DETERMINE EFFECTIVENESS OF POLY-VINYLPYRROLIDONE (PVP) AS KINETIC HYDRATE INHIBITORS USING DSC

By

MUHAMMAD IRSYADUDDIN BIN ROZALI
10841

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

MAY 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
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CERTIFICATION OF APPROVAL

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Approved by,

(MS. MAZUIN JASAMAI)

Mazuin Jasamai
Lecturer
Geoscience & Petreluem Engineering Department
Universiti Teknologi PETRONAS
Bandar Seri Iskandar, 31750 Tronoh,
Perak Darul Ridzuan, MALAYSIA.

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2011

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.

(MUHAMMAD IRSYADUDDIN BIN ROZALI)

ABSTRACT

Gas hydrates can form in both gas-producing and oil-producing wells, which can cause hazardous problems such as pipeline clogging and hydrates agglomeration. Gas hydrates is favorable in conditions of low temperature (0°C – 15°C) and high pressure (>600psia) in presence of natural gas and water in the form of vapor or moisture. In this condition, crystalline structures (gas hydrates) is formed. Hydrates plug have been serious economic concern in oil and gas production pipelines and affect flow assurance as well. The presence of gas hydrates in pipelines is causing serious operational problem and safety problems. Kinetic hydrate inhibitors (KHIs) are injected in order to delay the nucleation of hydrates within the residence time. The effectiveness of KHI is examined on the four different samples of water-in-oil emulsion by using Differential Scanning Calorimetry (DSC). Heat transfer is measured by DSC in different concentration of poly-vinylpyrrolidone (PVP) used as kinetic hydrate inhibitor. The result shows that sample with 0.7wt% of PVP is observed to be the most effective at delaying the hydrate formation time. Therefore, PVP can be considered to be applied as kinetic hydrate inhibitor in the oil and gas industry instead of conventional method, Thermodynamic Hydrate Inhibitor (THI) since KHI is used at low concentration thus it is cheaper and environmental friendly product.

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NOMENCLATURE

THI = Thermodynamic Hydrate Inhibitor

AA = Anti-Agglomerate Hydrate Inhibitor

KHI = Kinetic Hydrate Inhibitor

LDHI = Low Dosage Hydrate Inhibitor

PVP = Poly(N-vinylpyrrolidone)

PVCap = Poly(N-vinylcaprolactam)

VIMA = Poly(N-methyl-N-vinylacetamide)

PVVam = Poly(N-vinylvalrolactam)

PAPYD = Poly(acryoylpyrrolidine)

DSC = Differential Scanning Calorimetry

PEO = Thermoplastic polymer

$\frac{dQ}{dt} =$ Rate of heat production

$\frac{dh}{dt} =$ Rate of enthalpy change of the sample

$RC_s =$ Time constant of cell

$C_s =$ Heat capacity of the sample

$C_r =$ Heat capacity of the reference

$R =$ Thermal resistance between sample & heater

$T_s =$ Sample temperature

$T_p =$ Program temperature

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Gas hydrates are ice-like crystalline compounds that form at high pressure and low temperature conditions by hydrogen bonds of water molecules, with the assistance of natural gases. In other words, water physically entraps the molecules of a hydrate-former inside a hydrogen bonded solid lattice. Hydrate-former include nitrogen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, and butane which are the main components of natural gases [10][18].

The past two decades have seen the oil and gas industry moving towards deep-water exploration and production which is over 10,000 ft of water depth where pressures and temperatures are ideal for hydrate formation. This has brought new challenge for hydrate prevention in transportation.

There are a lot of theoretical and experimental works focused on studying gas hydrates. The modern studies of hydrates are aimed at three goals [11] :

- Prevention of formation and removal of large hydrate accumulations in natural gas production, transportation and processing systems.
- Development of natural gas reserves accumulated in earth in a hydrate state, and ecological aspects of gas hydrates.
- Creation of new technologies based on utilizing properties of hydrates, including making large amounts of hydrates for storage and transportation of gas in a hydrate state.

In order to protect a system against gas hydrate formation, the right chemical at the right dose rate need to be injected into the system. The conventional method of preventing hydrates is by using Thermodynamic Hydrate Inhibitors (THI) such as methanol and monoethyleglycol. THIs are used at high concentrations (10-60 wt %) which are costly on offshore developments and onshore processing facilities [8][10]. Currently there are two mechanisms of low-dose inhibition available as an alternative to THI; Anti-Agglomerate Hydrate Inhibitors (AA) and Kinetic Hydrate Inhibitors (KHI) [1][13]. Both AA and KHI are normally classified as Low Dosage Hydrate Inhibitor (LDHI) which added at low concentration (<1 wt %) [8].

AAs in general are surfactant based molecules, which allow the hydrate crystals to form but manage the size of the crystals so that they can be dispersed in hydrocarbon fluid. AAs are typically used for severe hydrate conditions and long shut-in period. On the other hand KHI's interface with the crystal nucleation process, thus delaying the onset of hydration for a significantly longer period of time. KHIs are typically used at more moderate sub-cooling and can be used at wide variety of water cuts [1][7][13].

KHIs are polymers which delay the rate of hydrate formation rather than affect the thermodynamics of the system. Increasing the concentration of the KHI will increase the time it takes for hydrate crystals to form.

The inhibition mechanism of polymers and surfactants is proposed as follows: Active molecules are found to adsorb strongly to the surface of a propagating hydrate crystal or pre-nuclear hydrate like clusters. In this process, they change the energy of the surface of hydrate crystal or cluster so change its growth characteristics. Some examples of known and patented inhibitors are poly-vinyl pyrrolidone (PVP), poly-vinylcaprolactam (PVCap), polymethyl-vinylacetamide (VIMA), poly-vinylvalrolactam (PVVam), and poly-acryoylpyrrolidine (PAPYD).

The objective of this study is to determine the effectiveness of polv-vinyl pyrrolidone (PVP) as kinetic hydrate inhibitor (KHI) by using Differential Scanning Calorimetry (DSC).

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Formation of gas hydrates in pipelines is causing serious operational and safety problems. In petroleum exploration and production operations, gas hydrates can cause partial or total blockages in pipelines and processing facilities. The problem is considered hazard in deepwater drilling, which can potentially block the blowout preventer (BOP) stack, kill lines and chokes, and obstruct the movement of the drill strings. This has brought new challenge for hydrate prevention in transportation. The crystallization of hydrate particles generally leads by forming solid plugs, to the blockage of pipelines, and thus to the shutdown of production facilities. The removal of hydrate plugs is generally difficult to achieve. A shutdown of several days or weeks may be necessary prior to the restarting of the production, and indeed, it may lead to pipeline abandonment as well.

The conventional method like THI is effective, but large concentrations are required which impacts the project profits. THIs are not cost saving as KHIs and AAs since they are added at high concentrations (10-60 wt.%) to shift the hydrate formation conditions to lower temperatures and higher pressures. On the other hand, KHIs only require low dosage to prevent the hydrate nucleation and growth with concentration range between 0.5-2 wt.% [2]. Besides, KHIs are discovered to be environmentally-friendly. However, further investigations on the effectiveness of KHIs have to be verified and comparisons between different inhibitors must be done before the industry can depend on the application of KHIs to the production system.

As an example of hydrate problems in oil production industry, there are more than 10 oil producing stations in both North and South are operation of Petroleum Development Oman. With desert environment, the ambient temperature in Sultanate of Oman can drop to as low as 5°C during winter, when hydrates form in several gases lift lines. The condition has caused affected wells to cease production, however being controlled temporarily by use of methanol as hydrate inhibitor.

Another case of hydrate formation problem occurred at offshore Dutch sector, where an unmanned platform tied back to an onshore terminal via a 17-km subsea pipeline. Although the sub-cooling was relatively low, 1-5°C, there were concern with both hydrate formation and corrosion occurring. THI injection was planned for hydrate prevention. However, due to the actual production temperature was unexpected and the high production of condensed water, MEG system was unable to treat the hydrates.

