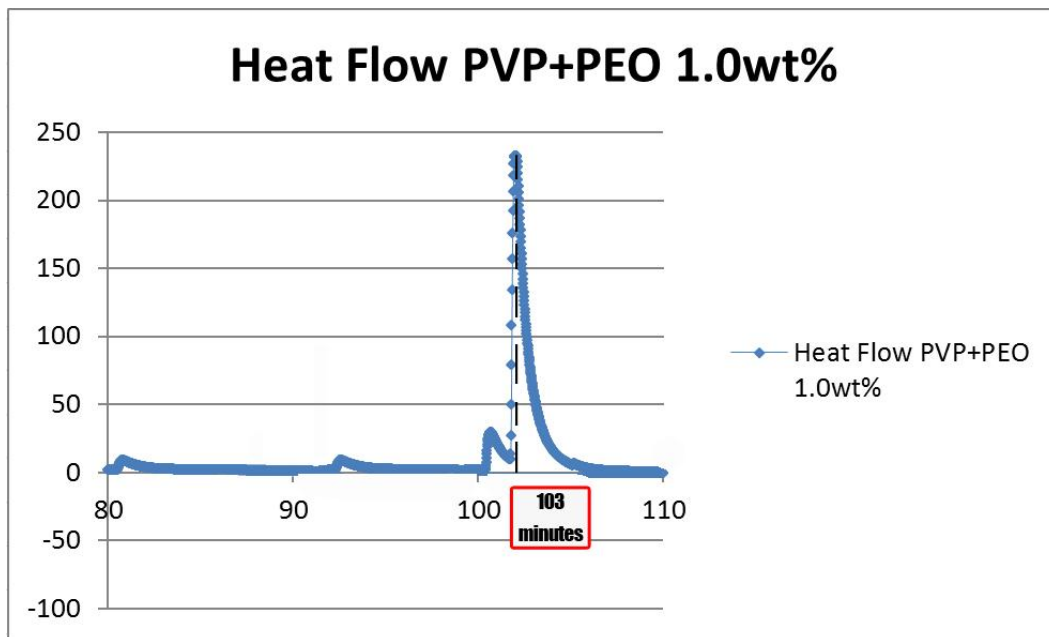


Figure 26 : Graph of Heat Flow (mW) versus Time(min) for PVP added with PEO 1.0wt%-**MS**

Excel

The graph above is the result of sample using bigger weight percent of PEO added to PVP, 1.0 wt%. It can be observed that the first peak indicating the ice formation is further delayed at 83rd minutes. Whereas, the induction time for hydrate to complete form of its bulk phase is at 103rd minutes. It can be deduced that by increasing the concentration of additives added to the kinetic inhibitor PVP will further enhance the induction time for hydrate first nucleation and successive growth.

Increment (%)PVP + PEO 1.0 wt% to blank sample

$$= \frac{\text{Ind. time PVP + PEO 1.0wt\%} - \text{Ind. time blank sample}}{\text{Ind. time blank sample}} \times 100\%$$

$$= (103 - 92) / 92 \times 100\%$$

$$= 11.95\%$$

This concentration gave the highest percent of increment based on the blank sample.

Sample	Percent of increment of induction time based on blank sample comparison (%)
PVP 0.1wt%	0
PVP 1.0wt%	6.52
PVP 0.07wt% + PEO 0.03wtT	7.61
PVP 0.7wt% + PEO 0.3wt%	11.95

Figure 27 : Table showing the tested sample with different concentration and composition with respect to induction time percent of increment.

