

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

by

Muhammad Hizbullah Bin Mawardi

Dissertation submitted in partial fulfilment of  
The requirement for the  
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(Petroleum Engineering)

May 2013

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## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MUHAMMAD HIZBULLAH B MAWARDI

CERTIFICATION OF APPROVAL

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(12742)

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In partial fulfilment of the requirement for the  
BACHELOR OF ENGINEERING (Hons.)  
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May 2013

## ABSTRACT

Parallel with current needs of oil and gas industry where hydrates formation caused a problem with flow assurance, new formulations are strived to yield a better Kinetic Hydrate Inhibitor (KHI) with high efficiency and low dosage required to inhibit a large scales of hydrate in flow lines. The formation of hydrates can cause flow interruption due to plugging and resulted in higher cost in maintenance and the usage of large dosage of inhibitor. Polyvinylpyrrolidone or PVP is a successful KHI and commonly known as Low Dosage Hydrate Inhibitor (LDHI). A natural polysaccharide from shrimp shells, linear polymer Chitosan ( $\beta$ -(1-4) linked 2-acetamido-2-deoxy- $\beta$ -D-Glucopyranose and 2-amino-deoxy- $\beta$ -D-Glucopyranose) is proposed to become an additive to enhance the performance of PVP as KHI. Therefore, this project aims to determine the capability of PVP with Chitosan to delay the formation of hydrate in comparison of using PVP only. Concentration of solution ranged from 0.1wt% to 1.0wt% to examine the optimum concentration of inhibitor required in weight percentage. The heat flux of exothermic and endothermic reaction of the tested inhibitor is examined by using Micro Differential Scanning Calorimeter ( $\mu$ DSC) against time to measure and compare the hydrate formation and dissociation mean time. PVP will be proven as conventional KHI with satisfying result and PVP with Chitosan as an addictive is expected to lengthen the induction time for hydrate to form greater than PVP alone. Polymer Chitosan is a green technology material with great future potential and the uses of Chitosan in oil and gas industry is a new step forward. As hydrates has been declared as long-term problems in oil and gas sector, research and studies regarding an improvement of known KHI is necessary to be applied in the industry.

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## Nomenclatures

|           |   |
|-----------|---|
| THI       | Thermodynamic Hydrate Inhibitor         |
| KHI       | Kinetic Hydrate Inhibitor               |
| KI        | Kinetic Inhibitor                       |
| AA        | Anti-Angglomerants                      |
| LDHI      | Low Dosage Hydrate Inhibitor            |
| CS        | Chitosan                                |
| PVP       | Polyvinylpyrrolidone                    |
| PVCap     | Polyvinylcaprolactam                    |
| VIMA      | Poly (N-methyl-N-vinylacetamide)        |
| PVVam     | Poly (N-vinylvalerolactam)              |
| PAPYD     | Poly (acryoyl pyrrolidine)              |
| PAMOR     | Poly (acryloylmorpholine)               |
| $\mu$ DSC | Micro Differential Scanning Calorimeter |
| HP        | High pressure                           |
| HCL       | Hydrochloric acid                       |

# CHAPTER 1

## INTRODUCTION

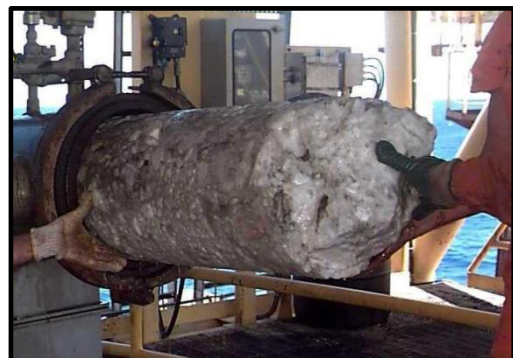
### 1.1 Background of Study

Lifting and transporting hydrocarbon is one of the major challenges faced in oil and gas industry where handling solid deposits such as wax, hydrates and asphaltene always become great issues and has been subject of long-standing problems. This phenomenon leads to safety hazard and very high economic losses (operation and maintenance cost). Moreover, current exploration focused on deep offshore operation with high pressure and low temperature which give the most addressable environment for hydrate to form (Xiao and Adidharma, 2009).

Hydrate exist in crystalline, ice-like solids formed molecule formed when the 'guest' molecule such as carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ) and nitrogen ( $\text{N}_2$ ) is altered by the addition or existence of water molecule in the system hence to create another molecule with different properties. Hydrocarbon which composes of this 'guest' molecule will transform into hydrates and cause blockage in hydrocarbon flow line (figure 1 and figure 2).



**Figure 1: Hydrate layer in pipeline**



**Figure 2: Hydrate cause blockage in pipeline**



Therefore, many initiatives have been developed to enhance the flow assurance of hydrocarbon such as the most regular traditional method is Thermodynamic Hydrate Inhibitor (THI) where glycol or methanol is used in large amount (about 30% of the volume). This situation resulted in higher operation cost by 150 Million USD/year<sup>3</sup>. THI were aims to disrupt the thermodynamic stability favourable zones for hydrates to form. The principles are keeping the operating temperature above or below hydrate formation pressure or introduce chemical injection to heat the gas above hydrates equilibrium pressure (Paez, Blok, Vaziri and Islam, 2001).

Non-thermodynamic inhibitor is widely in research and development phase due to their preferable dosage required and their mechanism by interfering the process of hydrates formation. They were classified as Low Dosage Hydrate Inhibitor (LDHI) and two common type of LDHI are Kinetic Hydrate Inhibitor (KHI) and Anti-Angglomerants (AA). KHI delays the induction time for hydrates to form and AA alter the structure of hydrate crystal by agglomeration of hydrates particles. The development of KHI is using polymer-based chemical and less toxic than chemical used in AA. KHI polymer is more environmental friendly and will not causing emulsions, which is a common problem faced in AA inhibitors. Studied shown Polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) are effective polymers as kinetic inhibitor and their enhancement to delay the hydrate formation induction time is still in on-going research (Fu, Cenegy and Neff, 2001).

## **1.2 Problem Statements**

### **1.2.1 Bad flow assurance as resultant of hydrate formation**

Hammerschmidt examine the causes of pipe blockage was hydrates and the research made in 1930's and once the pipe is plugged, there were limited options for removal process. The problem is expected to spread in most production wells and often occurred in cold-weather operations and matured well (Fu, Cenergy, Neff, 2001). Existence of water cause hydrates to form unless it removal (water) occurred at the most dew point but the operation in highly difficult and beyond operation cost. The safety hazard measure can occur in drilling operations when drilling fluid used in deep offshore form hydrates that cause major threats to the operation and personnel (Xiao and Adidharma, 2009). This situation is not only focused on gas well, in most operation including heavy oil extraction seems to release a light gas which can lead to hydrate formation. Hence the issues need to be taken care of at early stage of hydrates formation especially during essential stage of hydrocarbon operation; extraction, process and transportation (Paez, Blok, Vaziri and Islam, 2001).

### **1.2.2 Traditional method of Thermodynamic Hydrate Inhibitor is not preferable.**

Thermodynamic inhibitor is a successful method by shifting the equilibrium hydrate stability zone by adding chemical such as methanol. However, the exploration and operation of hydrocarbon moves to a deeper part of the sea deal with higher pressure and low temperature that closer to favourable environment for hydrates formation, required a large dosage of THI and the concentration reported up to 50wt%. Another chemical is recently introduced by injecting Sodium Chloride (salt) as THI, but the corrosion issues arise in the pipeline and may reduce the effectiveness of corrosion inhibitor (Xiao and Adidharma,, 2009). Therefore, the uses and development of effective kinetic inhibitor (KHI) with more environmental friendly with Low Dosage Hydrate Inhibitor (LDHI) classified is much preferred.

### 1.3 Objective and Scope of Study

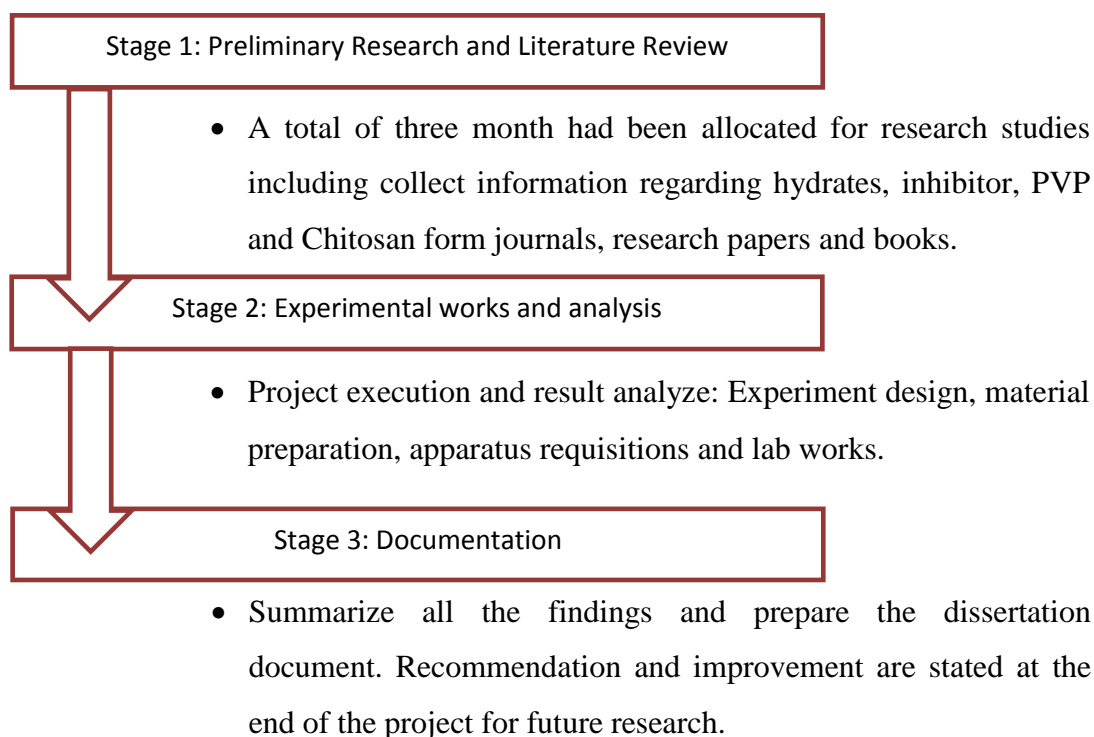
This project is aimed to:

1. Determine the practicability of Chitosan as an addition to PVP as KHI in increasing the induction time in hydrate formation.
2. Determine the best concentration of KHI resulted in the most optimum result to delay the hydrate formation with Chitosan as an additive.

The scope of study includes the laboratory procedure to determine the potential of polymer-based chemical added (Chitosan) to PVP. The parameter to be weighted in the experiment is the induction time of hydrate formation. The water soluble-based chitosan need to be prepared with concentration lower than PVP as Chitosan is an additive polymer. Chitosan is not a sole inhibitor but expected to give a longer time in hydrate formation when added to PVP. The experiment will be done by using Micro Differential Scanning Calorimeter ( $\mu$ DSC) which the heat flow will be observe and analyse the heat curve pattern against time.