Gas hydrates are likely to form in subsea flow lines, an technology for subsea application is often costly. In many cases, KHIs aid on lowering the cost as compared to classical inhibitors, and more environmentally-friendly. However, there is limited published information at this time. Therefore, both data verified from field tests and laboratory tests are highly required to verify the effectiveness of a KHI.

1.2.2 Significant of The Project

Through this project, data such as thermogram, heat flow, heat capacity, pressure-temperature graph, and enthalphy can be obtained. Using these values, analysis on isothermal studies can be done which allow the detection of transitions like crystallizes, phase changes and curing. Therefore, effectiveness of the PVP as KHI can be evaluated.

1.3 OBJECTIVES

- To analyze the temperature of hydrate formation at atmospheric pressure using Differential Scanning Calorimetry (DSC).
- To determine hydrate dissociation at different concentration of KHI (PVP).
- To determine the most effective concentration of PVP to be used as Kinetic Hydrate Inhibitor (KHI).

1.4 SCOPE OF STUDY

The scope of study for this project revolves around gas hydrates handling methods in petroleum production system. The first stage of study consists of researching for industry case studies to understand the gas hydrate handling procedures adopted in the production system. Besides, understanding the different properties and conditions that favor the formation of gas hydrates in the pipeline in different regions of the world, is essential before moving to the second stage of study.

In the second stage, the experiments will be carried out using the polymer identified as KHI. Further evaluation has to be done by measuring the hydrate formation in the sample of water-in-oil emulsions with Differential Scanning Calorimetry (DSC). Using PVP, its effectiveness acting as KHI will be measured based on these parameters:

- Concentrations (wt.%) of KHI required to prevent gas hydrates effectively
- Time in minutes/hours before the nucleation of hydrates.

Then, analysis and comparisons will be done base on the data gathered and research studies before.

1.5 THE RELEVANCY OF THE PROJECT

Hydrates formation is becoming problematic in the deepwater exploration. As there were need of an effective hydrate inhibitor which is also economic to use. Using poly(N-vinyl pyrrolidone) (PVP) as Kinetic Hydrate Inhibitor (KHI), engineers can overcome this problem. This also helps in deciding on investment on the particular field.

1.6 FEASIBILITY OF THE PROJECT

This project is fully experimental based. In the time given, the project could be done. This project can be done within seven months given that everything goes fine. The objective can be achieved if the procedures are closely followed.

CHAPTER 2

LITERATURE REVIEW

2.1. HYDRATE FORMATION

Gas hydrates have been studied by petroleum industry for more than 70 years, but up now, the major part of the research was linked to the problem of oil transportation, prevention or remediation of pipe lines plugging [6][16]. Gas hydrates are ice-like crystalline inclusion compounds that form at high pressure (>600psia = 4Mpa)) and low temperature (around 0°C to 15°C) conditions by hydrogen bonds of water molecules, with the assistance of gases such as methane, ethane, propane and butane. On the other hand, hydrocarbons heavier than butane generally do not form hydrates [6].

There are three common crystal structures for gas hydrates named SI, SII, and SH [3][6][14]. The network of the structure I is a centered face cubic system which appears with light components such as methane or carbon dioxide. Structure II network is of diamond type with 24 cavities per mesh. SII is the most common because of the normal distribution of hydrocarbons in petroleum. The structure H network of hexagonal type is constituted of 6 cavities. This SH appears for molecules of important size such as cycloalcanes, but at support gas as methane is always necessary in order to stabilize the structure. Figure 1 shows SI and SII structures.

Basically, gas hydrate formation is expressed by the following equation: [3]

$$G + nH_2O \rightarrow G.nH_2O$$

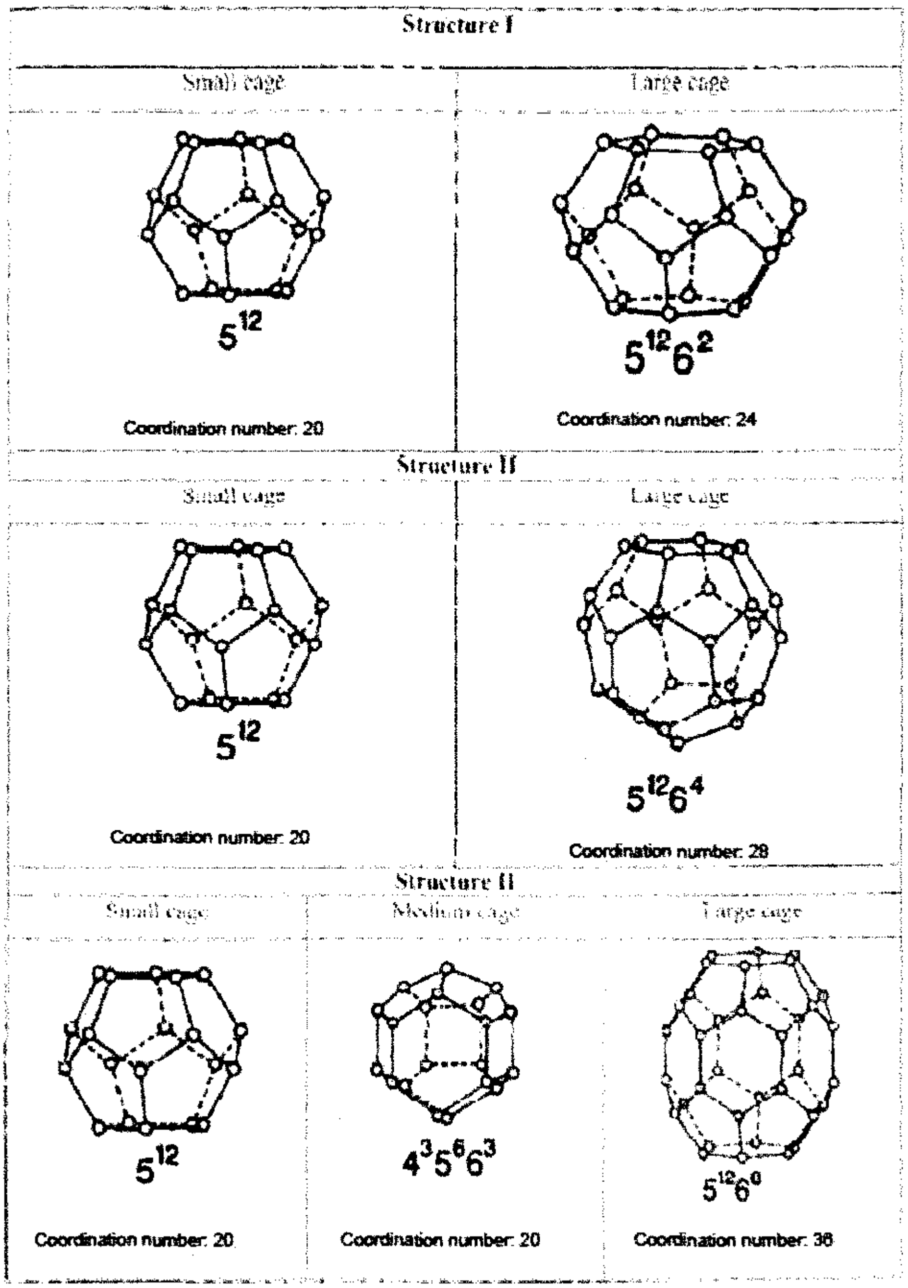


Figure 1- Cages and their coordination number in clathrate structures I, II and H (Mohamad Sabil, 2009)

From the equation, G represents natural gas molecules, n represents the mole of water when 1 mol gas is consumed, and $G.nH_2O$ represents gas hydrates. Formation of $G.nH_2O$ experienced these stages; from gas dissolution through metastable structures, to stable gas hydrates, shown in Figure 2.