4.5 Merge Sample in One Graph

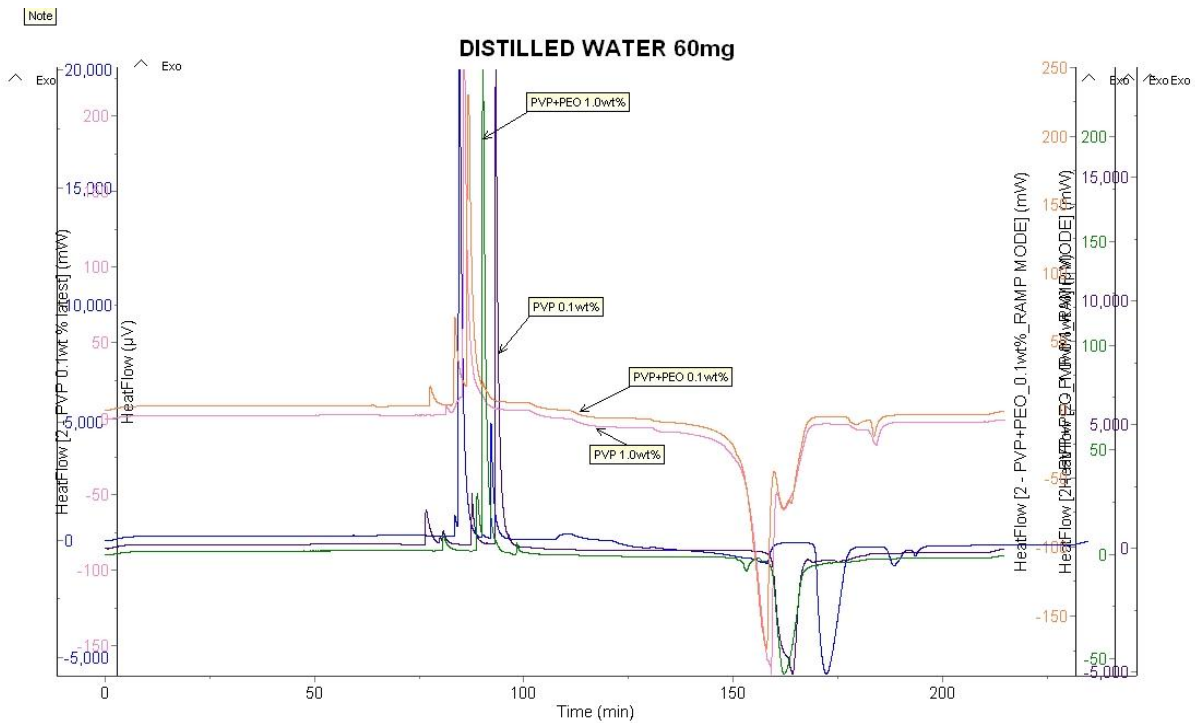


Figure 28 : Graph of Heat Flow (mW) versus induction time (min) for all sample.

This is a graph obtained using Calisto software at which all the curves representing the composition and concentration of kinetic hydrate inhibitor is merged in one graph. The blue curve representing the hydrate formation and dissociation for blank sample consists of deionized water. The blank sample serves as a reference sample to test on the effectiveness of PVP in lengthening the induction time for hydrate formation.

Due to the difference in the heat flow in those samples, 2 separate graphs have been generated to take a look on closer view of graph trend. (Next Page) :

1. Graph of Heat Flow (mW) vs Induction Time (min) for PVP 0.1 wt% & PVP +PEO 1.0 wt%
2. Graph of Heat Flow (mW) vs Induction Time (min) for PVP 1.0 wt% & PVP+PEO 0.1 wt%

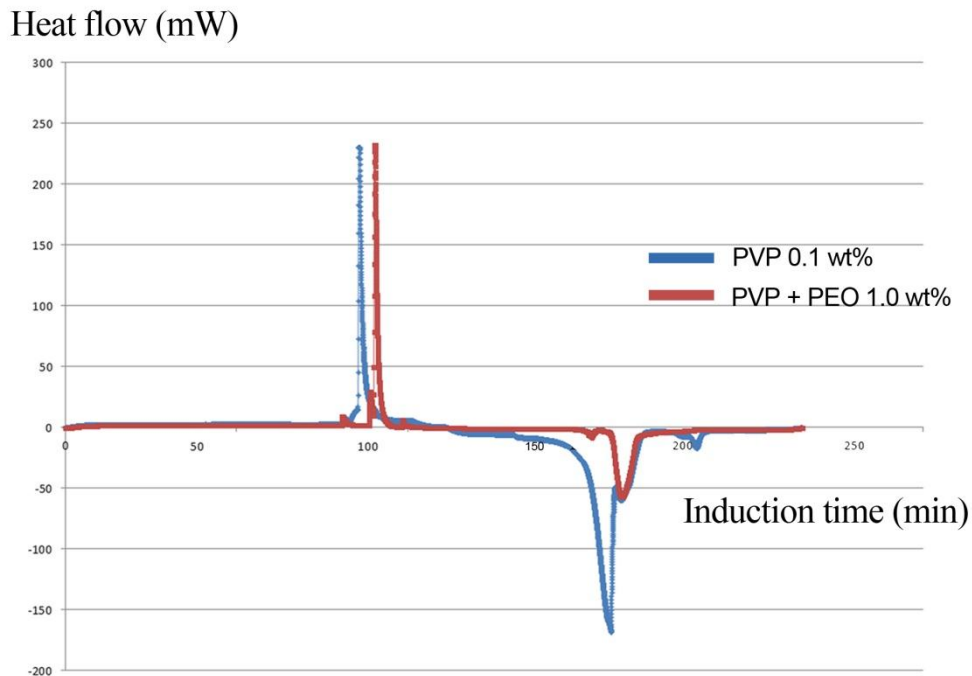


Figure 29 : Graph of Heat Flow (mW) vs Induction Time (min) for PVP 0.1 wt% & PVP +PEO 1.0 wt%

From the graph, it can be observed that the addition of PEO to the PVP will lengthen the induction time for hydrate formation. This can be proved by looking at the 2 highest peak from the graph above recorded at different time interval. For PVP 0.1wt% the induction time recorded is 92 minutes whereas the PVP+PEO 1.0wt% is 103 minute.