### 1.4 Feasibility of the Project

The project is divided into three (3) stages;

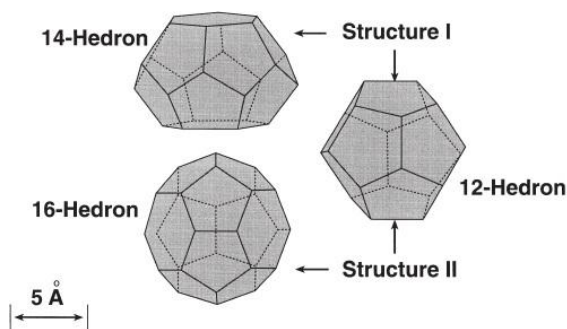


## CHAPTER 2

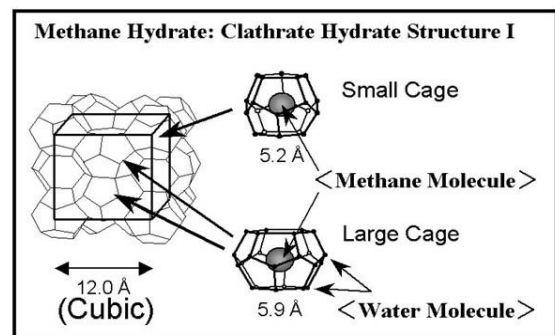
### LITERATURE REVIEW AND CRITICAL ANALYSIS

#### 2.1 Hydrates Formation and Characteristics

Hydrocarbon production consist of molecules that have higher tendency to act as ‘guest’ molecule in hydrates formation mainly by methane, followed by ethane, propane, iso-butane, sulphur dioxide, nitrogen, carbon dioxide and hundreds more that slightly contribute to hydrates formation (Paez, Blok, Vaziri and Islam, 2001). Hydrates are more favorable to form under certain condition of elevated pressure and low temperature (Cingoti and Sinquin, 1999). The formation of hydrates were not in chemical union with water but the molecule interact through Van der Waals dispersion type of force thus described by their crystalline structure. Structure I in figure 3 shows the pure methane hydrates structure but the existence of propane resulted in structure II (Notz, Bumgardner, Schaneman and Todd, 1996).



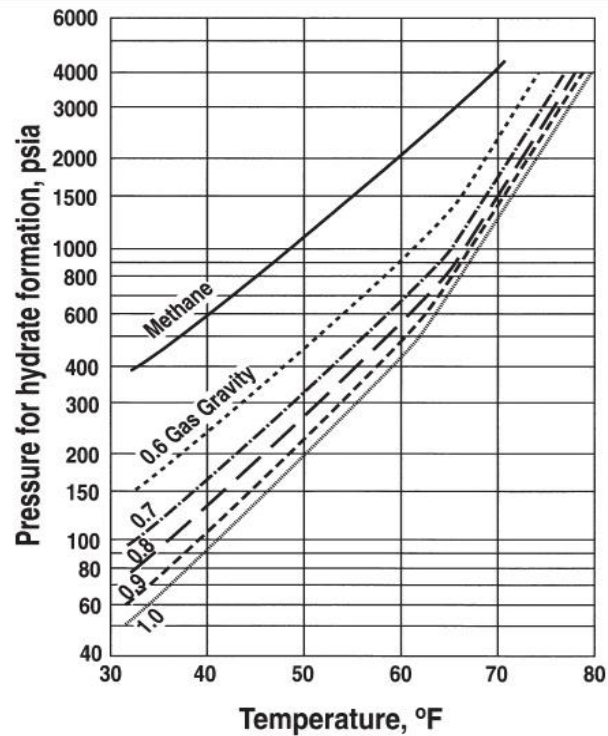
**Figure 3: Structure I & II cavities of hydrates**



**Figure 4: Small and large cage hydrate form**

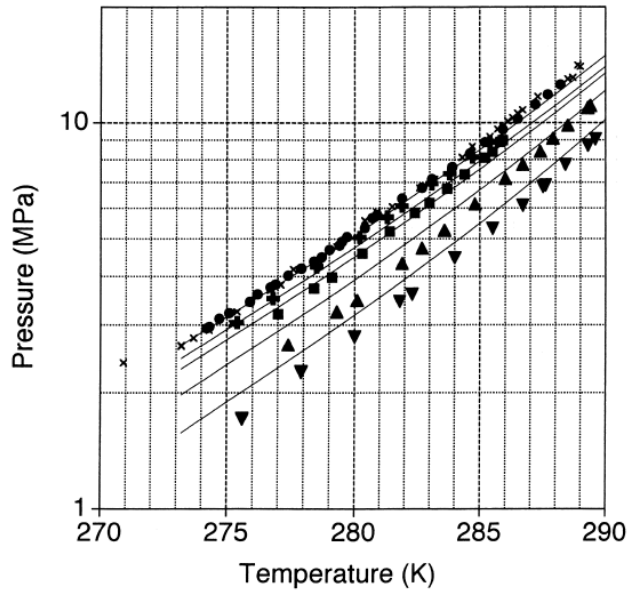
Figure 4 shows structures of cages of hydrogen (water) that make up the two crystals that commonly found in hydrocarbon production where each combination consists of small cages or either large cages. On the other hands we can verify that the formations of hydrates are based on these four principles; the presence of hydrate-forming components, the presence of water, favorable condition of pressure and temperature (Fu, Cenegy and Neff, 2001). This would be very important in order to consider the prevention method for hydrates formation. Any absence of these four elements would be impossible for the hydrates to form.

For any composition of hydrocarbon, a pressure versus temperature curve can be plotted to determine the most favorable area of hydrates formation with various gravities. As shown in the figure 5 with methane as an example, with appropriate pressure and temperature, methane hydrates are formed. The presence of heavier component as butane resulted in more easily of the hydrates to form (Notz, Bumgardner, Schaneman and Todd, 1996). This curve also helps to determine the proportion areas (with pressure and temperature) which are free of hydrates.

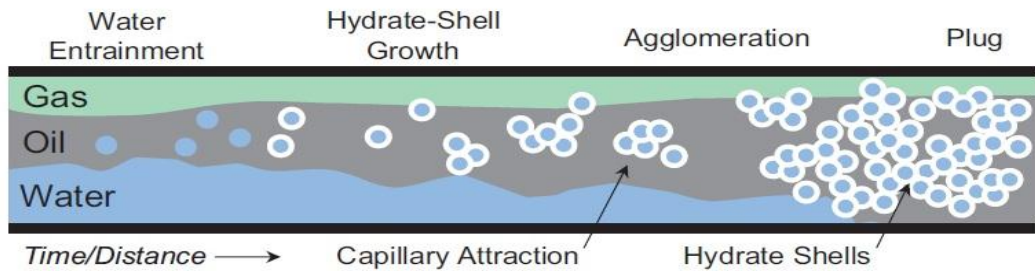


**Figure 5: Hydrates forming condition with various gravities**

The equilibrium conditions for gas hydrates depend on the hydrates forming composition. Relevant to this project which uses 99.9995% of methane, investigation of methane hydrates equilibrium curve had done by Sloan (1998) and compiled by Maekawa (2000). Figure 6 shown the equilibrium condition of methane hydrates with small amount of ethane in pure water. Solid curves are thermodynamically predicted by Sloan (1998) with the relationship favorable of pressure and temperature for hydrates to form.

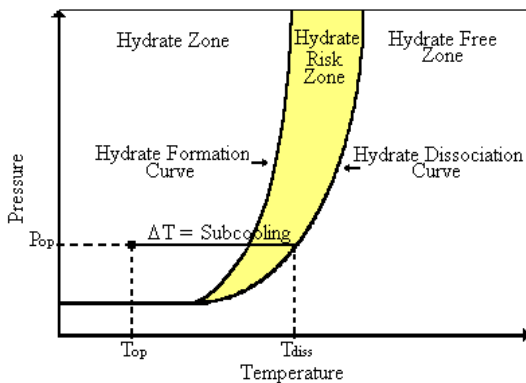


**Figure 6: Equilibrium Condition for methane hydrate**

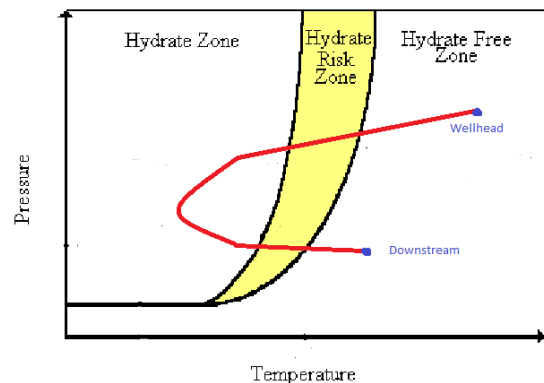


**Figure 7: Conceptual representation of hydrate formation**

Figure 8 below is the curve represent the relationship between pressure and temperature of hydrates forming regimes and figure 9 show the real cases where pipeline entering hydrates forming zones. This is the area of concern where inhibitor expected to perform during production. Sub-cooling ( $\Delta T$ ) as in figure 8 defines the difference temperature between the thermodynamic of hydrate formation and ambient temperature (Paez,Blok, Vaziri and Islam, 2001).



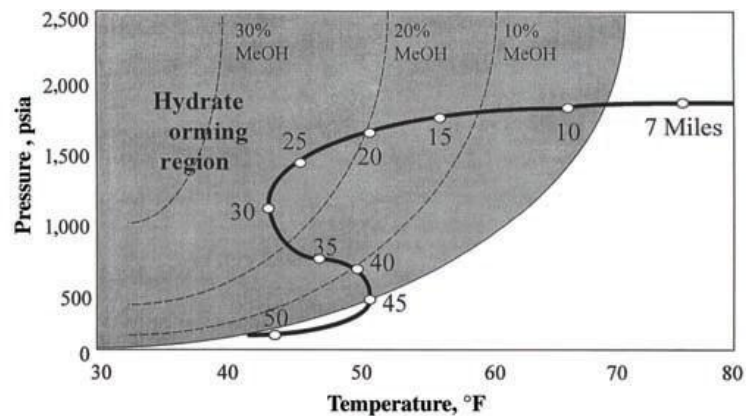
**Figure 8: Hydrate forming regime**



**Figure 9: Pipeline in hydrate form regime**

## 2.2 Thermodynamic Hydrate Inhibitor (THI)

THI prevent the formation of hydrates by keep the system out from hydrates stability zones. Since exploration and production go deeper into the sea and deal with higher pressure and low temperature, THI is not a preferable method due to a large dosage required (such as ethanol or methanol) to shift the hydrate equilibrium zones. Methanol is most successful in record but the large dosage resulted in higher cost and cause logistical difficulty in operation. Thermal hydrate inhibition technique also is not practically used due to restriction for short pipeline and permit heating when shut-in operation by deliver electricity to heat the formation. This method is much complex and also capital-intensive. Last option in THI is dehydration technique where temperature of the system remains above the dew-point. Non-existence of water causes no hydrates to form. However, this technique also required high capital-expenses by using large dosage of glycol and not suitable for subsea flow line (Talley and Mitchell, 1999).



**Figure 10: pipeline facing hydrate formation**

Figure 10 is an example of case-study of 7 miles pipeline facing hydrates formation zone and using methanol as Thermodynamic Hydrate Inhibitor (THI). The points along the line (pipeline) show the weight percentage of methanol injected into the flow line to prevent hydrates to form. The minimum weight percentage in this case is 23 wt% methanol (including safety factor) and the maximum up to 63 wt% (including safety factor) of methanol which is the weight percentage is more than the weight of the system (Sloan and Koh, 2009).

### **2.3 Kinetic Hydrate Inhibitor (KHI)**

Initiative of developing better hydrates inhibitor been done to enhance the commonly used thermodynamic inhibitor where the process deal with pressure and temperature to shift the thermodynamic equilibrium of hydrate formation (Fu, Cenegy and Neff, 2001). KHI is designed to delay or prevent the crystal growth of hydrates in flow line (Cingotti and Sinquin, 1999). Generally KHI is polymers and advantages as biological inhibitor towards green technology (Talley and Mitchell, 1999). The rapid growth of hydrates crystal in flow line known as catastrophic growth is a kinetic process, which means the formation is not instantaneously appear as crystal (Paez, Blok, Vaziri and Islam, 2001). The process introduces the induction time, in other words, the lagging time for the crystal to appear. The induction time is when the KHI (polymers) is expected to react to delay the hydrate formation. Moreover, the usage of KHI is commonly known as 'Low Dosage Hydrate Inhibitor' (LDHI) that effectively can inhibit hydrates at low concentration (<1 wt. %) (Fu, Cenegy and Neff, 2001).

