CHAPTER 1

INTRODUCTION OF NATURAL GAS HYDRATE

1.1 Hydrate History

Natural gas hydrates were first documented by Sir Humphrey Davy (1810, pg. 30) and to date, study and research about hydrates has been carried for over a century. Along these period there are many discovery has been made and vary of theories and hypotheses has been suggested by numerous researchers all around the world. Study about hydrate can be separated into three periods where the first period is from 1778 to 1934. Within this period, the focus is to create hydrates in laboratory and there was not much interest for hydrates during this time.

Second period of hydrates study began in 1934 to 1965 and it was initiated by Hammerschmidt when he found out that the obstruction that occur in the U.S gas pipelines was caused by ice-solid thing which is hydrates. Since then, the studies about hydrate grew sharply. During second period, the study is to investigate the condition that allows hydrate formation and methods to prevent it from happen.

Third period began at the mid of 1960s up till now. This period was drive by hydrates discovery in the deep water well in Yakutia. The focus of third period study is to study the molecular structure of hydrate, way to prevent it and develop methods to produce hydrates as it’s recognise as new source of energy in the coming decade.

Nowadays, there are three main hydrate issues to study. The first one is to create a new and economically way to produce gas from gas hydrates. A recent research published by researchers from British Petroleum and Texas A&M have estimated that world underwater reserves at 35 to 177 quadrillion cubic feet while proven world reserves of conventional natural gas amount to just 6 quadrillion cubic feet. Second, current focus of hydrate study is to determine the role of gas hydrate in past and future climate changes. Lastly, the area of recent studies is to find the best means to prevent hydrate formation in oil and gas production area as hydrates problems in the gas pipelines is keep increasing as the increasing of the wells at Arctic and at deep water locations like Gulf Mexico. Thus, the knowledge to prevent the hydrates formation is crucial in order to obtain optimum flow assurance in the pipelines.

1.2 Introduction of Hydrate

Natural gas hydrate is ice-like crystalline compounds that is formed from water and hydrate former molecules. Hydrate occurs when pressure, temperature, gas saturation, and local chemical conditions are combined and make them stable. Gas hydrates occurs in the pore spaces of sediments and may form cements, nodes, veins, or layers. They are found in sub-permafrost locations in a land in polar region and in most continental margins of the world in near sea-floor sediments approximately below 500m water depth, or roughly 1,600 feet. Normally gas hydrates is typically dominated by methane.

Figure 1: *Methane gas hydrate sample. Methane gas is trapped within this ice-like solid*

Nowadays, deep water exploration and production (E&P) are aggressively carried out by the petroleum company such as Shell, ExxonMobil and also PETRONAS. In deepwater conditions, the temperatures down to -1°C while the pressures up to 350 to 400BAR and with these conditions the risk for hydrate to occur is high.

In the earlier time, Thermodynamics approaches is use to counter hydrate problem. However, in deep offshore environments KHIs approaches may be ineffective and lots of oil company especially Shell and British Petroleum (BP) has invest lots of money to find better methods to control hydrate formation.

1.3 Project Background

New method which is kinetic hydrates inhibitors (KHIs) has been introduced in 1990s after researchers discovered natural inhibitors called anti-freeze proteins, AFPs, which exist in some fish that live in low temperatures and high pressure environment. To date, KHIs methods are widely used as the hydrate inhibitor in the petroleum industry because it offer low concentration of chemical and it’s much cheaper than THI’s method. Thus, reduce the OPEX and CAPEX of the company to control and preventing hydrate formation in their petroleum operation.

In this project, measurements of methane hydrate formation in the presence of PVP are carried out and phase transition of the sample will be recorded by DSC. DSC is the best technique to use because it can measure phase changing of the sample and the effect of PVP in controlling methane hydrate can be measured by studying the two graph that plotted by DSC in terms of time versus temperature to determine the delaying time of methane hydrate to form. In addition, hydrate phase change such as crystallization and dissociation processes can be obtained by analyzing heat change versus temperature curve to determine endothermic and exothermic processes. Endothermic indicate dissociation and exothermic indicate crystallization process that undergo by the sample.