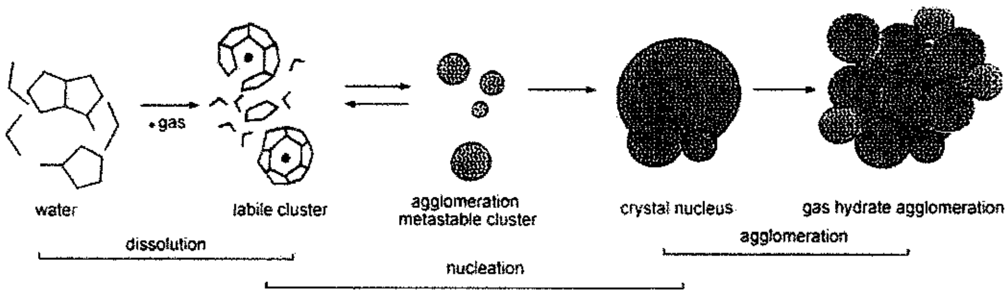


Figure 2 Gas hydrate formation process [10]

As shown in Figure 2, gas hydrate formation can be divided into gas dissolution, hydrate nucleation and agglomeration stages. Under condition of gas hydrate formation, water molecules form quasi-cavities by hydrogen bonds. When gases dissolve, gas molecules are entrapped intro these quasi-cavities and form labile clusters. These clusters could agglomerate together, which are in quasi-equilibrium with labile clusters until the species reach a critical radius to form stable hydrate nuclei. Finally the hydrates grow catastrophically when hydrate nuclei agglomerate.

2.2. HYDRATES CONTROLLING METHOD IN INDUSTRY

Hydrate formation is very expensive problem faced by the oil and gas industry, which must be solved in an economically and environmentally appropriate manner. The conventional method employed by the industry to prevent hydrates formation along the flow line is to add THI such as methanol or mono ethylene glycol (MEG), which shifts the hydrate formation conditions to lower temperatures and high pressures [2]. However, this method has significant economical impacts and technical limitations.

THIs are only effective at high concentrations with respect to the water rate (30 to 60 wt.%), which consequently results in high concerns about Health, Safety and Environment (HSE) risks. For instance, large quantity of methanol leads to high operational expenditure (OPEX), needs large size storage facilities, and cause serious problems in desalting operation and water management.

Therefore, studies have been carried out on the replacement of methanol or monoethylene glycol using Low Dosage Hydrate Inhibitors (LDHI). LDHIs can be efficiently used at dosages far lower than that of the THI, where the required concentration for these additives is expected to be in the range of 0.5-4.0 wt.% versus the water rate.

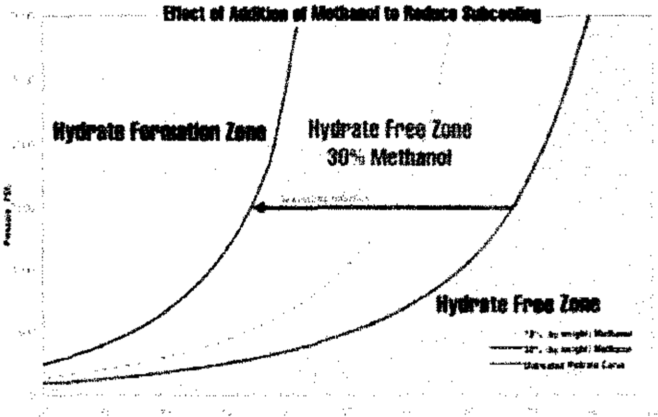


Figure 3 - Effect of additional methanol to reduce subcooling

There are two types of LDHI – Kinetic Hydrate Inhibitors (KHI) and the Anti-Agglomerators (AA). KHIs were initially discovered in 1991. KHIs are chemical products composed of active matters formulated in a solvent. KHI acts by delaying the hydrate nucleation step and by slowing down the growth of crystal in initial stage.

Therefore, the efficiency of KHI is depending on the maximum sub-cooling that the effluents have to bear, and the maximum residence time of the effluents inside the hydrate stability zone. Sub-cooling is the difference between the thermodynamic temperature of the hydrate formation and the ambient temperature. Thus, the maximum sub-cooling is obtained for the maximum operating pressure. The maximum residence time of the effluents inside the hydrate stability zone is obtained at the minimum gas flow rate. Tests are done to determine the minimum KHI dose rate to delay the formation time of hydrates.

2.3. TYPE OF KINETICS INHIBITORS & FIELD APPLICATION

KHIs are a class of low dosage hydrate inhibitor that have been used in the oil industry since about, 1995 to prevent plugging of oil, condensate and gas production pipelines with gas hydrates. This method is applied by injecting some substances which inhibit crystal structures to crease either by preventing nuclei agglomeration or by creating more crystallization centers, leading to a hydrate suspension. Then, the fluid can be transported through the pipeline without clogging the flow. The KHI used in the industry nowadays includes polymers and surfactants.

Polymers used as kinetic inhibitors comprise of several different types, where majority of them are active matters which are water soluble. Due to similarity in composition of water and gas hydrates, kinetic ice inhibitors have helped inspire the development of kinetic inhibitors. For example, PVP has been known for many years as a cyroprotectant for ice formation and also effective as KHI. The anti-freeze proteins (AFPs), found in some species of fish have also inspired KHI research in some oil companies. The polymers applied today in hydrates control are mostly patented KHI by companies.

KHIs which are water-soluble polymers, sometimes with additional organic molecules act as synergist enhancing the performance. KHIs delay the nucleation and usually also the crystal growth of gas hydrates. The nucleation delay time (induction time), which is the most critical factor for field operations, is dependent on the subcooling (ΔT) and pressure in the system as well as other factors such as the type of oil or condensate or the presence of other production chemicals such as certain corrosion inhibitor [19].

Type of water soluble polymers used include homopolymers, such as PVP and PVCap; copolymers such as poly-vinylpyrrolidone/vinylcaprolactam [P(VP/VCap)]; and terpolymers. PVP and PVCap are the most common used in the industry.

There are many studies in which polymers are suitable to use as KHI. In the study conducted by Karaaslan and Pariaktuna, different polymers have been tested in a high-pressure apparatus at high pressures and low temperatures with varying polymer concentration. A known hydrate inhibitor, poly(N-vinylpyrrolidone) (PVP) and a water soluble thermoplastic polymer (PEO) were determined the best kinetic inhibitors among them [8]. Figure 4 shows methane hydrate formation with different PVP concentration.

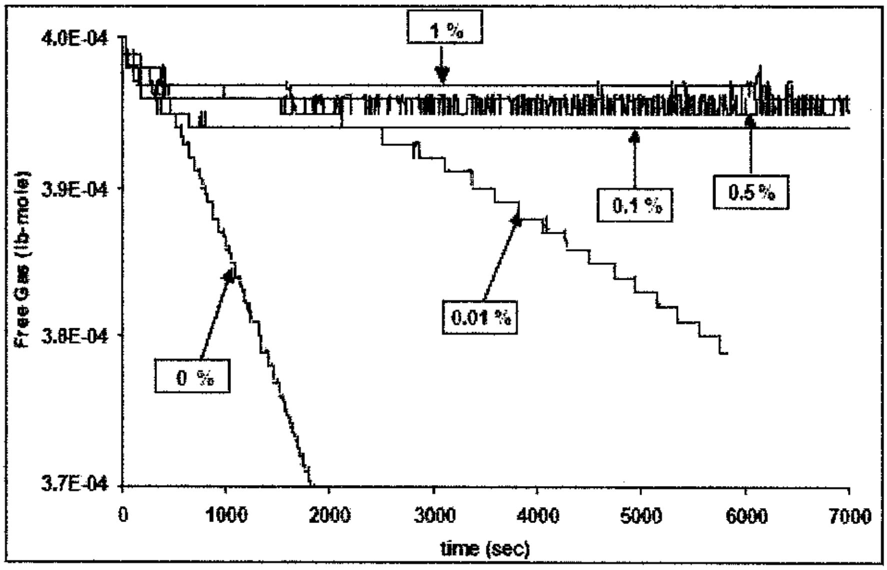


Figure 4 – Methane hydrate formation with 0, 0.01, 0.1, 0.5 and 1 weight % PVP solutions [8].