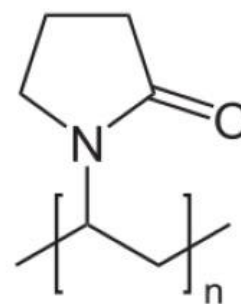
Most of the successful kinetic inhibitor that have been studied were polymer-based inhibitor; poly(N-vinylpyrrolidone) (PVP), poly(N-vinylcaprolactam) (PVCap), poly(N-methyl-N-vinylacetamide) (VIMA), poly(N-vinylvalerolactam) (PVVam), poly(acryoyl pyrrolidine) (PAPYD), and poly(acryloylmorpholine) (PAMOR) (Xiao and Adidharma, 2009).

### **2.4 Polyvinylpyrrolidone (PVP)**

PVP are polymer compound from monomer n-vinylpyrrolidone that has a long and repeating structure. The product of PVP commonly in white chalky powder are widely available and manufactured for medical, vehicle manufacturing, cosmetic and oil and gas industry. PVP comes with various viscosity and soluble in aqueous and organic solvent. This behavior is important to choose the suitable viscosity to be appropriately soluble in different flow line of hydrocarbon. PVP is non-toxic material hence less precaution in handling the polymers.



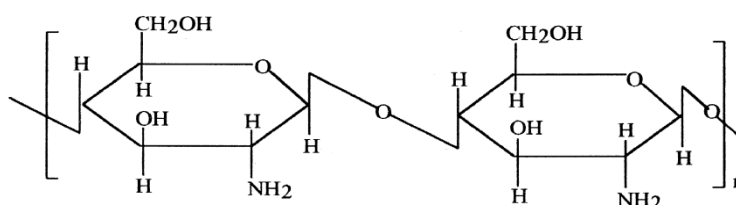
In oil and gas industry, PVP has successfully being used for cement set-time retarder, reduces speed of fluid loss, improve sealant properties, viscosity modifier in drilling mud and as kinetic hydrate inhibitor in gas flow line. Experiment and investigation has been done to determine the performance of PVP as KHI. PVP has ability to increase the induction time for the hydrates to form (Daraboina, Ripmeester, Walker and Englezos, 2011). There are several summaries of success fields using PVP as KHI instead of methanol and glycol to retard the formation of hydrates (Fu, Cenegy and Neff, 2001). But the using PVP in KHI can only be done if the hydrates formation curve is not too far away shifted from the hydrate proportion area (Ugur and Mahmut, 2002).



**Figure 11: PVP molecular structure**

## 2.5 Chitosan

Chitosan ( $\beta$ -(1-4) linked 2-acetamido-2-deoxy- $\beta$ -D-Glucopyranose and 2-amino-deoxy- $\beta$ -D-Glucopyranose) (figure 12) is a natural amino polysaccharide from crab and shrimp shells. The production of chitosan started from the recycle of waste product from sea food canning process industries in Oregon (Pillai, Paul and Sharma, 2009). Chitosan exist as white, hard, inelastic material (figure 13) after through fermentation process from Chitin, where alkali treatment is used to remove protein from chitin.



**Figure 12: Chitosan molecular chain**



**Figure 13: Chitosan production from shrimp shells**

The properties of chitosan are influenced mainly by its degree of deacetylation (DD) including its ability for water solubility. Chitosan is highly insoluble (based on their percentage in DD) and give a sensitive reaction with acid, alcohol and alkali. To unfold its molecular chains, the intermacromolecular hydrogen bonds and interchain hydrogen bonds of chitosan need to be destructed and reaction is successful with strong acid while reaction with alkali resulted in insoluble, aggregated each other. To produce a water-soluble chitosan is important to examine their ability with other polymers (Lu and Song, 2003).

Due to unique structural modification properties of chitosan, the application of this material in industries is wide ranging such as film forming ability in photography, fungistatic properties for cosmetic product, contact lenses manufacturing in ophthalmology, metal capture in wastewater, artificial skin and very wide uses in biomedical and many others applications (N. V. Ravi Kumar, 2000). However, chitosan is not much recognized in engineering application and perspective but intense activities are going on in the research and development of chitosan abilities. Chitosan used to be waste sediments in coastal area however for the past decade, chitosan has been classified as green-development material with great future potential.

## **2.6 Micro Differential Scanning Calorimeter ( $\mu$ DSC)**

A high-pressure micro differential scanning calorimeter ( $\mu$ DSC) by SETARAM Inc. will be used to determine the formation and dissociation of hydrate formation. This equipment using Peltier's principle to manipulate the heating and cooling degree of temperature near the high pressure cell. The HP  $\mu$ DSC can operate up to 400 bar and temperature range from -45 to 120 degree celcius with the lowest scanning rate of 0.001 °C/min (Xiao and Adidharma, 2009).

The scanning result will be presented in Calisto software of the heat flux versus time curve (DSC thermogram). Any exothermic (heat released) and endothermic (heat absorbed) reaction in the system will be examined and detected based on the peak in the heat flow curve. The induction time of hydrate formations will be determined by its onset time and the energy required for the heat process can be determined by calculating the area under the curve.

# CHAPTER 3

## METHODOLOGY

### 3.1 Project Flow and Activities

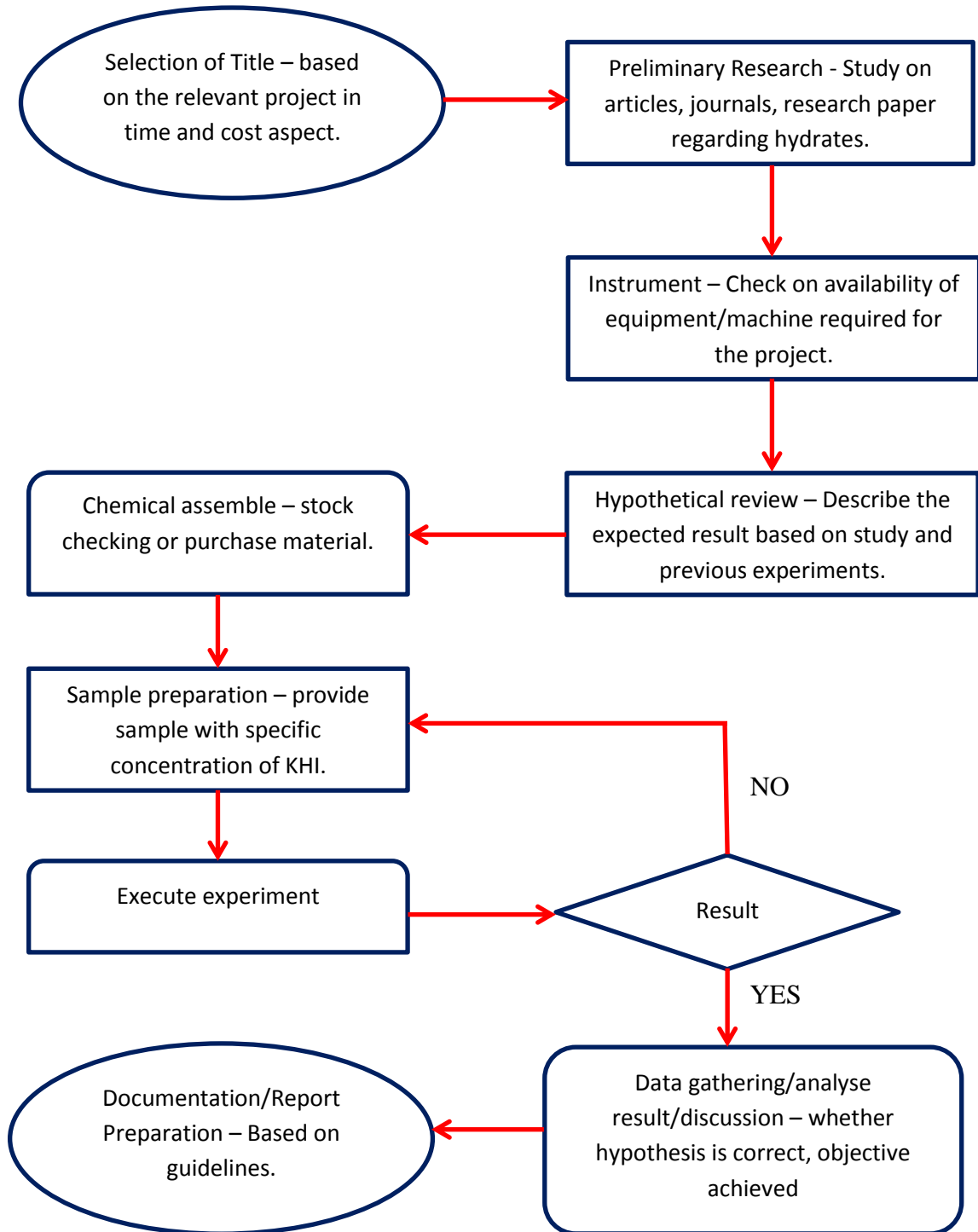


Figure 14: Project Flow and Activities

## 3.2 Gantt Chart and Key Milestone

### 3.2.1 Gantt Chart

**Table 1: Final Year Project 1**

| No | Details  | Weeks |   |   |   |   |   |   |                    |   |   |    |    |    |    |    |
|----|--|-------|---|---|---|---|---|---|--------------------|---|---|----|----|----|----|----|
|    |  | 1     | 2 | 3 | 4 | 5 | 6 | 7 | MID SEMESTER BREAK | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| 1  | Consolidation of FYP Topics                      | █     |   |   |   |   |   |   |                    |   |   |    |    |    |    |    |
| 2  | Topic assignments to students                    |       | █ |   |   |   |   |   |                    |   |   |    |    |    |    |    |
| 3  | Research for the topic assigned                  |       | █ | █ |   |   |   |   |                    |   |   |    |    |    |    |    |
| 3  | Preparation for Extended Proposal                |       |   |   | █ | █ | █ |   |                    |   |   |    |    |    |    |    |
| 4  | Submission of Extended Proposal                  |       |   |   |   |   |   | █ |                    |   |   |    |    |    |    |    |
| 5  | Research for the experimental procedure and work |       |   |   |   |   |   |   |                    | █ | █ | █  | █  | █  | █  |    |
| 6  | Research for the material properties             |       |   |   |   |   |   |   |                    |   | █ | █  | █  | █  | █  |    |
| 7  | Preparation for Proposal Defence                 |       |   |   |   |   |   |   |                    |   | █ |    |    |    |    |    |
| 8  | Proposal Defence                                 |       |   |   |   |   |   |   |                    |   |   | █  |    |    |    |    |
| 9  | Preparation for Interim Report                   |       |   |   |   |   |   |   |                    |   |   | █  | █  | █  |    |    |
| 10 | Submission of Interim Report                     |       |   |   |   |   |   |   |                    |   |   |    |    |    | █  | █  |