1.4 Problem Statement

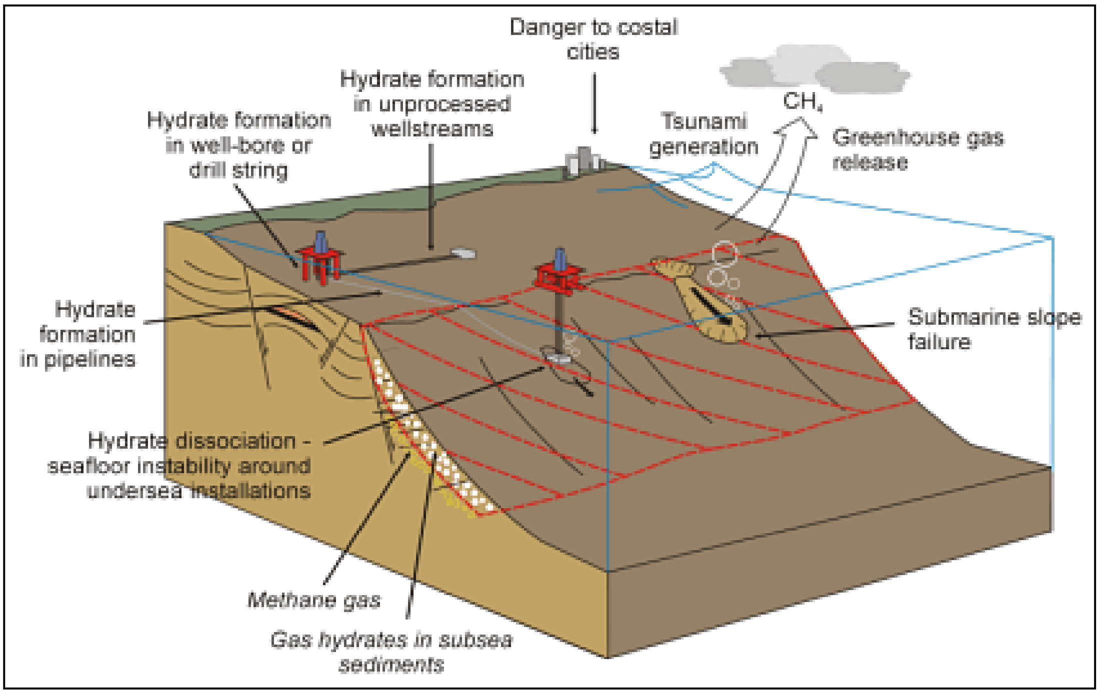


Figure 2: *Natural Gas Hydrates and its impact towards the nature, human and industry.*

Natural gas hydrate occurrence as a problem that need to be during E&P and transportation (Englezos 1993; Sloan 1998 which involving flow assurance, safety, new energy source, gas storage and transportation and also hydrate effect towards climate change.

According to A. Mohammadi (2011) the density of solid-hydrate 0.8-0.9s.p and this situation lead to safety issues such as it can damage offshore and onshore equipment and also threatening to human life that working in the field that deal with hydrate problem such as Macondo Prospect oil field in Gulf Mexico. In April 20, 2010 Deepwater Horizon Semi- Submersible Mobile Offshore Drilling Unit (MODU) that operates to drilling Macondo Prospect oil field has explode and the explosion killed 11 workers and 16 workers suffer physical injuries. Methane hydrate in the formation that was drilled is one of the factor that lead the explosion to happen. Expert from Halliburton and Carolyn A. Koh (professor at CSM and co-director of the Hydrate Center) told, cementing job that that carried out to prevent formation fracture has creates heat and cause the methane hydrate to destabilize. Then, the gas is released from the formation all at once and cause kick to happen because the surface pressure (pump pressure) and hydrostatic pressure (cement or mud) is not sufficient enough to overcome the sudden methane hydrate release gas and lead blowout to happen.

Figure 3: *Sudden release gas from methane hydrate caused blowout in Transocean Deepwater Horizon platform to explode in April 20, 2010.*

Besides that, hydrate methane can expand 164 times from its original volume. According to the calculation that made by Sara Madison, a student from Stanford University, 1 m^3 of methane hydrate contains 168.27 m^3 of methane gas at standard temperature and pressure (STP). So, when the hydrate plugs are heated it will cause the pipe the burst if the sudden increase in pressure is higher than the pipe rating pressure.

Secondly, is hydrate problem towards global climate changed and Milkov et al (2000) from Texas A&M University stated in his paper that, methane gas that released from the methane hydrate is a very effective greenhouse gas as it is ten times more potent than carbon dioxide. Global warming cause sea water temperature rises and trigger hydrate destabilization and then, methane is released to the atmosphere.

Third is about hydrate as an energy source. According to data that released by researchers from British Petroleum and Texas A&M, the estimated that world underwater hydrate reserves is 35 to 177 quadrillion cubic feet while proven world reserves of conventional natural gas amount to just 6 quadrillion cubic feet. A study by Ginsburg and Soloniev (1995) showed that the estimated worldwide hydrate reserves is about 8.7 x10^{15} m^{3} where 5.7x10^{15} m^{3} (in continental)and 3x10^{15} m^{3} (in oceans). So, many researches were carried out in order to find the suitable method to produce methane hydrate as an alternative to the existing energy source. To date, there are two fields that produce methane hydrate namely Messoyakha in western Siberia and Mallik that located at Beaufort Sea, Canada.