PVP, $(C_6H_9NO)_n$ is one of the earliest kinetic inhibitors with a relatively simple structure [3]. PVP is soluble in water and usually used as clarifying agent, stabilizer, bodying agent, tableting adjunct, and dispersing agent in the industry.

In Texaco field, methanol was successfully replaced by PVP in three gas wells and a ½-mile long gas line in southwestern Wyoming. In the five gas pipelines in east Texas, there was much reduced plugging with the use of PVP. The wellhead/pipeline pressures ranged from 150 to 2,500 psi and temperature ranged from 45 to 60°F [14].

On the other hand, surfactant is surface-active agent, which stabilizes the mixture of oil and water by reducing surface tension at interface between oil and water molecules (keep mixture from separating into layers). Surfactant-type inhibitors can reduce the risk of hydrates sticking to the pipe, minimizing the chance of hydrate plug formation. Some of these surfactants can make oil-in-water emulsions that interfere with the hydrate crystallization process. The surfactants selected in application of controlling hydrates are primarily those known as effective stabilizers for water in oil emulsions. Therefore, surfactants should have a direct effect on the hydrate formation process.

2.4. EXPERIMENTS

Both laboratory tests and field tests have been carried out on different samples using kinetic inhibitors to examine its effectiveness on gas hydrate prevention. For laboratory test, the apparatus for assessing the effectiveness of kinetic inhibitors that have been used include rocking cell chambers, flow loops, and Differential Scanning Calorimetry (DSC).

2.4.1. Rocking Cell Chambers

Rocking Cell apparatus is widely used in petroleum industry to determine the effectiveness of kinetic inhibitors. Generally, Rocking Cell consists of cylindrical tubes (cell) which contain the produced fluids used for testing purposes. A stainless steel ball fits in the cell and moves from one end of the cell to another [17]. Visual and non-visual techniques are used to track the ball movement, which indicates whether or not there is a hydrate blockage in cell.

The main advantage of this technique is that it allows for direct observation of the formation of gas hydrates. If gas hydrates are formed, then those will be spotted through a glass window. If the formation of the hydrates is such that it impedes the movement of the ball, then that will also be spotted and it is usually considered catastrophic [14]. This becomes useful when AA is being analyzed. As AA allow gas hydrates to be form, but they must be limited in size and be dispersed to allow the movement of the ball

The disadvantage is that a qualitative system must be used to evaluate the results and to rate the AAs. Besides, unless a light transparent enough condensate is used for the oil phase; the poor opacity of the oil phase makes it very difficult to evaluate the data. The type of glass used in the cell also limits how high in pressure the test can go. Therefore, several tests are required to obtain a significant result. As a result, it turns to be difficult to get consistent results due to the subjective evaluation of each test.

2.4.2. Flow Loops

Flow loops can better simulate the conditions of the system compared to Rocking Cells. Flow loops were being introduced for kinetic inhibitor effectiveness evaluation in 1990. Most flow loops are available in the industry are hundreds of feet in length. In general, flow loops are configured with a pipe-in-pipe setup, where the inner pipe carries the production fluids, and the outer pipe carries the heat transfer liquid. The production fluids are circulated using multiphase pumps. To evaluate AAs using flow loops, it will be difficult as they can crush a blockage formed upstream of the pump.

Although the heat transfer rate is high from the liquid in the outer pipe to the produced fluids in the inner pipe, the heating/cooling capacity required for hundreds of feet of 6-8 inches ID pipe is very large. Besides that, it is very expensive to utilize flow loops to attain the desired low temperature for heat exchange system [17]. Therefore, the industry is continuously looking for new methods to evaluate effectiveness of kinetic inhibitors.

2.4.3. Differential Scanning Calorimetry (DSC)

An alternative technique is by using **Differential Scanning Calorimetry (DSC)** – allowing to measure thermodynamic as well as kinetic properties of hydrate formation in PVP solution. This technique, DSC, consist in measuring thermal flux between two measurement cells and permits to detect any endo or exothermic phenomenon and especially any phase transition or change of state [4][6].

Basically, DSC consists of monitoring the heat exchanges between the sample and reference, either vs. time at constant temperature or vs. temperature during heating or cooling program.

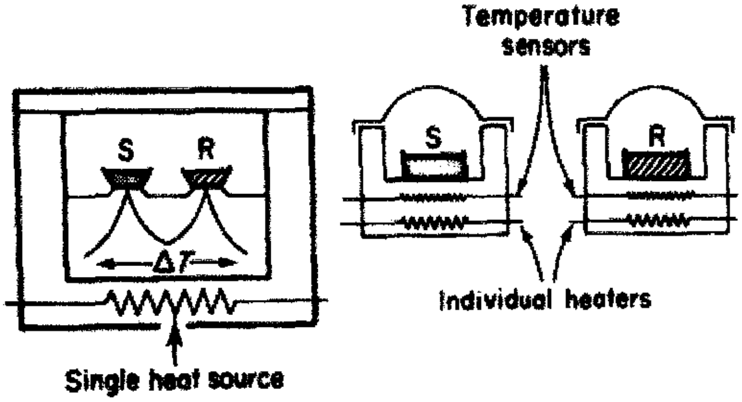


Figure 5 – Heat flux DSC and power-compensation DSC

As shown in Figure 5, the sample and reference are contained in identical crucibles, which can be opened or sealed, depending on the experimental conditions required. Both crucibles are placed in a thermoregulated furnace that imposes the temperature program. In simplest DSC, a thermocouple is used to measure the temperature difference between the two crucibles at one point of their walls (generally the bottom). The more complex DSC devices use Calvet principle to very precisely measure the heat exchanger [4]. The two cylindrical crucibles are placed into two independent heat sensors, formed from a large number of thermocouples surrounding the crucible. Each thermocouple measures the temperature difference between the crucible and the furnace in the radial direction as shown in Figure 6.

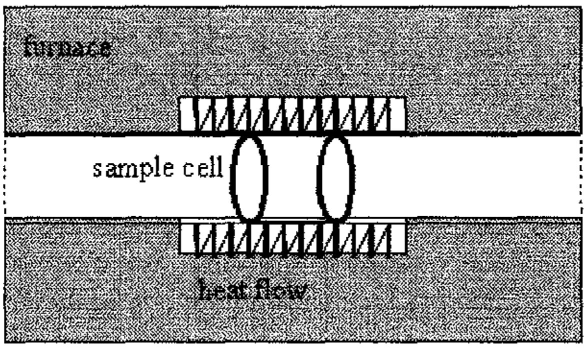


Figure 6 – Section of Calvet-type DSC showing one of the two sensors [4].

The fundamental equation of DSC is the following [5]:

$$\frac{dQ}{dt} = (C_s - C_r)\frac{dT_p}{dt} - RC_s\frac{d^2Q}{dt^2} - \frac{dh}{dt}$$

The power registered by the calorimeter, dQ/dt, is composed of three terms: first is to used to compensate the difference between the heat capacities of the sample (C_s) and the reference (C_r); the second one represents the transitory phenomena caused by the release (or absorption) of heat by the sample, R being the thermal resistance between the sample and the heater, and RC_s being the time constant of the cell containing the sample. The third one represents the production of heat by the sample (h).