**Table 2: Final Year Project 2**

| No | Details   | Weeks |    |    |    |    |    |    |                    |    |    |    |    |    |    |    |
|----|---|-------|----|----|----|----|----|----|--------------------|----|----|----|----|----|----|----|
|    |   | 15    | 16 | 17 | 18 | 19 | 20 | 21 | MID SEMESTER BREAK | 22 | 23 | 24 | 25 | 26 | 27 | 28 |
| 1  | Finalize procedure                                  | █     | █  |    |    |    |    |    |                    |    |    |    |    |    |    |    |
| 2  | Preparing experiment material, conform lab schedule |       | █  | █  |    |    |    |    |                    |    |    |    |    |    |    |    |
| 3  | Execute project's work / experiment                 |       | █  | █  | █  | █  |    |    |                    |    |    |    |    |    |    |    |
| 3  | Result analysis and discussion                      |       |    |    | █  | █  | █  |    |                    |    |    |    |    |    |    |    |
| 4  | Submission of progress report                       |       |    |    |    |    |    |    |                    |    |    | █  |    |    |    |    |
| 5  | Preparation of Pre-SEDEX                            |       |    |    |    |    |    |    |                    |    |    | █  | █  | █  |    |    |
| 6  | Pre-SEDEX   |       |    |    |    |    |    |    |                    |    |    |    | █  |    |    |    |
| 7  | Submission of draft report                          |       |    |    |    |    |    |    |                    |    |    |    | █  | █  |    |    |
| 8  | Submission of technical paper and dissertation      |       |    |    |    |    |    |    |                    |    |    |    |    | █  |    |    |
| 9  | Oral presentation                                   |       |    |    |    |    |    |    |                    |    |    |    |    |    | █  |    |
| 10 | Submission of project dissertation                  |       |    |    |    |    |    |    |                    |    |    |    |    |    |    | █  |

### 3.2.2 Key Milestone

| No | Activities   | Date             |
|----|--|------------------|
| 1  | Finalizing the project title from project supervisor | Feb, 2013        |
| 2  | Research via journals, articles, book                | Feb, 2013        |
| 3  | Identify objective and problem statement             | Feb, 2013        |
| 4  | Research on literature review                        | Feb, 2013        |
| 5  | Plan methodology and project flow                    | Feb, 2013        |
| 6  | Submission of Extended proposal                      | 27 Feb, 2013     |
| 7  | Proposal defense with panel and supervisor           | 13 March, 2013   |
| 8  | Submission of interim report                         | 17 April, 2013   |
| 9  | Sample preparation and experiment work               | May – July, 2013 |
| 10 | Submission of progress report                        | 12 July, 2013    |
| 11 | Submission of final draft report                     | 1 August, 2013   |
| 12 | Submission of technical report                       | 1 August, 2013   |
| 13 | Pre-SEDEX (Poster Presentation)                      | 14 August, 2013  |
| 14 | Final project presentation                           | 19 August, 2013  |

**Table 3: Project Key Milestone**

### 3.3 Material

#### i) Polymer sample

Two polymers; polyvinylpyrrolidone (PVP) and chitosan will be used in this experiment. PVP and Chitosan will be prepared as water-soluble samples with varying percentages of concentration.

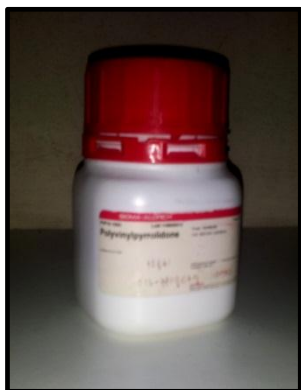


Figure 15: Polyvinylpyrrolidone



Figure 16: Chitosan

#### ii) Hydrochloric acid (HCL)

HCL is used to prepare a water-soluble chitosan with a low percentage of HCL as solvent.

#### ii) Distilled water (H<sub>2</sub>O)

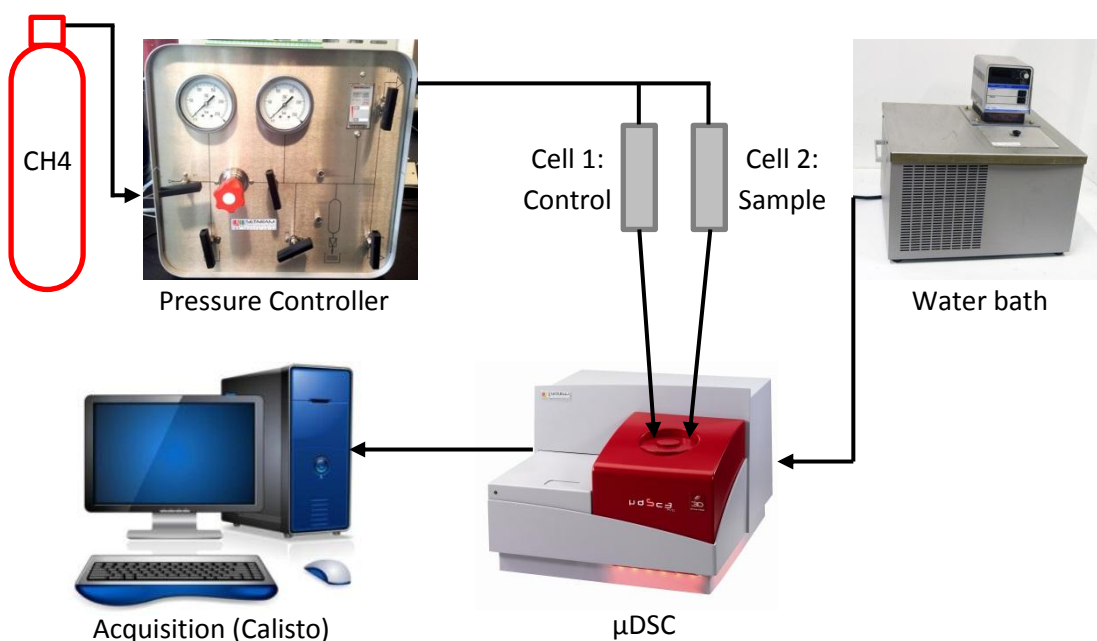
Distilled water is used as an aqueous solution for solution preparation and to run one blank sample as a control measure.

#### iii) Methane gas (CH<sub>4</sub>)

Methane with 99.9995% purity is used as a 'guest' molecule to form methane hydrates.

### 3.4 Apparatus

To examine the samples with transferred heat flux, Micro Differential Scanning Calorimeter ( $\mu$ DSC) by SETARAM Inc. will be used. Figure 17 shows the  $\mu$ DSC equipment set up consist two high-pressure vessels made up from Hastelloy C276 with custom holder to allow Peltier's principle of heating and cooling around the vessels, pressure controller, water bath and computer with Calisto software displayed.



**Figure 17:  $\mu$ DSC equipment set-up**

Cell 2 contain tested sample and cell 1 contain blank sample (distilled water) as control sample to allow comparison (reference) of heat flux in both cells. Methane will be used as the hydrates formers, a guest molecule that will be surrounded by water molecule. Methane hydrate structure belongs to hydrate structure I. Methane is flammable, which potentially hazard hence need an extra precaution in handling methane. The  $\mu$ DSC can operate up to 400 bars and temperature range of -45 to 120 degree Celsius and the scanning allowable is from 0.001  $^{\circ}\text{C}/\text{min}$  to 5  $^{\circ}\text{C}/\text{min}$ . Calisto programme will display the thermogram of heat flux versus time and water bath is functioned to run  $\mu$ DSC engine.

### 3.5 Procedure and Method

#### 3.5.1 Sample preparation

Sample of PVP and PVP + chitosan will be prepared by simple processing technique and chitosan dilution with low concentration acid. The concentration percentage of samples PVP + chitosan will be prepared in proportion of 7:3. 70% of weight percentage PVP + 30% of weight percentage chitosan as chitosan is proposed to be an additive to enhance PVP performance as kinetic inhibitor. Data of sample with tested concentration is tabulated in table below;

| No of Sample | Concentration | No of Sample | Concentration                    |
|--------------|---------------|--------------|----------------------------------|
| 1            | 0.1 wt% PVP   | 5            | 0.07 wt% PVP + 0.03 wt% chitosan |
| 2            | 0.5 wt% PVP   | 6            | 0.35 wt% PVP + 0.15 wt% chitosan |
| 3            | 0.7 wt% PVP   | 7            | 0.49 wt% PVP + 0.21 wt% chitosan |
| 4            | 1.0 wt% PVP   | 8            | 0.7 wt% PVP + 0.3 wt% chitosan   |

**Table 4: Concentration of PVP solution and PVP + chitosan solution**

#### i) PVP solution preparation

PVP (solute) is weighted on the electronic beam and diluted with 100 ml of distilled water with fixed stirring rate and stirring period of one hour.

*Mass percentage of solution,*

$$= \frac{\text{Mass of solute PVP (g)}}{100 \text{ ml of distilled water}} \times 100\%$$

#### ii) PVP + Chitosan solution preparation

PVP and chitosan is weighted separately with ratio of mass percentage PVP to chitosan 7:3. Three drops of HCL ( $\pm 0.15$  ml) is poured into 100ml of distilled water as solvent to dilute PVP + chitosan with fixed stirring rate and stirring period of one hour.

*Mass percentage of solution,*

$$= \frac{\text{Mass of solute PVP + chitosan (g)}}{100 \text{ ml of distilled water} + \pm 0.15 \text{ ml of HCL}} \times 100\%$$



### 3.5.2 Method

The experiment work started with sample preparation a day before tested with  $\mu$ DSC for each sample. A total of eleven (9) samples are tested; one sample for blank sample (distilled water), four samples for PVP solution and four samples for PVP + chitosan solution. The mass of 30 mg is fixed to each sample for  $\mu$ DSC experiment. The tested sample in cell 2 will be connected to methane gas while the control sample in cell 1 will be connected to inert gas (nitrogen). The cell is cleaned up with distilled water pressurized air for each run and the gas line from pressure controller to  $\mu$ DSC is purged with a small amount of methane to flush out any gas left inside to avoid history defect.

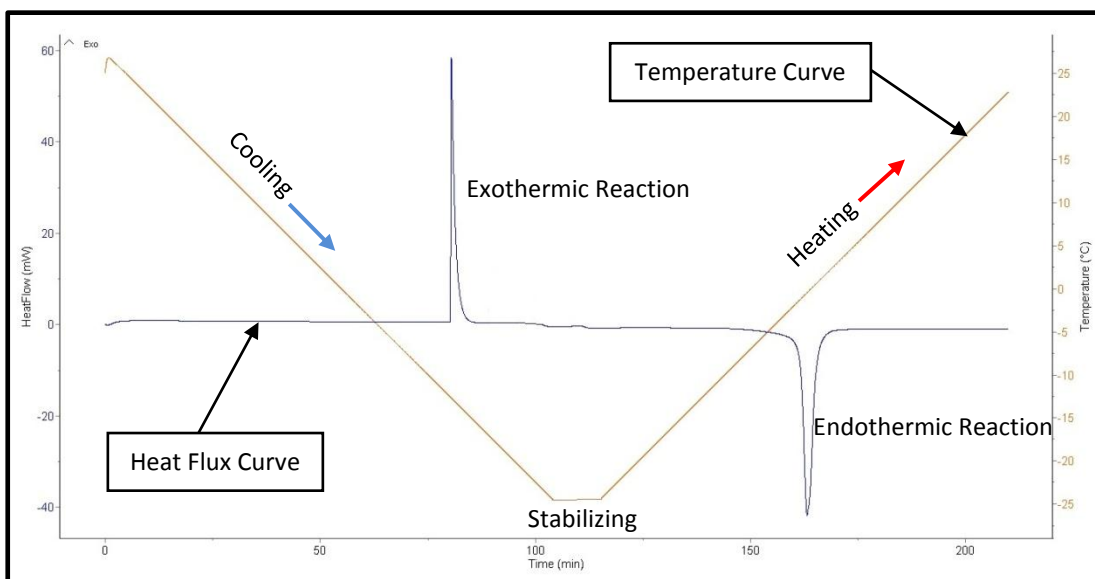
The experiment is conducted in ramped mode of non-isothermal cooling and heating process. The pressure is kept constant for all samples at 40 bars. The scanning rate is fixed for 0.5 °C/min from 25 °C to -25 °C for cooling process where hydrates formation is expected to form and -25 °C to 25 °C to examine the dissociation of hydrates in heating process. Stabilizing period is set for 10 minutes to allow the temperature of the sample is fully distributed in the cell. Table 5 show the design of the experiment in ramped mode.

| No. | Temp (°C) |     | Scanning rate<br>(°C/min) | Duration<br>(min) | Gas                           | Remarks     |
|-----|-----------|-----|---------------------------|-------------------|-------------------------------|-------------|
|     | Start     | End |                           |                   |                               |             |
| 1   | 25        | 25  | -                         | 5                 | Methane<br>(CH <sub>4</sub> ) | Starting    |
| 2   | 25        | -25 | 0.5                       | 100               |                               | Cooling     |
| 3   | -25       | -25 | -                         | 10                |                               | Stabilizing |
| 4   | -25       | 25  | 0.5                       | 100               |                               | Heating     |
| 5   | 25        | 25  | -                         | 10                |                               | Finish      |

**Table 5: Cooling and heating stage (ramped mode)**

Figure 18 shows the display of thermogram heat flux versus time. The induction time of hydrates to form is the parameter analyzed by determine the onset time of the exothermic peak while the endothermic peak shows the hydrates dissociation process. Ice formation and dissociation curve is expected to displayed prior to hydrates formation due to the process will record any exothermic and

endothermic reaction in the cell. The pressure line is not stated due to pressure is fixed throughout the experiment.