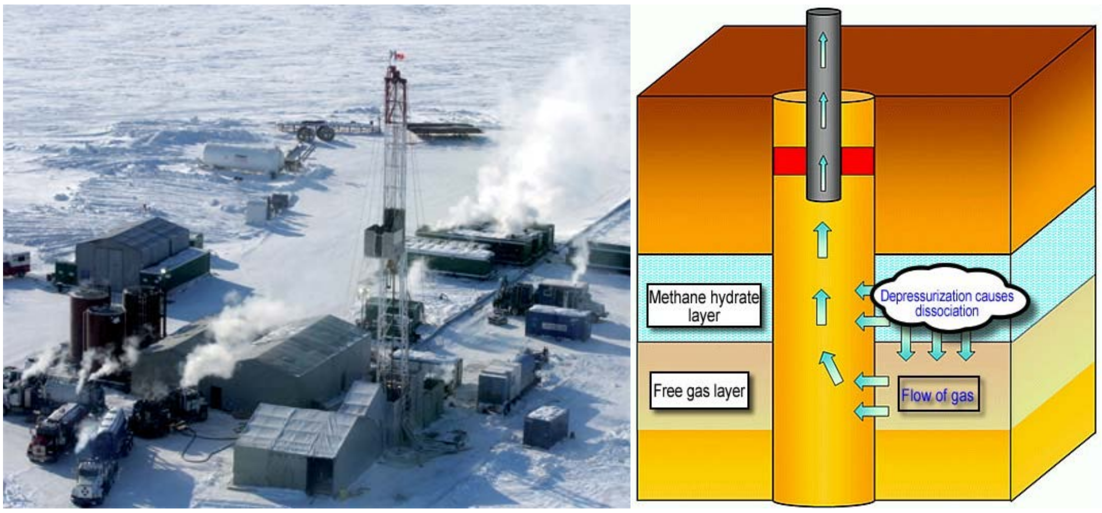


Figure 4: ***(left),*** *Mallik Site that located in Beaufort Sea, Canada and* ***(right),*** *a diagram showed natural gas hydrate in Mallik field is produced by reducing the pressure inside the well causing the methane hydrate to decompose.*

A fourth and fifth issue is the main driver of this project where the issues are about hydrates in gas storage and transportation pipeline and how it affects pipe flow assurance. Hydrate plugs in the pipeline causing the pipe to operate below its optimum flow capacity. If the hydrate blockage is too severe, production will be stop and clearing the blockage lines is a consuming task that can take as long as 20-day. When this situation happens, production time is affected and oil operator will lost lot of money. Because of these reason, all oil and gas company try to maintain their pipeline or operation system temperature and pressure outside the hydrate formation envelope.

In the earlier times, hydrate formation is control by using thermodynamic approach either by physical or chemical approach. For physical approach, insulation or pipeline burying were applied to the pipelines and by doing this, fluid temperature within the pipe is held outside the hydrate formation range because heat is induced to the pipe. On the other hand, chemical approach is applied by injecting THI's such as methanol or glycols into the fluid system at the wellhead and the injected chemical will bond with water molecules and the addition of methanol, ethanol, or glycols to the aqueous phase shifts hydrate equilibrium behaviour to lower temperatures. As a result, there is no free water left for the gas to bind with and no hydrates could be formed.

However, THI's approach requires lot of inhibitor chemicals as they are added at high concentration, 10%-60% wt of the aqueous quantity. Thus, the flow assurance costs are increasing year by year. In addition, methanol is hazardous due its toxicity and flammability. Methanol is toxic to human because excessive exposure during handling the methanol causes central nervous system depression, headache, dizziness and nausea.

As E&P of hydrocarbon goes deeper, the usage of THI's is no longer efficient as the required volume and concentration that needs to be injected to the system is increasing and also costly. According to the statement that released by a consortiums named Deep Star which focuses on Gulf Mexico deepwater development technology, British Petroleum need to spend more than $100,000,000 per year for hydrate prevention in their pipeline via methanol injection.

To date, new method to counter hydrate formation is available and Kinetic Hydrate Inhibitors (KHI's) offer lots of advantages compare to THI's.

1.5 Significant of the Project

KHI's does not shift the hydrate equilibrium conditions but it decrease the rate of hydrate to form by delaying hydrate formation process for a period longer than the free water residence time in the gas pipeline.In addition, KHIs effectiveness has been proven at concentrations as low as 0.5 wt% of the free water phase. Moreover, only small volume and low concentrations are needed for it to work so the chemical costs to ensure flow assurance can be reduced.

The purpose of this project is to extend the studies of methane hydrate formation in the presence of kinetic (PVP) inhibitor by using Differential Scanning Calorimetry (DSC). In addition, few projects about the study of PVP towards the formation of methane hydrate by using DSC can be found.

Kinetic (PVP) Inhibitor is chosen because it has the strongest polar charge than polyvinylpyrrolidone (PVP), N,N-dimethylaminoethyl methacrylate (VC-713) and co-polymer of N-vinylpyrrolidone-co-N-vinylcaprolactam (VP/VC).