DSC can be used in three types of applications [4]:

1. Thermodynamic: measurement of heat capacities, transitions (melting, crystallization, polymer transitions, glass transition etc.), purity determinations, and the study of dispersed phases.
2. Kinetics: relation between temperature, time and degree of advancement of a reaction (isothermal studies – Figure 7, measurement of kinetic with constant scanning rate or with different scanning rate). It is then possible to determine order of reaction and the activation energy.
3. Analytical: measurement of corresponding energy allows the determination of the component mass.

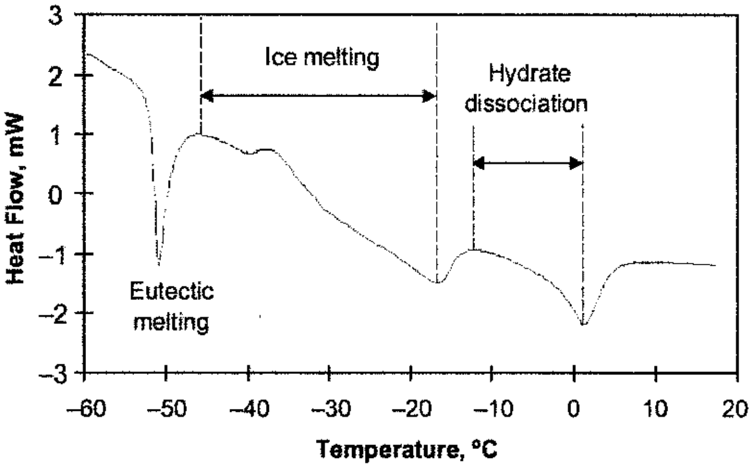


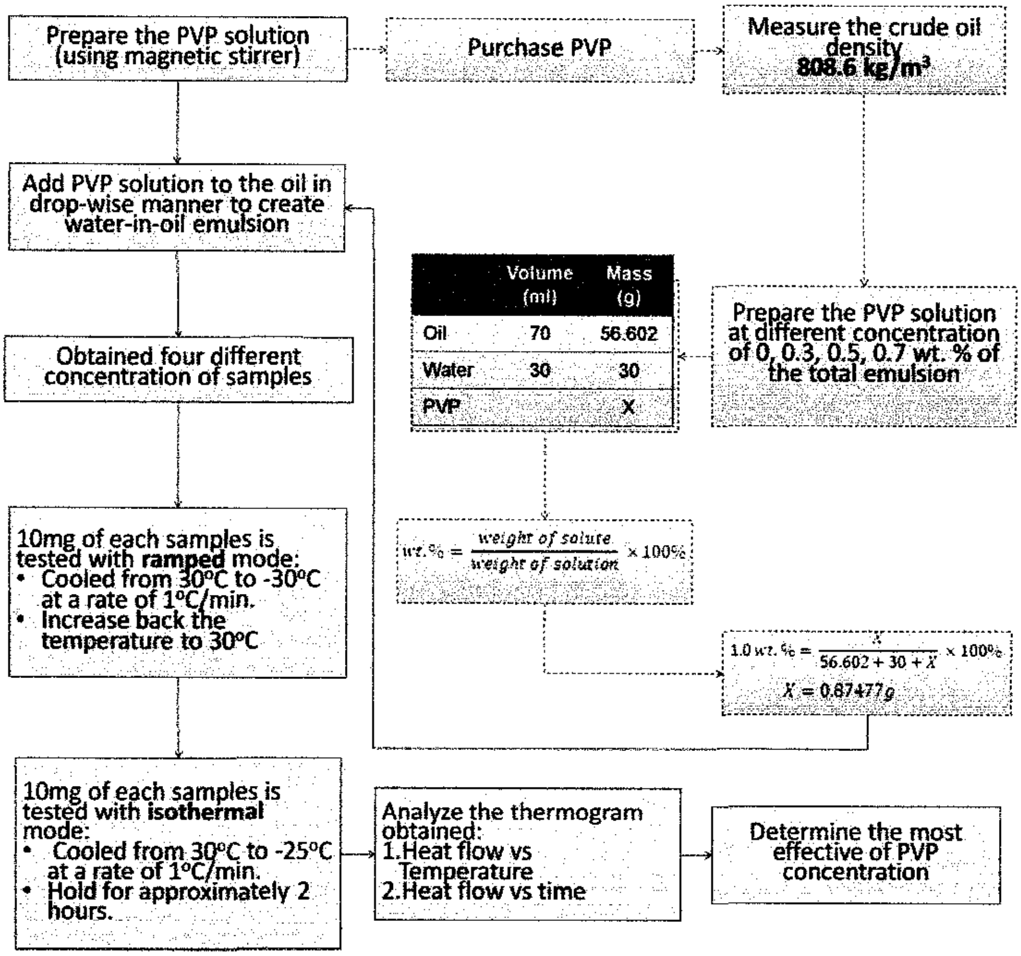
Figure 7 – Example of thermogram of a water-in-oil emulsion at 90 bar [14].

CHAPTER 3

METHODOLOGY

3.1. RESEARCH METHODOLOGY

Figure 8 below describes the overall methodology and general flow of this project.



	Volume (ml)	Mass (g)
Oil	70	56.602
Water	30	30
PVP		X

$$wt.\% = \frac{weight\ of\ solute}{weight\ of\ solution} \times 100\%$$

$$1.0\ wt.\% = \frac{X}{56.602 + 30 + X} \times 100\%$$

$$X = 0.87477g$$

Figure 8 – Flowchart representation of Project Methodology

3.1.2 Conditions that favor gas hydrate formation

There are four factors that can contribute to the hydrates formation:

i. High pressure (>600psia=4MPa)
ii. Low temperature (32°F to 60°F or 0°C to 15°C)
iii. Water (either in the form of liquid or water vapor)
iv. Hydrate formers (C_1, C_2, C_3, C_4, CO_2, N_2 and H_2S)

The common hydrate problem in the petroleum industry is methane hydrate. But this project used nitrogen as carried gas instead of methane due to limited availability of the methane gases. There are slightly difference between methane hydrate phase behavior and nitrogen hydrate phase behavior as shown in the figure 9 and figure 10.

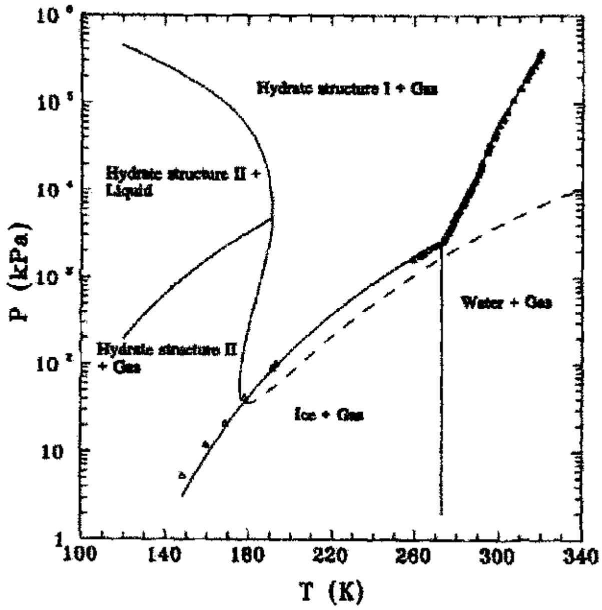


Figure 9 – Calculated phase diagram for methane hydrate. The dashed line represent an unstable equilibrium line between hydrate structures I and II and gas, where it cuts the ice-gas-hydrate equilibrium line there is a change in the stable hydrate structure. (Lundgaard and Mollerup, 1992)