**Figure 18: Thermogram heat flux versus time**

# CHAPTER 4

## RESULT AND DISCUSSION

### 4.1 Effect of Polymer Polyvinylpyrrolidone (PVP) on Hydrate Induction and Dissociation Time

Induction time for hydrate to form is the main criteria in comparison of different inhibitor performance and to determine the optimum concentration of kinetic inhibitor. Induction time can be described as the elapsed time of methane hydrate crystallization which can be detected, where the total time taken for the nucleus formation and growth to their detectable size (Xiao and Adidharma, 2009).

Four samples are successfully tested with a few run for each samples due to no hydrate formation in some run and strange heat flux curve behavior caused by impurities or history defect. The tested samples are blank sample (distilled water), 0.1wt% of PVP, 0.5 wt% of PVP, 0.7 wt% of PVP and 1.0 wt% of PVP. The result of all concentrations will be plotted on the same graph and zoomed into specific time range separately (exothermic and endothermic) to visualize better in comparing and interpreting the data.

#### 4.1.1 Formation of Hydrate

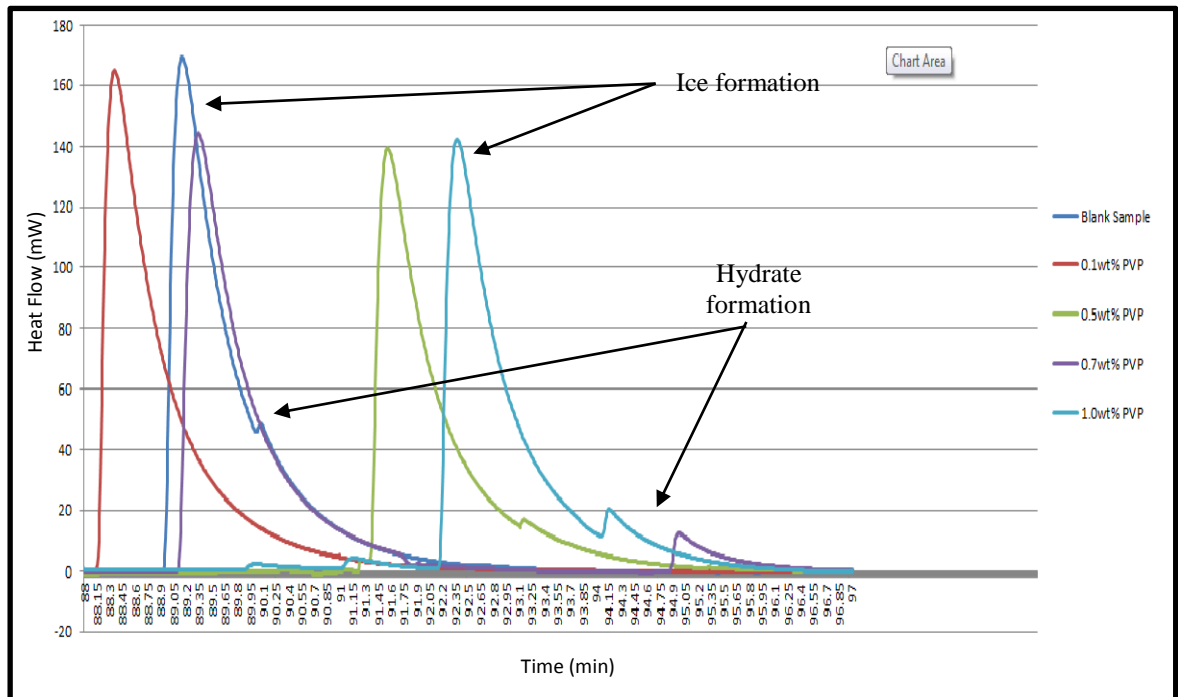
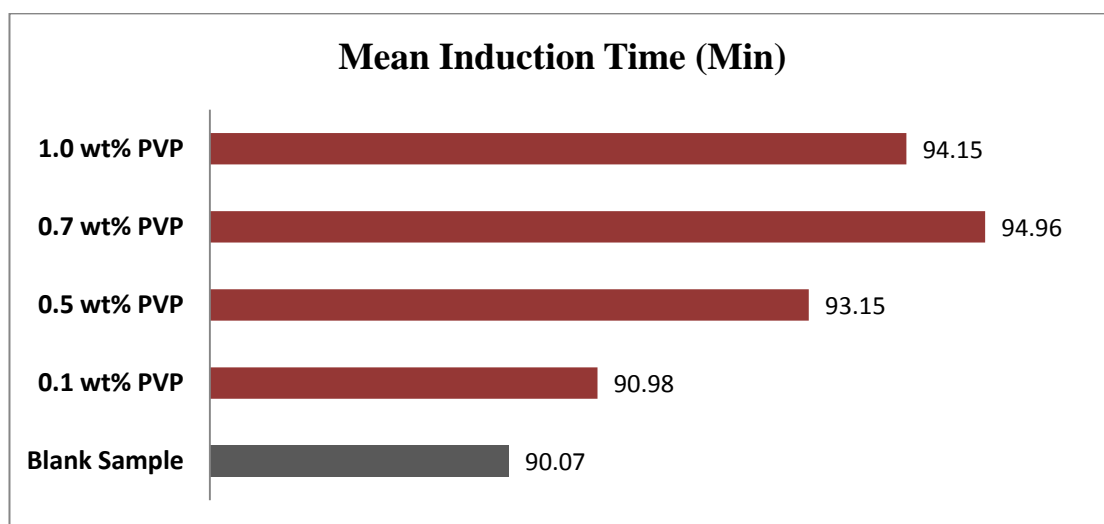


Figure 19: Methane hydrate formation curves

Figure 19 shows the trending of four samples of PVP with different value of concentration and one blank sample for reference. The result shown the exothermic curves with two (2) exothermic peaks are identified for each curve. The result in figure 19 displayed the heat flow versus time range zoomed from 88<sup>th</sup> minutes to 97<sup>th</sup> minutes ( $\pm 10$  minutes).

The first highest exothermic peak for each sample represents the ice formation of the sample and the second highest peak can be interpreted where hydrate formation take place. Theoretically, in lower pressure (30 bars – 100 bars) used to test hydrate formation, the formation of ice will take place before the hydrate formation whereas hydrate will form first for operating pressure 200 bars and above and the difference temperature of ice formation regardless of applied pressure in the experiment will not exceed 2 °C (usually from -16 °C to -18 °C) (Hester, Davies and Lachance). The energy consumed for the exothermic process to take place can be calculated by total area under the curve. The size of the peak for ice formation is greater than hydrates formation. This explained the hydrate formed is smaller in size whereas the size of ice formed is bigger due to the entire sample is converted into ice. In order for hydrate to formed, the sample needs to be in contact with the gas molecule which is methane and that define only a thin-layer hydrate is formed.



**Figure 20: Hydrate induction time**

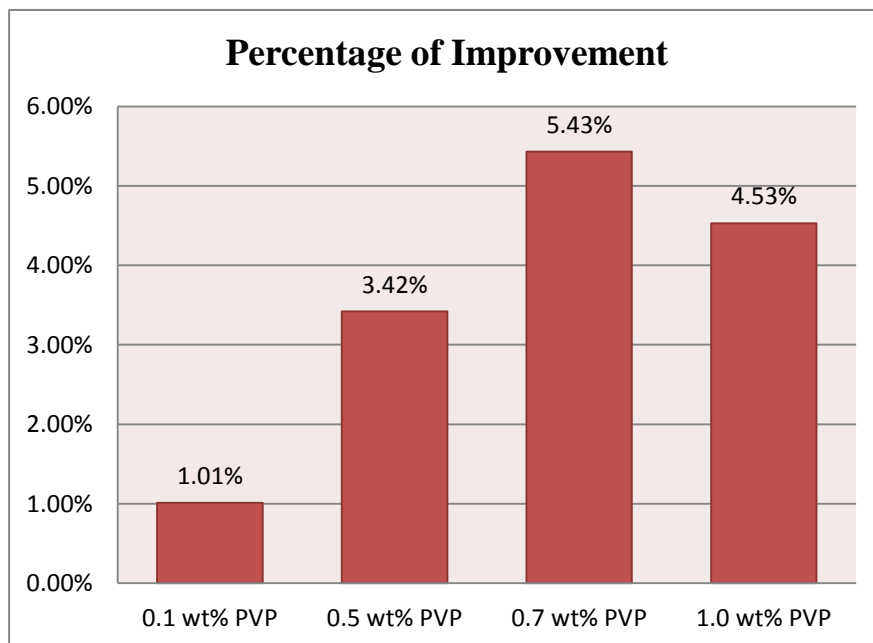
Figure 20 show the mean induction time for three concentration of PVP inhibitor to delay the formation of methane hydrate. This tabulation of data proved the ability of PVP as conventional KI where all PVP solution samples were resulted

in longer mean induction time for hydrate to form. 0.1 wt% of PVP delayed for 0.91 minutes while 0.5 wt% of PVP shows the induction time is delayed for 1.12 minutes. 0.7 wt% of PVP resulted in longest delayed time for hydrate formation which is 4.89 minutes and 1.0 wt% of PVP delayed for 4.08 minutes. This situation can be explained that the 1.0 wt% of PVP might not the optimum concentration of PVP inhibitor. The optimum concentration value is much closer to 0.7 wt% of PVP. The characteristic of successful kinetic inhibitor is the ability to delay the formation of hydrate with concentration of 1.0 wt% or less (Xiao and Adidharma, 2009).

Each sample that resulted in longer induction time shows an improvement to retard the hydrate formation process. The improvement percentage can be determine by the equation below and figure 21 show the improvement percentage of all three samples of kinetic inhibitor PVP tested.