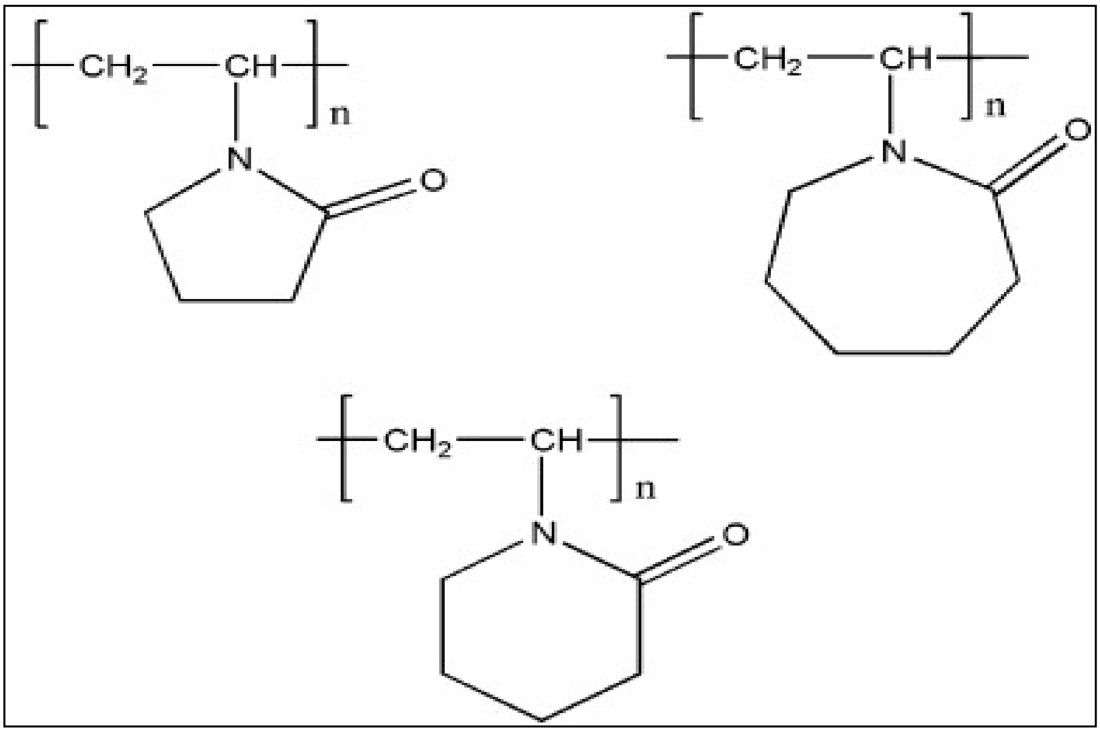


Figure 5: *structures of poly (N-vinyl pyrrolidone) (PVP)* ***(top left),*** *poly(N-vinyl piperidone) (PVPip)* ***(bottom)*** *and poly(N-vinyl caprolactam) (PVCap)* ***(top right).Rachel O'Reilly (2011).***

As reported by D. Dalmazzone in June 2002, DSC is one of the most commonly used techniques of thermal characterization of physico-chemical transformations. It consists of monitoring the heat exchanges between a sample and a reference, either vs. time at constant temperature or vs. temperature during a heating or cooling program.

During the experiment, sample will be put at atmospheric pressure and at temperature ranging from -25 to 50°C. In addition concentration of PVP that introduced into artificial seawater/ pure water-methane system will be vary. Then, the effectiveness of PVP will be studied through the result of a DSC experiment because it will give a curve of heat flux versus temperature or versus time.

By using this method six parameters of methane hydrate will be studied which are hydrate structure, how it is formed, dissociated and prevented with time at specific temperatures and pressures.

1.6 Scope of Study

This project is conducted to study kinetic of hydrate formation at different concentration of PVP by using DSC to cool the sample to -30’C and then heat the sample to 30’C at rate of 1°C/min by setting the DSC to the ramp mode for heating and cooling process. Then, the induction time to form hydrate will be studied base on graph that plotted by DSC.

1.7 Objective of the Project

The objectives of this project as the following:

1. To investigate the effect of PVP as inhibitor to natural gas hydrate formation.
2. To determine the amount of sufficient concentration of PVP to delay natural gas hydrate formation.
3. To determine the formation rate of natural gas hydrate based on the induction time.

1.8 Feasibility of the Project

In University Technology PETRONAS, a research team has been established specifically in the flow assurance research. Therefore, equipments, chemicals and guidance are available for this research to be completed within the time framework.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrate Molecular Structure

There are three structures of natural gas hydrates which are structure I, sI, structure II, sII, and structure H, sH. sI is the simplest of the hydrate structure and it consists of 46 water molecules forming eight number of cavities that consists of two small and six large cavities. The small cage is dodecahedron, a 12 sided polyhedron where each face is a regular pentagon and designated as $5^{12.}$ The large cage is tetradecahedron, a 14-sided polyhedron with 12 pentagonal faces and two hexagonal faces and designated as $5^{12}6^{2}$. sI formers molecules including methane, ethane, carbon dioxide and hydrogen sulphide.