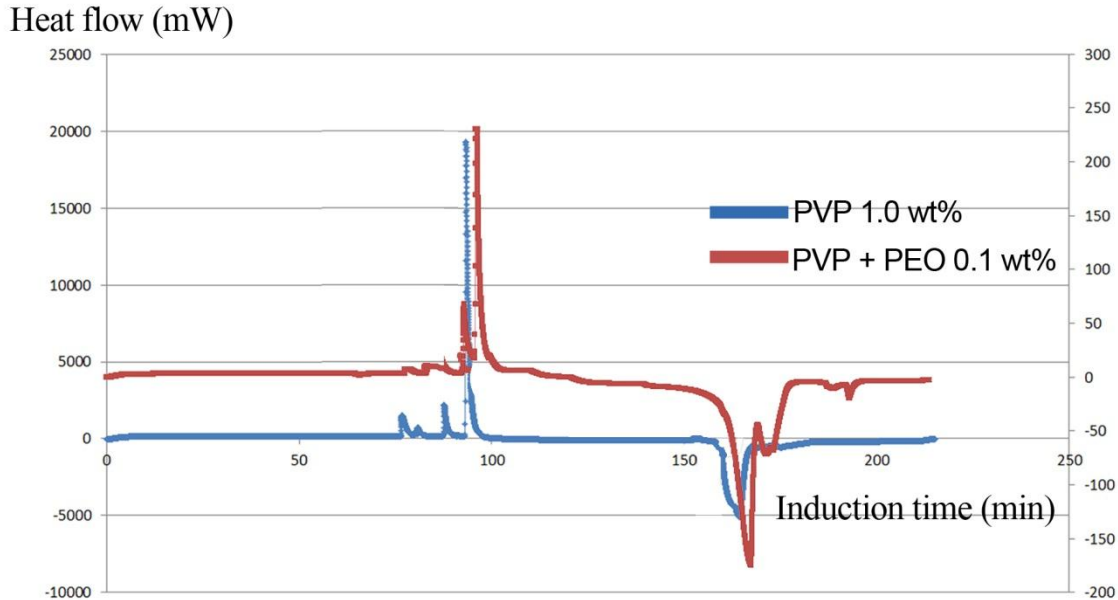


Figure 30: Graph of Heat Flow (mW) vs Induction Time (min) for PVP 1.0 wt% & PVP+PEO 0.1 wt%

From the graph, it can be observed that the addition of PEO to the PVP at different concentration will also lengthen the induction time for hydrate formation. For PVP 1.0wt% the induction time recorded is 98 minutes whereas the PVP+PEO 0.1wt% is 99 minute.

It has been proved that all the inhibitors have potential to inhibit the growth of hydrate except for PVP 0.1wt%. The reason for the ineffectiveness of PVP 0.1wt% may be due to very low concentration.

Comparing all of the data, the most promising formulation of new kinetic hydrate inhibitor is PVP+PEO 1.0wt% since it yield the longest induction time for hydrate to form.

4.6 Comparison with Calcium Magnesium Acetate(CMA)

SAMPLE COMPOSITION & COCENTRATION	ICE FORMATION (MIN)	HYDRATE FORMATION (MIN)
PVP 0.1WT%	85	92
PVP 1.0WT%	83	98
PVP 0.07WT% + PEO 0.03 WT%	88	99
PVP 0.7WT% + PEO 0.3 WT%	83	103
CMA 0.1WT%	89	110
CMA 1.0WT%	86	104

Figure 31 : Table recording the Ice Formation and Hydrate Formation time (min) for all the samples PVP, PVP+PEO, and Calcium Magnesium Acetate(CMA).

The value of induction time tabulated above is interpreted in the form of bar chart. Since the concern of this project is on induction time, the bar chart representing the induction time with respect to sample is plotted.