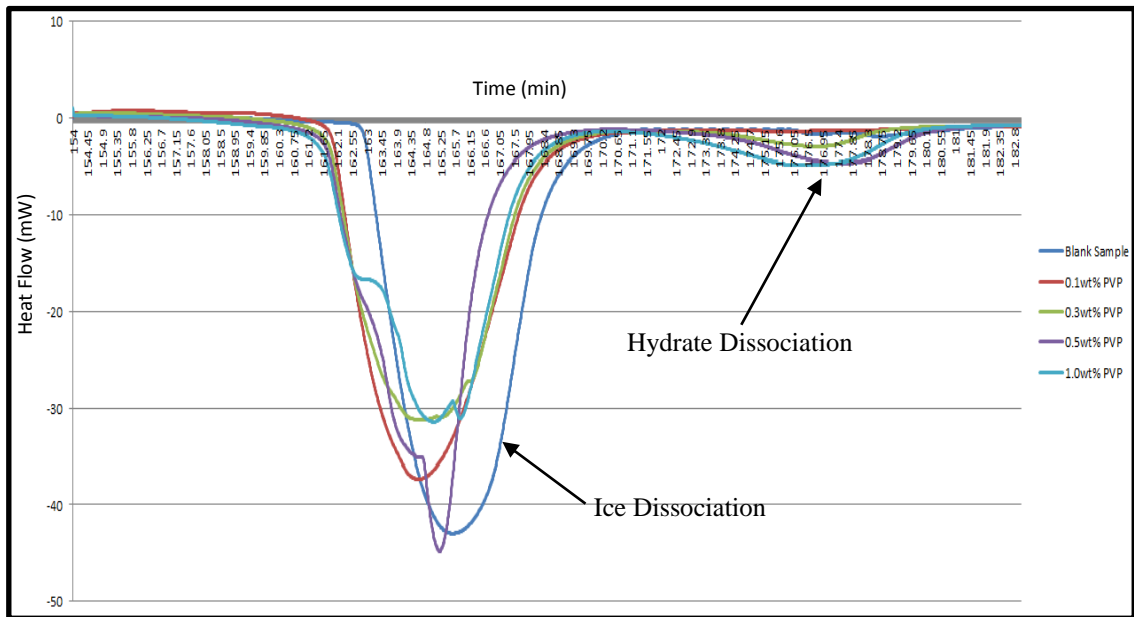
*Percentage of Improvement (%)*

$$= \frac{\text{Induction time of KI sample} - \text{Induction time of blank sample}}{\text{Induction time of blank sample}} \times 100\%$$



**Figure 21: Hydrate induction time improvement percentage**

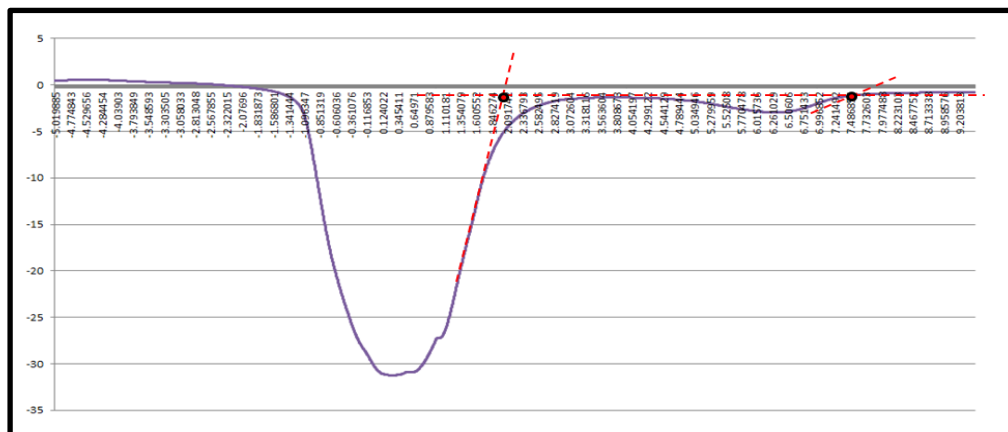
### 4.1.2 Dissociation of Hydrate



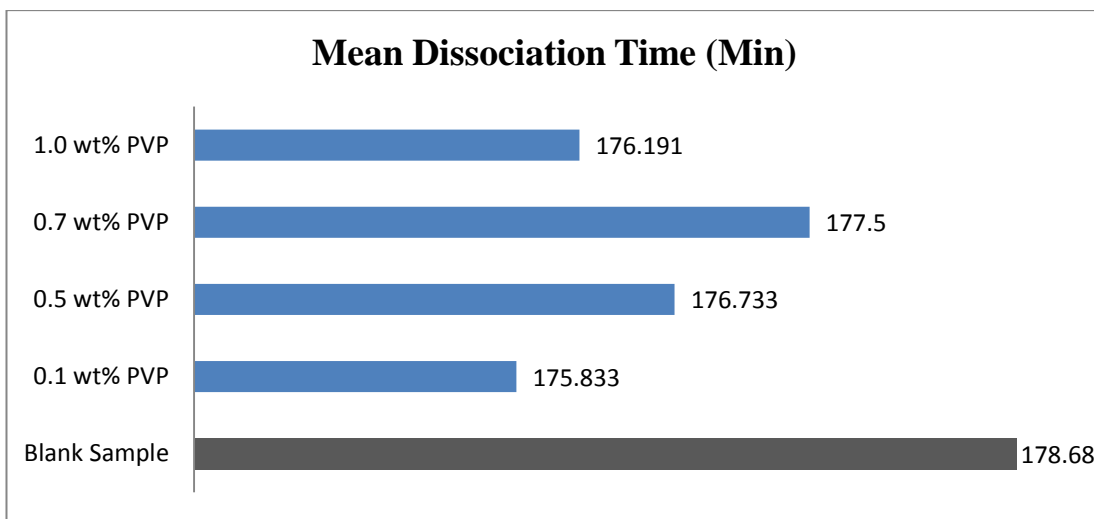
**Figure 22: Methane hydrate dissociation curves**

Figure 22 display the result of endothermic reaction curve zoomed at 154<sup>th</sup> minutes to 183<sup>rd</sup> minutes of experiment. The first endothermic peak represents the ice dissociation curve and the second peak for hydrate dissociation. The energy required or the magnitude of the ice and hydrate dissociation shown by the area under the curve. As in figure 22, the magnitude of ice dissociation is bigger than hydrate dissociation is explained as in exothermic situation where the size of ice formed is bigger whereas hydrate formed is just a thin-layer sized. Hence, ice needs more energy (heat) for dissociation.

To determine the dissociation temperature for ice and hydrate, the intersection point between the baseline and returning peak is observed as shown in figure 23.



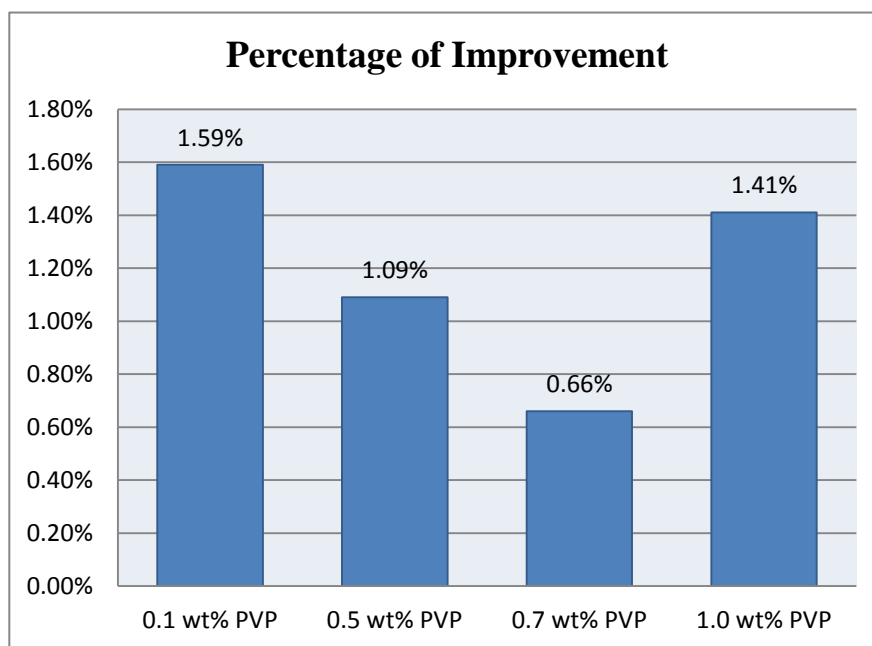
**Figure 23: Example to determine temperature for 0.5 wt% of PVP**



**Figure 24: Mean dissociation time for hydrate**

Figure 24 is the data tabulated for mean dissociation time taken for each sample with blank sample as the reference. All PVP samples resulted in lesser dissociation time for hydrate to dissociate as compare to blank sample. The result displays a positive measure for PVP as kinetic inhibitor which give a shorter time taken for hydrate dissociation. 0.1 wt% of PVP show the shortest time for hydrate dissociation at 175.83 minutes and 1.0 wt% is the second shortest give 176.19 minutes. 0.7 wt% and 0.5 wt% of PVP gives 177.5 and 176.73 minutes of mean dissociation time respectively. This behaviour of dissociation is not necessarily in correct measure as 0.1wt% of PVP should yield the shortest time for hydrate to dissociate. 0.7 wt% of PVP also shows unfavourable mean dissociation time. As in figure 22, the peak for hydrate dissociation is not clear and usually flattens. Difficulty in measuring the exact figure for dissociation mean time occurred and error while measuring the energy required for the endothermic process due to the area under the graph is not fixed as in exothermic curve.

Figure 25 demonstrates the effectiveness of tested PVP samples as kinetic inhibitor by their percentage of improvement for dissociation time of the methane hydrate.



**Figure 25: Improvement percentage of hydrate dissociation time**

#### **4.2 Effect of Polymer Polyvinylpyrrolidone (PVP) with Chitosan as an Additive on Hydrate Induction and Dissociation Time**

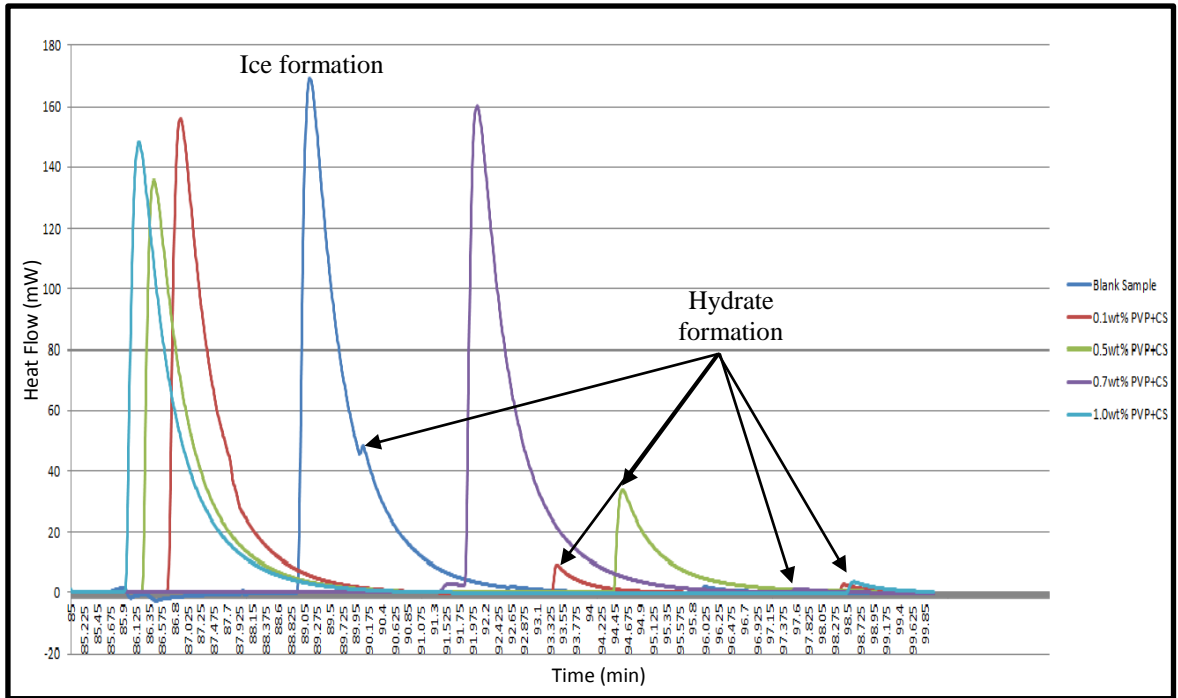
Blank sample as fixed variable used in data tabulation of PVP inhibitor with four (4) other tested samples of PVP with chitosan are plotted in the same plane graph to measure the mean time form induction and dissociation of hydrates. As previous data interpretation in 4.1, the heat flux curve behaviors determined the result of exothermic and endothermic reaction in the system. The concentration value of tested samples for PVP with chitosan inhibitor is as table 6.