On the other hand, sII consists of 136 molecules of water forming 24 cavities that consists of 16 small and 8 large cavities. The small cage is dodecahedron, a 12 sided polyhedron where each face is a regular pentagon and designated as 5^{12}. The large cage is hexadecahedron, a 16 sided polyhedron with 12 pentagonal faces and four hexagonal faces, designated to $5^{12}6^{4}$. sII formers molecules are nitrogen, propane and iso-butane.

Lastly is sH structured which is quite complicated compared to sI and sII. sH has 34 water molecules, forming 6 number of cavities that composed of 3 small, 2 medium and 1 large cavities. The small cage has the shape of a pentagonal dodecahedron, designated as 5^{12} and irregular dodecahedron with three square faces, six pentagonal faces and three hexagonal faces and designated as $4^{3}5^{6}6^{3}$. While the large cage has an irregular icosahedrons shape with 20 sided polyhedron, twelve pentagonal faces and 8 hexagonal face $5^{12}6^{8}$. sH formers molecules include methane and twelve sH forming molecules.

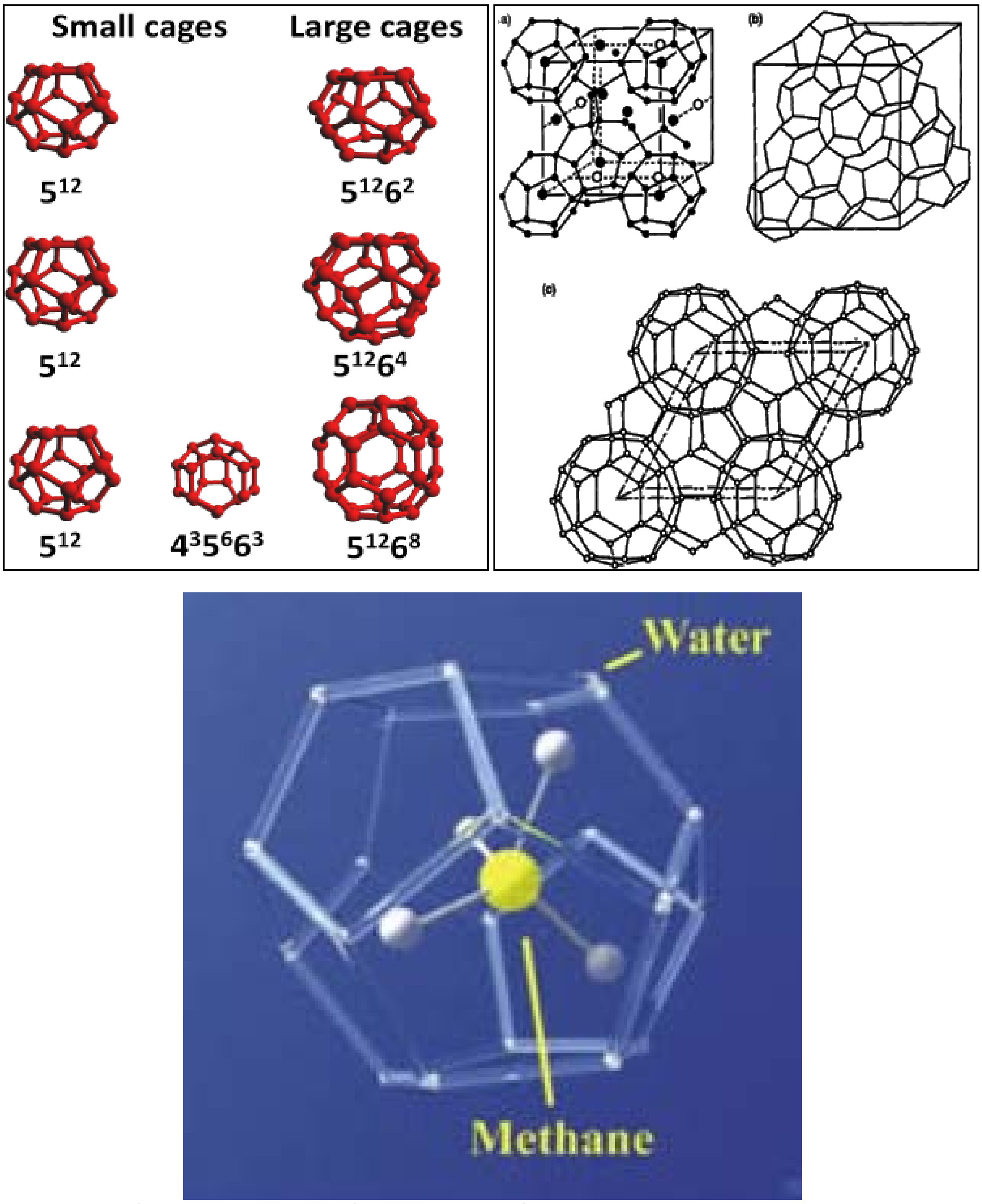


Figure 6: ***(left)*** *hydrate structures, from top: cages of sI, sII, and sH (Husebø, 2008),* ***(right)*** *unit cells of hydrate structure I(a), II(b) & H(c) (Sloan 1998),* ***(bottom)****, methane gas molecule surrounded by a cage of water.*

The summary of hydrate cages geometry as shown in table 1.