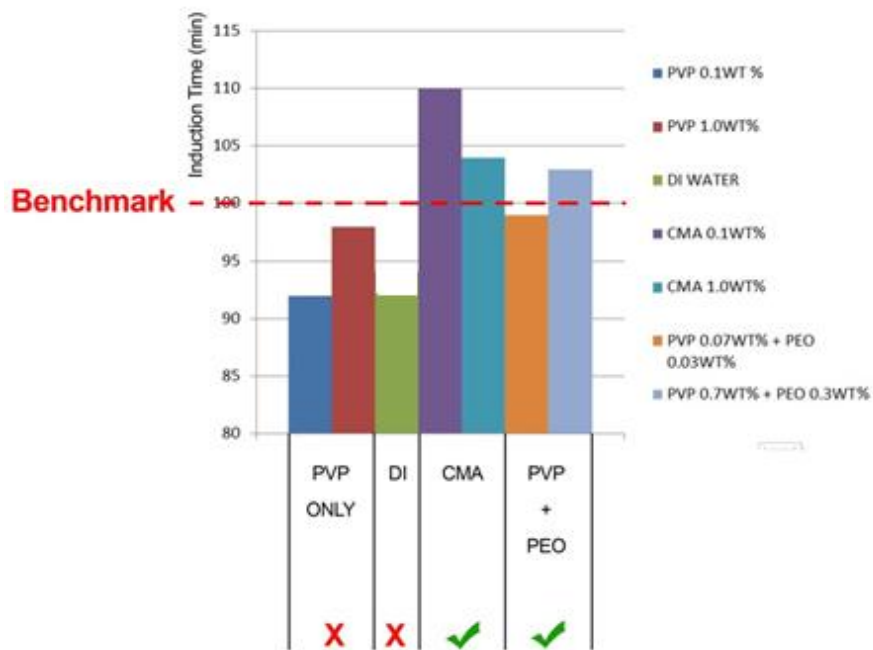


Figure 32 : Bar Chart Comparison of PVP, PVP+PEO, and CMA

The benchmark for this experiment is fixed at 100 minutes. If the sample recorded induction time for hydrate more than 100 minutes, it is considered effective. The samples with effective result are ticked (✓).

- CMA is proven to enhance the induction time of hydrate since both concentration 0.1 wt% and 1.0 wt % more than 100 minutes.
- PVP with addition of PEO also lengthen the induction time of hydrate but not as good as in CMA. The best concentration is found to be 0.7wt% PVP + 0.3wt % PEO.

CHAPTER 5 : CONCLUSION & RECOMMENDATION

5.1 Conclusion

- Addition of PEO to PVP will further enhance the time taken for hydrate to form. PVP has an active molecules in its polymer branch make it feasible to combine with this thickening agent, the PEO. By means of adsorption, the PEO will attach to the bulk phase of hydrate to prevent hydrate from sticking to one nuclei to another, thus preventing agglomeration that may kill the well or production. Via the injection of this type of KHI, more fluid is recovered as the fluid produced are given sufficient time to come to surface rather than sticking to hydrate formers in the well such as methane, ethane and carbon dioxide(structure I hydrate) .
- The best concentration for the new KHI has been defined to be 0.7wt% PVP plus 0.3wt% PEO. PVP serves as the backbone for the additives to attach on its active branch. 1.0wt% is considered to be low concentration and obey the rules that the KHI should exhibit Low Dosage Hydrate Inhibitor(LDHI) properties. Thus the concentration of the PEO and PVP should not be more than 5.0%. Even though the weight percent or the concentration used is very low, but the degree of subcooling for KHI is expected to be as equal as 50 weight percent thermodynamic inhibitor(THI).
- By comparing the result of induction time recorded for PVP+PEO and CMA, it is obvious that both kinetic hydrate inhibitors exhibits almost same value of induction time. The best sample is 0.7wt% PVP with addition of 0.3% PEO, which gives the induction time above 100 minutes.

5.2 Recommendations

To ensure that the new formulation is compatible with the formation and also producing fluids, author suggests that the study on the effect of this type of KHI towards formation and pipeline.

Author also recommends that this project can also initiate the study on reducing the emission of greenhouse gases (GHG) from the production by injecting back the carbon dioxide emitted into a chamber to form artificial or man-made hydrate. It is very important to know the favorable condition for hydrate formation and dissociation.

Added by Dr Shiraz, his personal request is to replace the water sample with hydrated oil. In his honored opinion, he asked author to use hydrated oil because it simulates the true scenario of flow assurance in real field. Hydrated oil may contain high water cut. Thus, it is a good idea to use it as a sample instead of using deionized water.

For future improvement, this project can be done using different sample of hydrate formers such as methane and ethane gas. This project utilizes only carbon dioxide as hydrate formers. To make it applicable for all type of hydrate gas, the experiment sample must be replace with other structure of hydrate such as structure II and H.

Further recommendation to be made is that, the study can be made accordance to other instrumentation such as using Hydreval to check on the integrity of result or using other PVT equipment. By using other instrument, the effectiveness of new formulation kinetic hydrate inhibitor can be verified because using PVT tools can provide insight to the 3D properties of hydrate.

Lastly, author also suggests to varies more on the concentration of sample. In this experiment, each type of sample has only 2 concentrations which are 0.1wt% and 1.0wt%. For future works, the concentration is varies in between 0.1 to 1.0wt% such as 0.2, 0.5, 0.7 and 0.9wt%.

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