| No | wt% of PVP and Chitosan        | Total wt% of sample |
|----|--------------------------------|---------------------|
| 1  | 0.07wt% PVP + 0.01wt% Chitosan | 0.1wt%              |
| 2  | 0.35wt% PVP + 0.15wt% Chitosan | 0.5wt%              |
| 3  | 0.49wt% PVP + 0.21wt% Chitosan | 0.7wt%              |
| 4  | 0.7wt% PVP + 0.3wt% Chitosan   | 1.0wt%              |

**Table 6: PVP with chitosan concentration values**

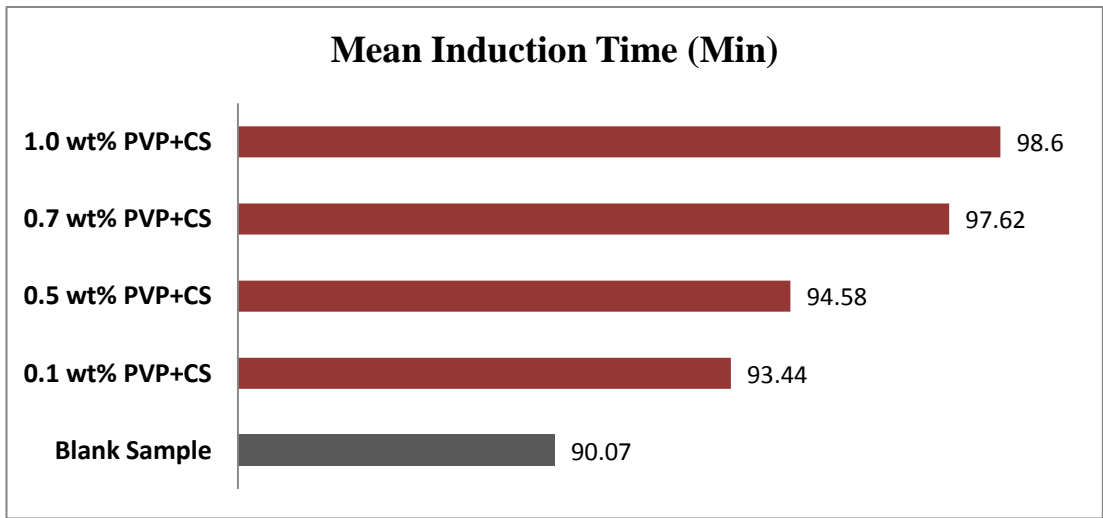


### 4.2.1 Formation of Hydrate



**Figure 26: Methane hydrate formation curves (PVP + CS)**

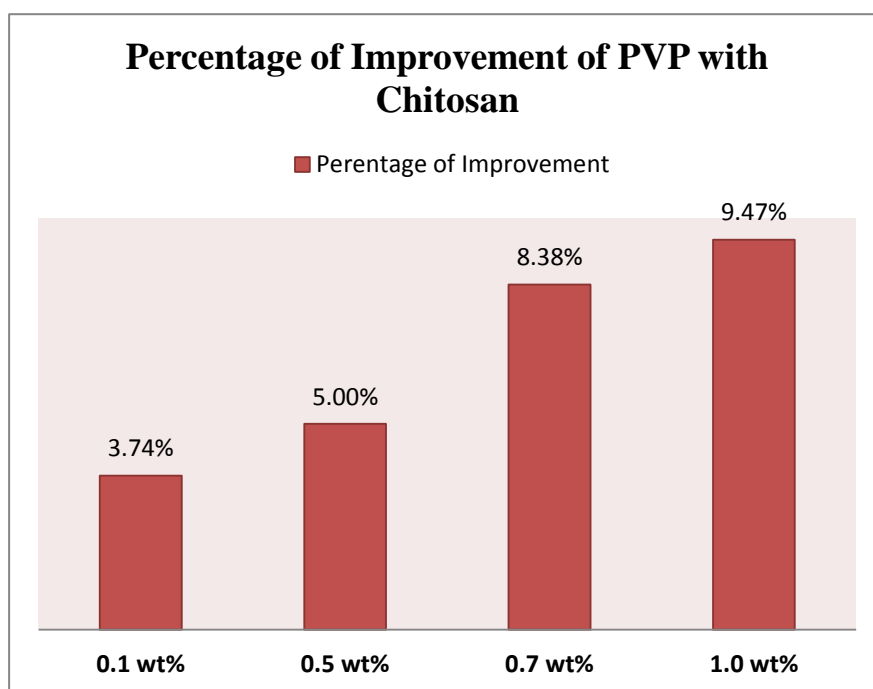
Figure 26 displays the hydrate formation heat flux zoomed from 85<sup>th</sup> minutes to 99<sup>th</sup> minutes of cooling process. The explanation regarding the size of each ice and hydrate formation peaks are the same with PVP samples in 4.1 as ice formed is bigger than thin-layered hydrate which portrays the energy required for the exothermic process. The hydrate formation mean induction time for PVP with chitosan as an additive as figure 27.



**Figure 27: Hydrate induction time for PVP with Chitosan**

All PVP with chitosan samples shows a positive result to prove chitosan ability to enhance the PVP performance as kinetic inhibitor. 1.0 wt% of PVP+CS resulted in the longest induction time delayed for 8.53 minutes and 0.1 wt% of PVP+CS gives the shortest, 3.3717 minutes delayed. 0.5 wt% and 0.7 wt% of PVP+CS gives 4.505 minutes and 7.547 minutes accordingly. In PVP with chitosan inhibitors, the optimum concentration observed is closer to 1.0 wt% due to its longest induction time differed from previous PVP inhibitor which 0.7 wt% is the closest optimum concentration. Briefly, the different is caused by the weight percentage of chitosan used. This experiment used weight percentage of PVP+CS with ratio of 7:3. This might not be the optimum ration to maximize the capability of chitosan to enhance PVP performance as kinetic inhibitor.

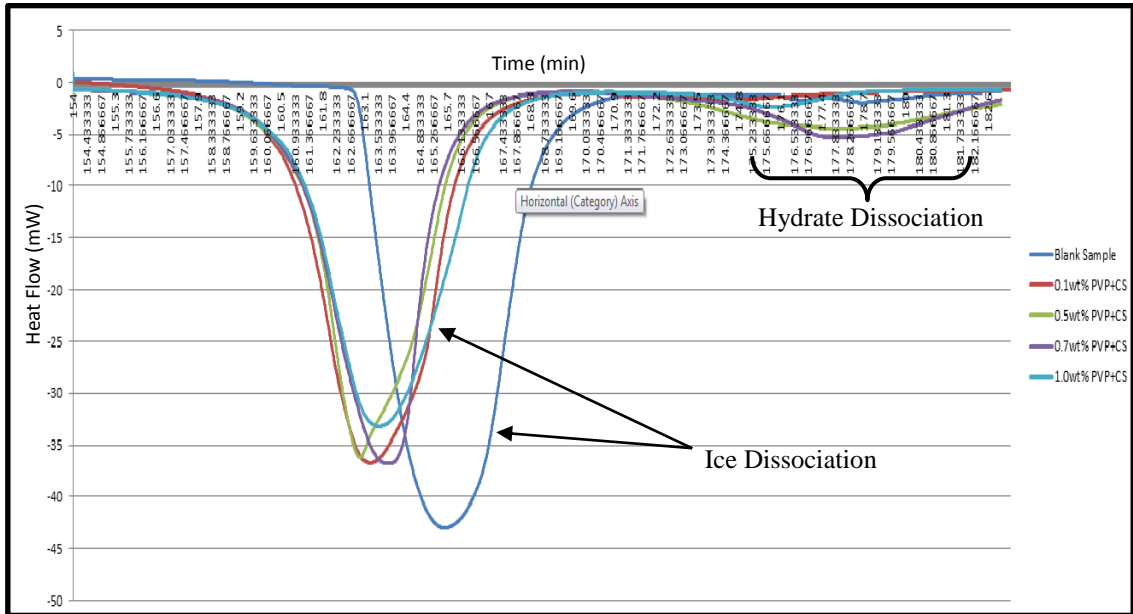
Figure 28 present the percentage of improvement of inhibitor PVP with chitosan in delay the hydrate formation with blank sample as the reference.



**Figure 28: Percentage improvement of PVP with chitosan (Formation)**

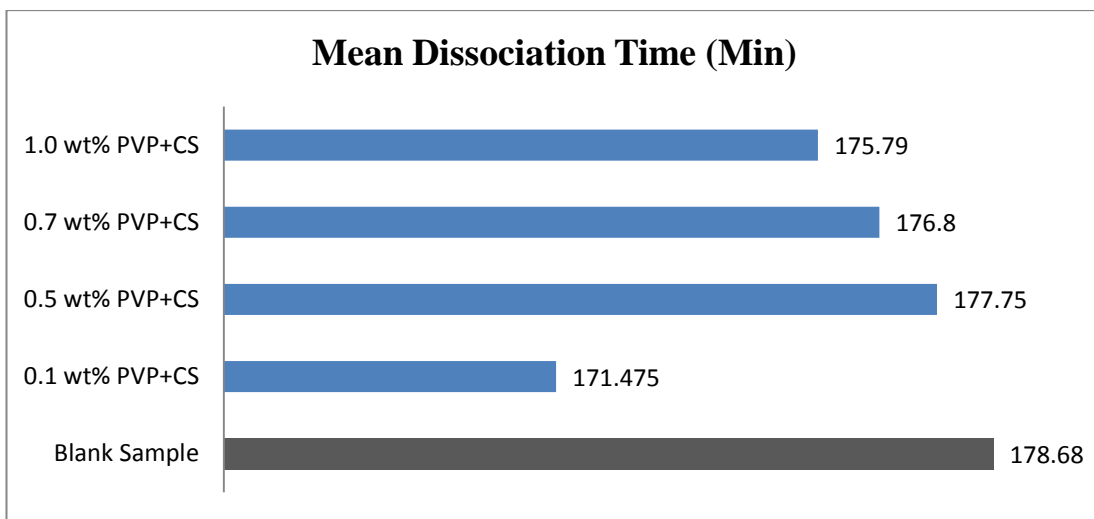
## 4.2.2 Dissociation of Hydrate

Figure 29 show heat flux of endothermic process for ice and hydrate dissociation zoomed from 154<sup>th</sup> minutes to 183<sup>rd</sup> minutes. The first and second endothermic peak represents the ice and hydrate dissociation with blank sample as fixed variable.