Structure	**I**		**II**		**H**		
Cage	Small	Large	Small	Large	Small	Medium	Large
Designation	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$	5^{12}	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
Average cage radius	3.95	4.33	3.91	4.73	3.91	4.06	5.71

Table 1: *Geometry of hydrate unit cells and cavities*

2.2 Hydrate formation

Methane hydrate will form where sufficient gas and water present at favourable pressure and temperature. According to (Sloan 1998), natural gas hydrate like methane will form at high pressure (>15MPa) and low temperature condition (<25°C).

While (Makagon 1999) stated in his book that there are three conditions that must be satisfied for hydrate to form where the process should be thermodynamically favourable where $\Delta G < 0$, there are access to hydrate forming constituents that consists of water and hydrate former and lastly, removal of hydrate formation latent heat through heat transport during hydrate formation.

A rule of thumb regarding hydrate formation at various water depths (Barker 1988b) can be used where;

Water Depth, ft	Risk of Hydrate Formations Problems
<1500	A hydrate problem will not probably be occur
≤1500	Without inhibition, hydrate problem may occur
≤2000	Without inhibition, hydrate problem will occur
≥3000	Insufficient experience; salt alone will not suffice

Table 2: *empirical rules to define locations in which inhibition is necessary*

The diagram shows about the phase boundary of hydrate zone and free hydrate zone. To the left of the boundary is the area where hydrate formation will occur. In this region water or ice co-exist with methane hydrate. Moving the right of the boundary is free hydrate zone. In this region dissociation of methane hydrate happen where water and ice are co-exist with gas methane. So, a combination of low temperature and high pressure is needed to support methane hydrate formation.

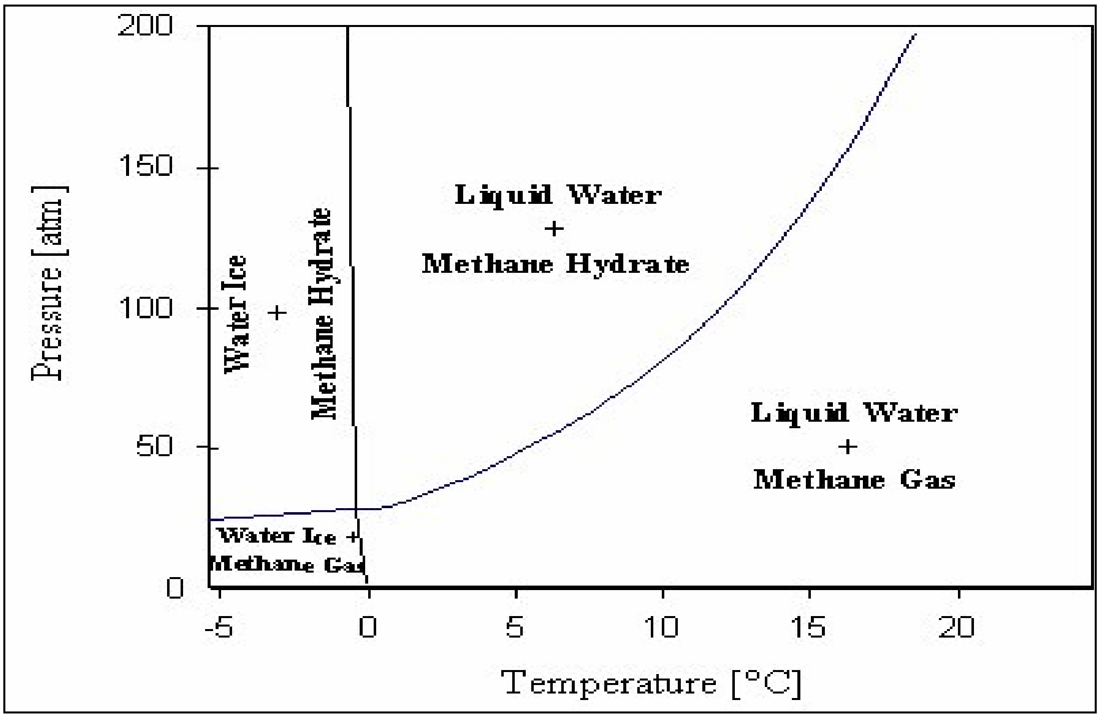


Figure 7: *Phase diagram of pressure versus temperature for methane which form hydrate*

2.3 Gas Hydrate Phases

2.3.1 Nucleation

Nucleation is a process where small hydrate crystals which is nuclei grow and disperse in order to obtain critical size before they continue to grow, at a specific temperature and pressure. As this is a microscopic process, many theories and hypothesises exist to explain this poorly understood phenomenon and most of the theory is based on the water freezing process. Besides, many theories and molecular models of hydrate nucleation focus on the surface of vapour-liquid interface as hydrate initiation occur at this place. Nucleation can occur either homogeneously or heterogeneously, but Mullin (1993:182-183) notes that homogeneous nucleation is not a common event.