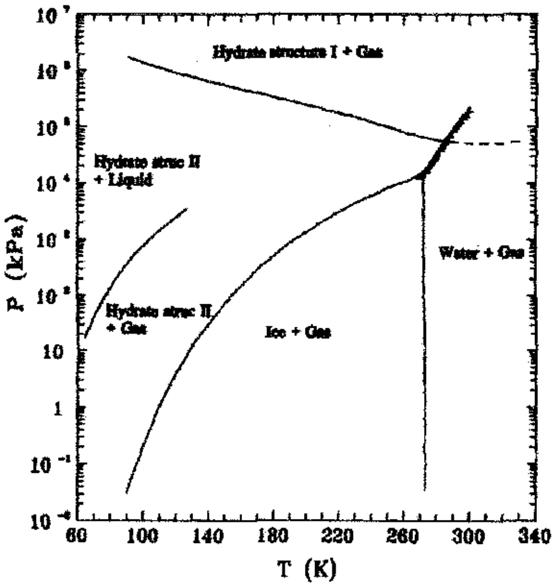


Figure 10 – Calculated phase diagram for nitrogen hydrate. The solid line at the top of the diagram represents the equilibrium line between hydrate structure I, II and gas. The dashed extension represents an unstable equilibrium line between hydrate structure I and structure II (Lundgaard and Mollerup, 1992)

3.1.3 Type of kinetic hydrate inhibitor

Among the many polymers used in the industry as KHI, the most common ones are poly-vinylpyrrolidone (PVP) and poly-vinylcaprolactam (PVCap), which are water soluble homopolymers. Due to cost constraints and polymer availability, poly-vinylpyrrolidone (PVP) will be tested in this project.

Polyvinylpyrrolidone (PVP) is a white to tan powder which is supplied in two molecular weight forms. PVP used in this experiment is lower molecular weight category which is about 40,000 MW. It is first diluted in water to create PVP solution before mix with the crude oil in drop wise manner to create water-in-oil emulsion samples.

3.1.4 Experimental apparatus

Differential Scanning Calorimetry (DSC) is used to measure the thermal properties of the water-in-oil samples prepared using the magnetic stirrer. The equipment available in the laboratory is product of *Perkin Elmer Pyris 1 DSC.*

DSC is defined as a technique in which the difference in energy inputs into a substance and a thermally inert reference material is measured as a function of temperature while the substance and reference are subjected to a controlled temperature program. DSC measures the amount of heat flow into the samples (endothermic) and away from the samples (exothermic) when the specimen undergoes thermal transition.

Table 1 – Technical specification of Perkin Elmer Pyris 1 DSC

Technical Specification
Perkin Elmer Pyris 1 DSC
• An intracooler allowing temperature range of -60°C to +600°C • An air shield to prevent moist air from settling into and maintaining the sample holder region dry and frost-free. • Samples as small as 1 mg can be analyzed at rates of up to 300°C per minute. • Specific heat capacity measurement • Power compensating calorimetry

In the DSC thermogram of Perkin Elmer, the Y axis is usually expressed in mW or W/gm. The latter is a normalized unit (heat flow / weight of sample). For the Y-axis, analyst need to be aware of heat flow convention whether endothermic is pointing up or down. Both conventions are acceptable. Thermal events will appear as deviations from the baseline. The X-axis can be displayed as either temperature or time. The area under the curve is usually calculated as the integration of heat flow over time. The unit under the curve is therefore mJ or J/gm.

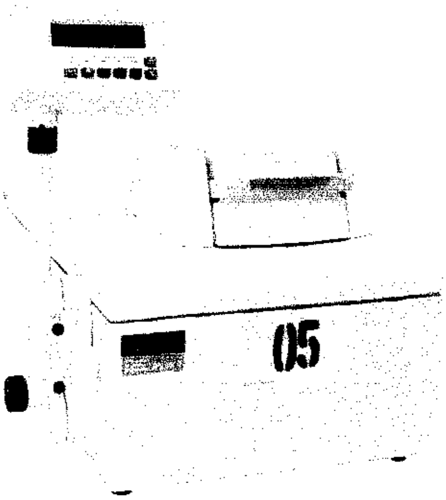


Figure 11 – Perkin Elmer Pyris 1 DSC

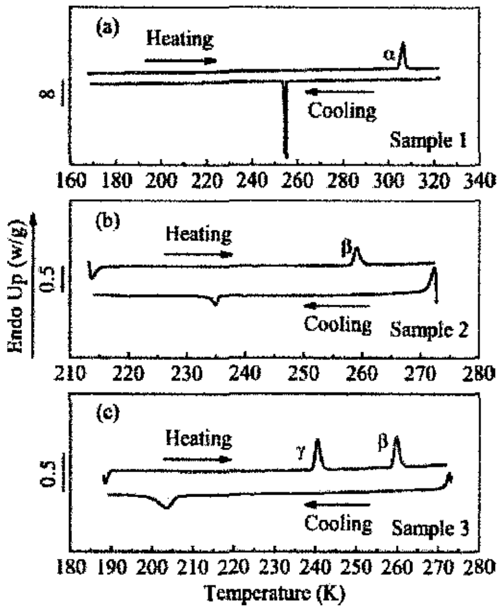


Figure 12 – Samples of thermogram generated by *Perkin Elmer Pyris 1 DSC*

3.2. PROJECT ACTIVITIES

Table 2 – Project activities planned for Final Year Project

Activities	Starting Month	Finishing Month
Survey on the availability of suggested Experiment Apparatus	1st March 2011	4th March 2011
Study on method to calculate data obtained from DSC and how to analyze them	5th March 2011	31st March 2011
Study on the methodology and prepare for the proposal defense.	1st April 2011	8th April 2011
Study on the optimum amount and sample preparation for DSC experiment.	11th April 2011	1st June 2011
Experiment on effect of temperature (with constant pressure) on hydrates formation and dissociation with and without PVP [ramped mode]	3rd June 2011	10th June 2011
Experiment on effect of contact time (hold 6 hours at -25°C) on the solutions with and without PVP. [isothermal mode]	10th June 2011	17th June 2011
Analysis of the data	17th June 2011	20th July 2011
Report documentation	21th July 2011	1st Sept 2011

3.3. GANT CHART & KEY MILESTONE

Table 3 – Gantt chart and Key Milestone through the Final Year Project

	1ST SEM				2ND SEM			
Activity	F	M	A	M	J	J	A	S
Selection of Project Topic	🟥							
Preliminary Research Work	🟥							
Submission of Extended Proposal Defense	🟦							
Survey on the availability of suggested Experiment Apparatus		🟥						
Purchase unavailability things. Study on how to prepare the solutions.		🟥						
Defense proposal. Present details on methodology of the experiment			🟦					
Sample preparations. Water-in-oil emulsion at different wt% will be prepared. 100ml of each sample.				🟥	🟥			
Experiment on effect of temperature (with constant pressure) on hydrate formation and dissociation with and without PVP (ramped mode)					🟥			
Experiment on effect of contact time (hold 6 hours at -25°C) on the solutions with and without PVP (isothermal mode)					🟥			
Completion of the temperature determination at which hydrates formation and dissociation at different concentrations of emulsions.						🟦		
Completion of determination of the time at which hydrates form at different concentrations of emulsions.						🟦		
Data analysis						🟥	🟥	
Report documentation							🟥	🟦

🟥 Process

🟦 Milestone

3.4. TOOLS

In this project, DSC is the major tool used. Equipments such as PVP and nitrogen gas can be obtained in the lab. The entire needed graphs can be obtained from DSC software. DSC used in the UTP lab is Pyris 1 (power-compensation DSC) from Perkin Elmer.

CHAPTER 4

RESULT AND DISCUSSION

4.1. HYDRATE FORMATION IN EMULSION

Initially, the ramped mode test was used in the DSC to measure the effects of temperature towards the formation of hydrates in water-in-oil emulsion samples. Four different samples were prepared which are:

i. Emulsion without PVP
ii. Emulsion with 0.3wt% PVP
iii. Emulsion with 0.5wt% PVP
iv. Emulsion with 0.7wt% PVP

10mg of each sample were first examined by ramped mode. In ramped mode, samples were cooled from 30°C to -30°C at a rate of 1°C/min, and heated back to 30°C at the atmospheric pressure. Nitrogen gas is used as the carried gas during the cooling process.