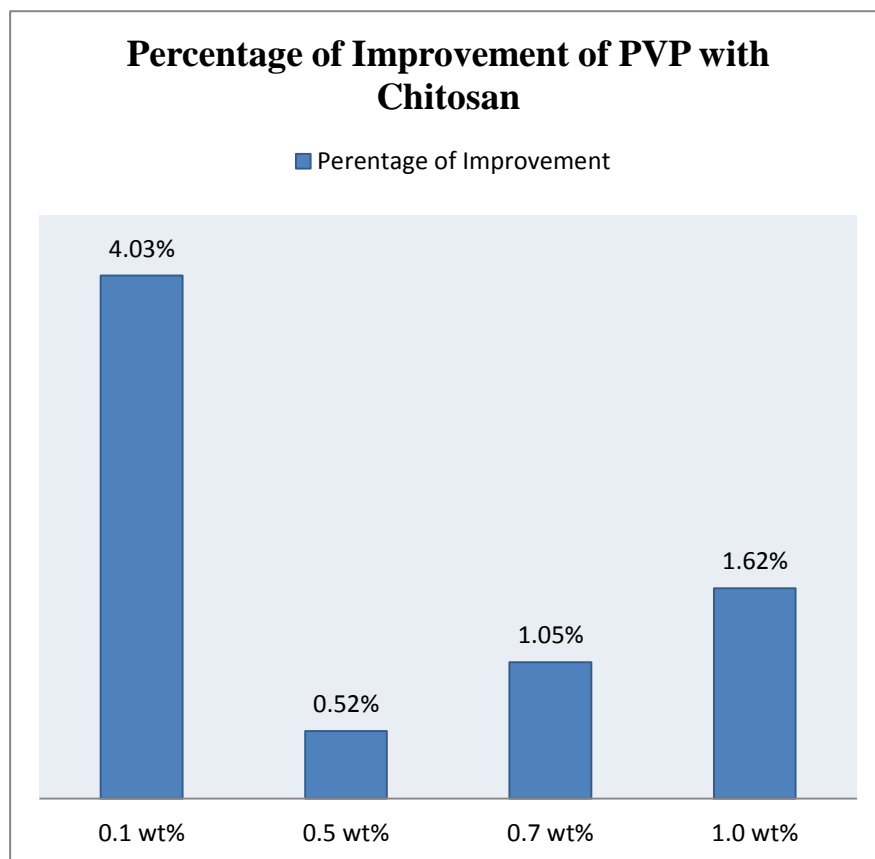


**Figure 29: Methane hydrate dissociation curves (PVP + CS)**

Hydrate dissociation curve (endothermic) is important to analyze the formation curve (exothermic) if the two peaks appeared in the formation curve were about the same in size by calculating the area under the peak as dissociation curve are more distinctive between ice and hydrate dissociation peak than formation curve. With high scanning rate of 0.5 °C/min method used, the exothermic process is much sensitive for any exothermic process occurred throughout the experiment rather than the heating process in endothermic (Xiao and Adidharma, 2009). The hydrates mean dissociation time for inhibitor PVP + CS and their increment in percentage of improvement are tabulated in figure 30 and figure 31 respectively.



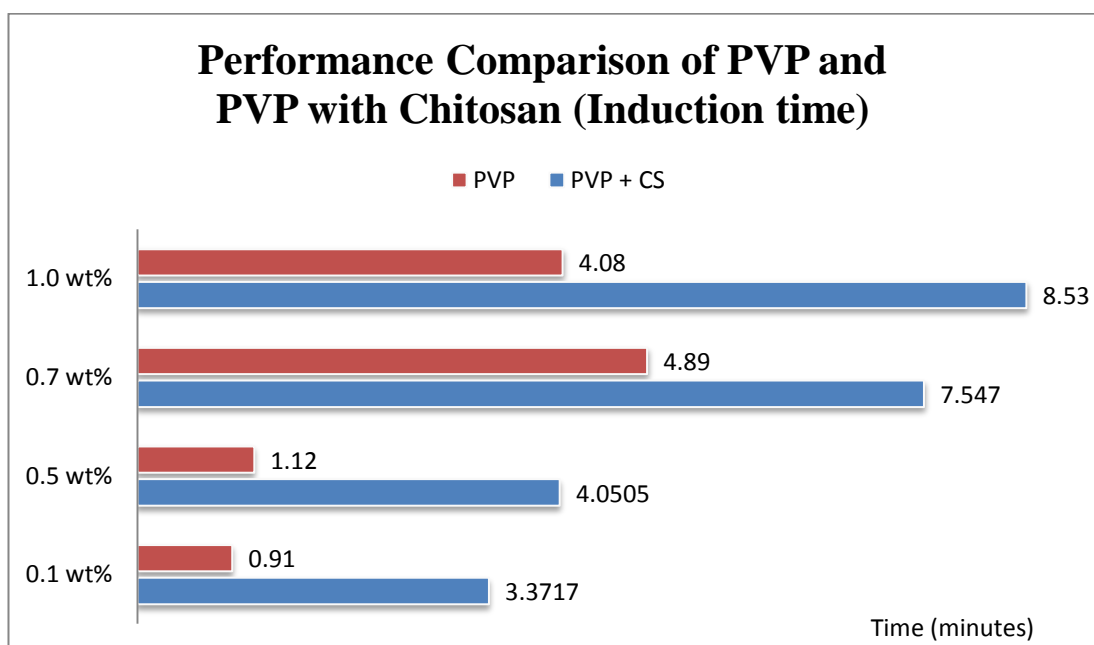
**Figure 30: Mean dissociation time for hydrate of PVP with chitosan inhibitors**



**Figure 31: Percentage improvement of PVP with chitosan (dissociation)**

### 4.3 The Performance Comparison and Analysis of Kinetic Hydrate Inhibitor between PVP and PVP with Chitosan as an Additive

The performance of successful kinetic inhibitor is measure by the ability of the inhibitor used to adsorb onto the hydrate surface which by time dependent, prevent the hydrate to form by acting as the ‘guest’ into the hydrate cage (Sloan, Koh and Sum, 2010). It is necessary to understand the concept of kinetic inhibitor to analyze the enhancement of any sub-material added to the known KI. Figure 32 shows the comparison of two type of tested inhibitor; PVP and PVP with chitosan as an additive with their respective result of induction time in delaying the formation of hydrates.



**Figure 32: Performance comparison of PVP and PVP with chitosan**

Data tabulated in figure 32 proved the enhancement of KHI is successful with the addition of chitosan. Based on the result, as in average, the performance in terms of the time delayed for hydrate to form of PVP with chitosan added is twice longer instead of PVP alone. This enhancement with chitosan allowed PVP to inhibit hydrate formation in larger hydrate stability zone since PVP is not suitable to be used if the hydrates formation curve is too far away shifted from the hydrate proportion area (Ugur and Mahmut, 2002).

The positive result explained that chitosan is able to lower down the sub-cooling degree of kinetic inhibitor PVP. Sub-cooling is the necessary parameter since KHI are ranked based on their sub-cooling degree (Sloan, Koh and Sum, 2010). For an example in this experiment at 40 bars of operating pressure, how much degree of sub-cooling is lowered when chitosan is added.

The ratio 7:3 of PVP and chitosan to prepare the sample solution is a trial procedure since chitosan are proposed to become an additive, sub-material for inhibitor PVP. The optimum concentration hence needs to be specified in determine the optimum ratio for PVP and chitosan. This specification required information in sub-cooling degree for comparison and the degree of deacetylation (DD) of chitosan since the main properties of chitosan depends on its deacetylation degree. The experiment run with chitosan having DD of 70% - 97% which is high and required acid (HCL is used in the solution preparation) to unfold the molecular chain of chitosan. This resulted on slight changes in viscosity of the solution. However this slight alteration is ignored due to the experiment mainly aims to determine the practicability of chitosan to enhance PVP performance as KI. How chitosan works with PVP to produce a better kinetic inhibitor is unsure which further research is needed to focus on the reaction in nucleation process of hydrate. However by the properties of chitosan and referring to the chemical structures, assumptions made where chitosan membrane 'helps' PVP in adsorb onto the hydrate surface in the growing cages of hydrate hence prevent or delay the hydrates formation. This phenomenon can be related with industrial application where chitosan membranes are used to transport chloride ions in aqueous solution (Wan, Creber, Peppley and Bui, 2003). In the present of excessed deionized water, chitosan membrane will swell hence will utilized by PVP molecule. This might be related as figure 32, result shown the lower weight percentage of PVP+CS solution (0.1 wt% PVP+CS), the higher the improvement of particular inhibitor which can up to three (3) times instead of PVP alone.

#### **4.4 Uncertainties**

##### **i) Exothermic and endothermic curve behavior**

The heat flux versus time curve displaying exothermic and endothermic reaction is not consistent in aspect of curve behavior. This include the cases where the top is flattens instead of peak, the exothermic or endothermic peaks appeared more than twice and no hydrate formation peak in several run.

##### **ii) Sample effectiveness**

Some of the samples were prepared 2 to 3 days before run the  $\mu$ DSC experiment (maximum for one day as planned). The samples were kept in the storage room at ambient temperature and may cause slight affection.

##### **iii) Errors**

Error which might cause defect in the result and data observed form the experiment are the history effect in  $\mu$ DSC equipment, the presence of impurities in sample and incorrect measure in balance and scale.

## CHAPTER 5

### CONCLUSION & RECOMMENDATION

#### 5.1 Conclusion

The performance of conventional kinetic inhibitor PVP is studied and the enhancement with the addition of chitosan has been investigated. Chitosan not able to inhibit hydrates by itself however successfully act as an additive to enhance the performance of PVP as kinetic inhibitor by twice longer the induction time for hydrate to form. The optimum concentration for PVP and PVP with chitosan is carried out and the effectiveness of both inhibitors to delay the methane hydrate formation in order for PVP,  $0.1\text{wt}\% < 0.5\text{wt}\% < 1.0\text{wt}\% < 0.7\text{wt}\%$  and for inhibitor PVP with chitosan as an additive,  $0.1\text{wt}\% < 0.5\text{wt}\% < 0.7\text{wt}\% < 1.0\text{wt}\%$ .

The mechanism and behaviour of chitosan with PVP in improving the kinetic inhibitor is still on-going research. Progressive studies on producing better formulation of LDHI never meet the end line as hydrate is categorized as long-standing problem in oil and gas operation.

In summary, research proved the ability of other polymers which are highly potential as KHI than PVP but the enhancement of PVP with chitosan is a step forward initiative in oil and gas sector. Chitosan, a great future potential material used to known as the second most abundant polymers, hence it is sustainable strategy to produce an inhibitor enhancer which is greener, less expensive and biodegradable.



## 5.2 Recommendation

Future work in this project is important as many parameters need to be manipulated with sophisticated explanations. The recommendations are based on perspectives from other hydrate researcher and from the author's findings throughout the project work are executed.

- The experiment can be enhanced by varies the pressure to investigate the behavior of hydrate formed in low and high pressure. In addition, the higher the pressure set for the experiment, the better the result since the environment is closer to the real cases.
- The optimum concentration of chitosan to be added with PVP should be determined by varies the ratio value of PVP and chitosan.
- Further studies regarding nucleation process and reaction in closer observation (e.g. using electron microscope) should be executed to investigate the chitosan behavior with PVP on the surface hydrate.
- To make the result is applicable for the most gases and situations, experiment on determine the hydrate formation in structure II or structure H (beside structure I) is recommended.
- Instead of using deionized water, it is recommended to use hydrated oil since the water cut in hydrated oil is higher and which closer to the real cases.
- To stimulate the true scenario of flow assurance, the impact of tested inhibitors toward pipelines should be investigated. The uses of low percentage of strong acid (HCL) which may affect in corrosion and the hydrocarbon fluid itself are recommended.
- The economic analysis should be done to compare the cost of using Chitosan as an additive with other kinetic hydrate inhibitors available before applied in the industry.

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