However, most of the theories have focused that the site of hydrate nucleation is located at the water-gas interface because vapour-liquid interface is preferred for the hydrate formation not only due to the lowering of the Gibbs free energy of nucleation but also due to high concentration of water and guest molecules, which is required for hydrate nucleation.

As suggested by Long (1994) and Kvamme (1996), hydrate nucleation process begin when the guest molecules are transported to the water interface. Then, the gas will absorb on the aqueous surface. In order to fit into a suitable cavity these molecules migrates around the water interface via surface diffusions. At a suitable location, guest molecules is entrap within the water cavities. After that, cluster join and grow on the surface side to achieved hydrate critical size by addition of water/ gas or cavities joining along the water interface.

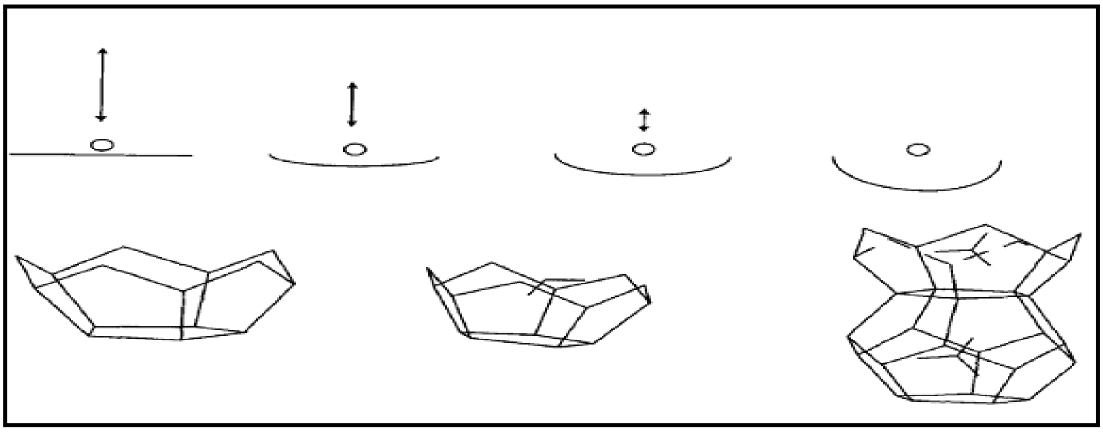


Figure 8: *Adsorption of gas molecules onto labile hydrate cavities at gas-water interface. (Long 1994)*

2.3.2 Dissociation

At present, the knowledge about hydrate dissociation remains largely unknown. However, many experiments had shown that hydrate dissociation can be obtained through heat transfer. As an example, Jamaluddin et al. (1989) used the model of Kim et al (1987) to obtain hydrate dissociation with heat transfer relation. As a result, dissociation happens when pressure was within 70% of the equilibrium pressure and when it came to 28% of the dissociation pressures; both heat transfer and intrinsic kinetics became important.

In addition, dissociation process of hydrate occurs whether the system is in steady state or unsteady state. Under steady state condition, pressure of the system not changing with time;

$$\frac{\partial p}{\partial t} = 0$$

On the other hand, unsteady state unsteady state is where pressure is changing with respect to time.