Heat flow vs. temperature data were gathered and plot in the graph. From this graph, phase transitions can be determined by looking at the dips and peaks of the graph which represent the total heat flow in (endothermic) or out (exothermic) of the samples. Figure 13 shows a thermogram (heat flow vs. temperature) of the samples.

Based on the Figure 13 generally, hydrate started to form at -23°C during the cooling process. The hydrate formation dips shown are the indication of heat released (exothermic) by the samples in order to transform into another physical state, which is from water-in-oil emulsion to hydrate crystalline state. As the temperature gets lower, the hydrate formed earlier remains as the solid phase.

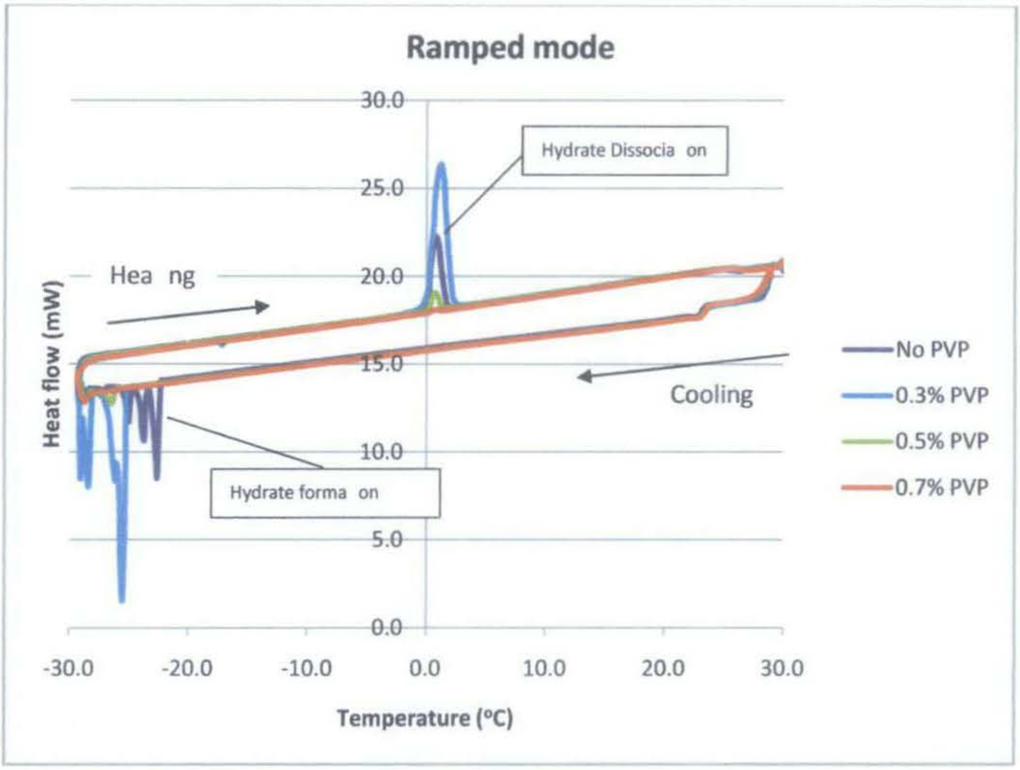


Figure 13 - Hydrate formation and dissociation trends of water-in-oil emulsions through cooling-heating process during ramped mode test

As the samples undergo heating process, there are peaks of hydrate dissociation which can be seen at the temperature mere 0°C. This is indication of hydrates formed earlier during the cooling process being dissociated. Heat is absorbed (endothermic) by the samples in order to transform from solid to liquid phase.

The results of different concentrations of PVP yield from ramped mode test are quite similar, whereby the hydrate formed as samples undergo cooling process and hydrate dissociation trends can be observed while temperature increases slowly. Thus, this shows the tendencies of hydrate formation in the emulsions as the temperature changes. However, to examine the effectiveness of kinetic inhibitor in delaying the hydrate nucleation, the samples must be tested with isothermal mode in DSC.

4.2. KINETIC INHIBITOR EFFECTIVENESS

During isothermal test, the DSC was used to form hydrate at -25°C isothermally. In order to observe the effectiveness of PVP acting as a kinetic hydrate inhibitor, comparison will be made focusing on the hydrate formation peaks during the isothermal mode of six hours. The result is shown as displayed in Figure 14.

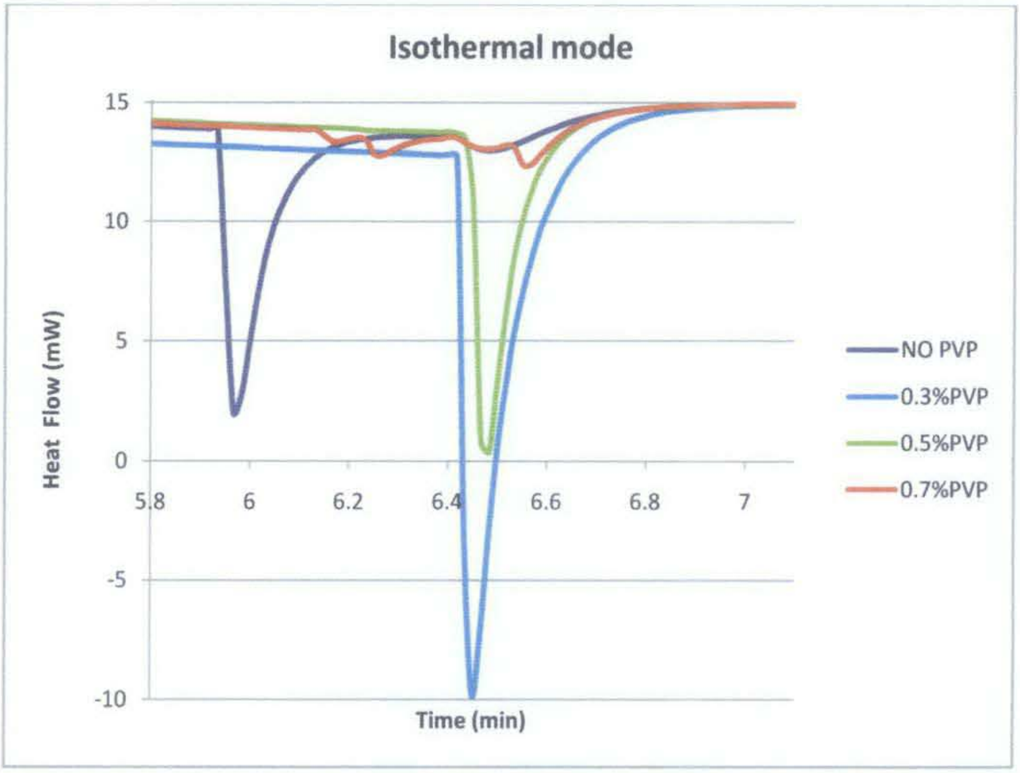


Figure 14 – Hydrate Formation Peaks in DSC during Isothermal Mode Test, of samples with and without PVP

Figure 14 shows hydrate formation peaks of the water-in-oil emulsions tested, with and without addition of PVP as kinetic hydrate inhibitor. The comparison is made between each sample by looking at hydrate formation time. Referring to heat flow curves as shown, emulsion without PVP tends to form hydrate earlier which is at 5.9 minutes followed by emulsion with 0.3wt% PVP at 6.4 minutes. Both samples of emulsions with 0.5wt% and 0.7wt% PVP formed hydrates at 6.45 minutes and 6.52 minutes respectively.

This indicates that the water droplets nucleate over a longer period of time, as compared to the sample without kinetic inhibitor added. Statistically, PVP is verified to be effective as a kinetic inhibitor at delaying the hydrate nucleation time.

Furthermore, the different concentrations of PVP added to the samples showed small changes from 0.3wt%, 0.5wt% and 0.7wt%. The changes in the concentration of PVP do not affect much on the hydrate formation peak. This implies that low concentration of kinetic inhibitor is required on acting effectively at delaying the hydrate nucleation time.

Therefore, this suggests that PVP can be considered to be applied on controlling the hydrate formation in the petroleum production systems. As the hydrate nucleation time increases along with the addition of polyvinylpyrrolidone (PVP), the residence time of production fluids in the flowline as non-crystalline phase will increase. Thus, this will prevent the hydrate to form in the region with tendencies of forming hydrates.

4.3. ENVIRONMENTAL ISSUES

Environmental issue is one of the drawbacks of the most widely used chemical hydrate prevention – thermodynamic inhibitor such as methanol (MeOH) and monoethylene glycol (MEG).

Both methanol and MEG are only effective at high concentrations with respect to the water rate (30 to 60 wt %) resulting in potentially high concerns about Health, Safety and Environment (HSE) as they can contribute to toxicity of the overboard produced water discharge. Moreover, the refineries tend now to limit the methanol concentration allowed in the oil and condensate which can cause serious problems in desalting operation and water management (IPTC 13765, 2009).

Treating the hydrates using polyvinylpyrrolione (PVP) as kinetic hydrate inhibitor (KHI) can be effective at very low concentrations. Therefore, the handling cost required for this non-toxic chemical are much lower as compare to methanol or MEG.

[10]. Lee J.D. and Englezos P. 2005, *Enhancement of The Performance of Gas Hydrate Kinetic Inhibitor With Polyethylene Oxide*, British Columbia, Canada: Elsevier Ltd.

[11]. Makagon, Y.F. 1997. *Hydrates of Hydrocarbons*, Tulsa, Oklahoma: PennWell Publishing Co.

[12]. Makogon Y.F., Makogon T.Y. and Holditch S.A. 1999. *Gas Hydrate Formation and Dissociation with Termodynamic and Kinetic Inhibitors*, Houstan, Texas: SPE 56568

[13]. Moore J.A., Vers L.V. and Conrad P. 2009, *Understanding Kinetic Hydrate Inhibitor and Corrosion Inhibitor Interactions*, Houstan, Texas, USA: OTC 19869

[14]. Notz P.K., Bumgardner S.B., Schaneman B.D. and Todd J.L. 1995. *Application of Kinetic Inhibitors to Gas Hydrate Problems*, Houstan, USA: Offshore Technology Conference.

[15]. Oskarsson, H., Nobel, A., Lund A., et al. *New Technique for Evaluating Antiagglomerate Gas-Hydrate Inhibitors in Oilfield Applications* 2005

[16]. Ostergaard K.K., Masoudi R., Tohidi.B., Danesh.A., Todd.A.C., 2005. *A general correlation for predicting the suppression of hydrate dissociation temperature in the presence of thermodynamic inhibitors*. Journal of Petroleum Science and Engineering 48(1–2),70–80

[17]. Sanford, Elizabeth A., Golczynski, Thomas S., Hampton, Brian J., Alapati, Rama R. and Lee, Jeremy. *Successful LDHI Qualification for Produced Fluids in a Flexible Riser at 10°F* (SS-FA) 2009

[18]. Sloan E.D. 1998. *Clathrate Hydrate of Natural Gases*, second edition, New York: Marcel Dekker, Inc.

[19]. Villano L.D. and Kelland M.A. 2010. *An investigation into the kinetic hydrate inhibitor properties of two imidazolium-based ionic liquids on Structure II gas hydrate*, 2010Elsevier Ltd. 0009-2509.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

Based on research, studies and experiments carried out throughout this period, it is proven that the employment of poly-vinylpyrrolidone (PVP) as kinetic hydrate inhibitors in oil with probable hydrate formation is able to increase the flow assurance of the system. The experimental data obtained from Differential Scanning Calorimetry (DSC) shows accurately on the effectiveness of PVP in delaying the hydrate nucleation. Since PVP is very effective in low concentration (<2.0wt%), it is proven that PVP is much more effective as hydrate inhibitor compare to conventional inhibitors like methanol and monoethylene glycol (MEG).

The objectives are achieved throughout this project. Hydrates to form in the water-in-oil emulsion samples are determined to be at temperature of -23°C, and dissociate at temperature merely 0°C. Adding the kinetic hydrate inhibitor; in this project, polyvinylpyrrolidone (PVP) – aid in delaying the hydrate nucleation time. Hydrates in the sample of water-in-oil emulsion without PVP tend to form earlier which is at 5.9 minutes. In the other hand, hydrates in the samples of water-in-oil emulsion with PVP of 0.3wt%, 0.5 wt% and 0.7 wt% nucleate later which are at 6.4 minutes, 6.45 minutes and 6.52 minutes respectively. Therefore, 0.7wt% of PVP concentration is determined to be the most effective PVP as kinetic hydrate inhibitor (KHI).

5.2. FUTURE WORK RECOMMENDATION

PVP is categorized as kinetic hydrate inhibitors – means it just delay the hydrate formation within the residence time (an hour or more). When applied in the industry, it is very effective in reducing the capital and operational expenditures but at the same time it cannot solve all the problems regarding hydrates.

For example, when the system is shutdown for long period of time, PVP cannot prevent the hydrates problem. Modifications can be carried out through the combination of other inhibitors like thermodynamic inhibitors (THIs) or anti-agglomerators (AAs). However, this requires further verifications from the laboratory experiments and field applications.

REFERENCES

[1]. Alapati R., Sanford E., Kiihne E. and Vita E. Champion Technologies. 2010. *Proper Selection of LDHI for Gas-Condensate Systems, in the Presence of Corrosion Inhibitors*, Houston, Texas, USA: OTC 20896

[2]. Boxall J., Greaves D., Mulligan J., Koh C., Sloan E.D. 2008 *Gas Hydrate Formation and Dissociation from Water-in-oil Emulsions Studied Using PVM and FBRM Particle Size Analysis*, British Columbia, Canada: ICGH 2008

[3]. CuiPing T., XingXue D., JianWei D., DongLiang L., XiaoYa Z., XiangYang Y. and DeQing L. 2010. *Kinetic Studies of Gas Hydrate Formation With Low-Dosage Hydrate Inhibitor*, Guangzhou, China: Science China Press and Springer-Veriag Berlin Heidelberg.

[4]. Dalmazzone D., Dalmazzone C., and Herzhaft B. 2002. *Differential Scanning Calorimetry: A New Technique To Characterize Hydrate Formation in Drilling Muds*, June 2002 SPE Journal.

[5]. Gray A.P. *"A simple Generalized Theory for the Analysis of Dynamic Thermal Measurements," Analytical Calorimetry*, R.J. Porter and J.F. Johnson (eds.), Plenum Press, New York City (1968) Vol. 1, 209.

[6]. Herzhaft B. and Dalmazzone C. 2001. *Gas Hydrate Formation in Drilling Mud Charactarized With DSC Technique*, New Orleans, Louisinia: SPE Annual Technical Conference & Exhibition.

[7]. Huo Z., Freer E., Lamar M., Sannigrahi B., Knauss D.M. and Sloan E.D. 2001. *Hydrate Plug Prevention by Anti-Agglomeration*: Elsevier Science Ltd.

[8]. Karaaslan U. and Parlaktuna M. 2002. *Kinetic Inhibition of Methane Hydrate by Polymers*, Ankara, Turkey: Fuel Chemistry Division Preprints 2002, 47(1), 355.

[9]. Khalik M. Sabil, 2009. Phase Behaviour, *Thermodynamics and Kinetics of Clathrate Hydrate Systems of Carbon Dioxide in Presence of Tetrahydrofuran and Electrolytes*. PhD Thesis, Delft University of Technology, Netherlands.