$$\frac{\Delta P}{\Delta t} \neq 0$$

2.4 Hydrate Prevention

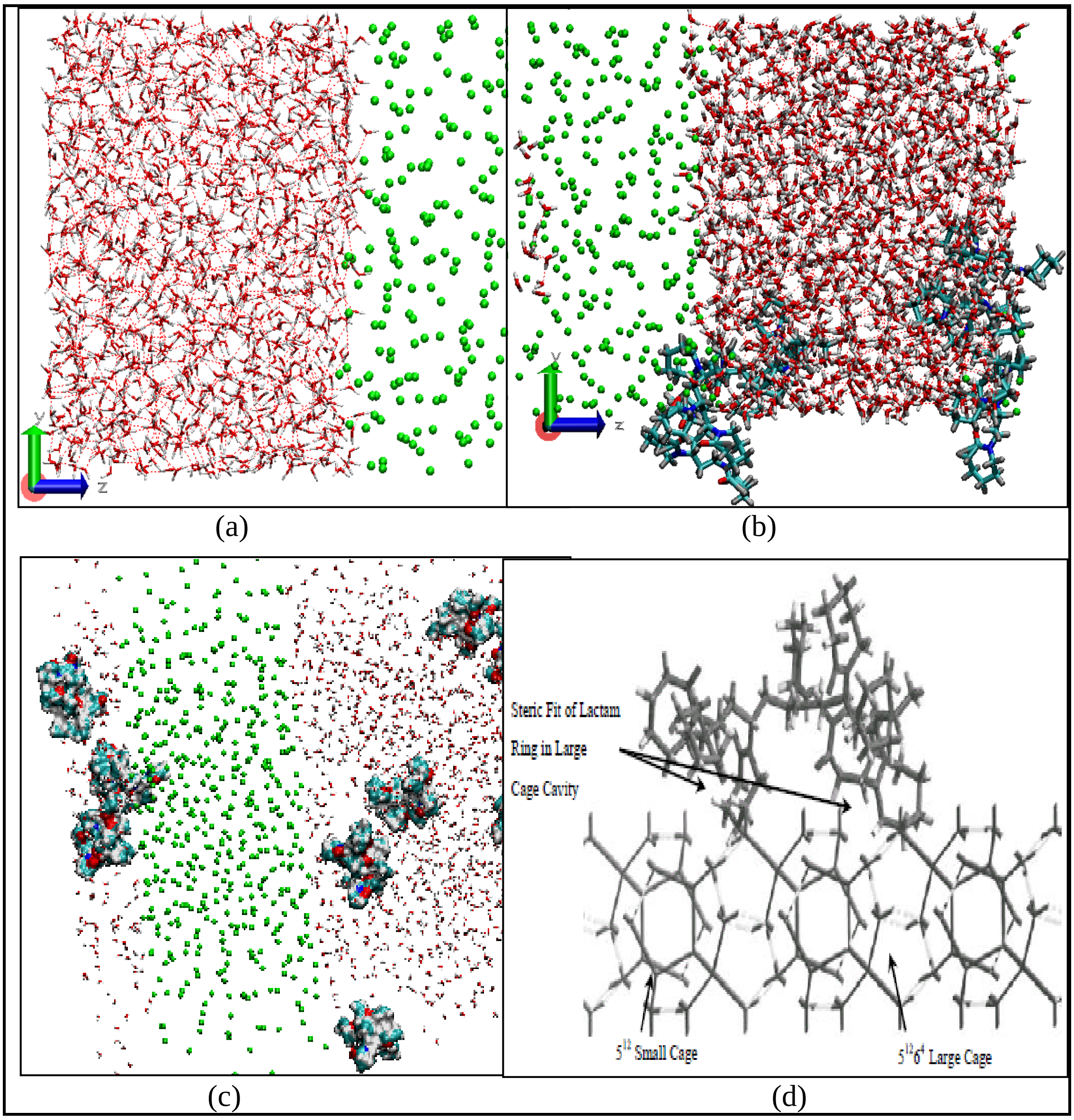
As mentioned before, there are two commonly used methods to control hydrate formation which are THIs and LDHIs (KHIs and AAs).

THIs is an inhibitor that changes the energy of intermolecular interaction and changes thermodynamic equilibrium between molecules and water and gas. As a result, KHIs shift the hydrate formation equilibrium conditions and cause the hydrate formation boundary moves to the left (Sira et al 1990).

On the other hand, KHIs control hydrate formation by decreasing hydrate formation rate for a period longer than the free water residence in the pipeline (Sloan and Koh, 2008). There are four typical types of KHIs which are polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PVP-CAP), N-vinyl pyrrolidone/ N-vinylcaprolactam/ N,N-dimethylaminoethyl methacrylate (VC-713) and co-polymer of N-vinylpyrrolidone-co-N-vinylcaprolactam (VP/VC).

Each of these four polymers is effective to prevent hydrate formation at different pressure, temperature, water salinity and salt concentration. For instance, Long et al (1994) have shown that PVP is proven to be effective at high temperature, 285.6K, but as the temperature decreases such as at 277K PVP, it will cause the hydrate formation process occurs more rapidly. At 0.5 wt%, VC-713 is proven effective at pressure as high as 6.9MPa but at pressure greater than 10MPa, more inhibitor is needed to be injected for inhibition.

KHIs are worked by preventing the hydrate nuclei growth because KHIs will adsorb on the hydrate faces and change water-gas interface ability for the diffusion-adsorption (Sloan and Koh, 2008). This situation cause hydrate growth to slow down or stop as KHIs will block the diffusion of hydrate formers to the existing hydrate surface.



(a) (b)

(c) (d)

Figure 9: ***(a)*** *water molecules are red & white lines, and methane are green balls,* ***(b)*** *PVP as KHI injected to the system at t1,* ***(c)*** *PVP attach at hydrate surface and blocking hydrate to grow,* ***(d)*** *close-up view of PVP adsorbed on the structure blocking the hydrate surface to grow more*

2.5 Past Research

Larsen et al (1998) from the Norwegian University Science and Technology, Norway use tetrahydrofuran THF and ethylene oxide EO aqueous solutions to form structure II and and sI hydrates, respectively to study effect of KHIs polymers (PVP, PVCap and VC-713) at concentration as low as 0.1 wt. % at low supercooling temperature They observed the hydrate growth by using Plexiglas cell. As a result, PVP showed the best inhibition performance compare to PVP and VC-713 because PVP has good stabilizing effect on partial cavities due to the large pendant group of PVP and provide strong enough adsorption on water-THF interface. The shape of THF hydrates before and after inhibition process as shown below;

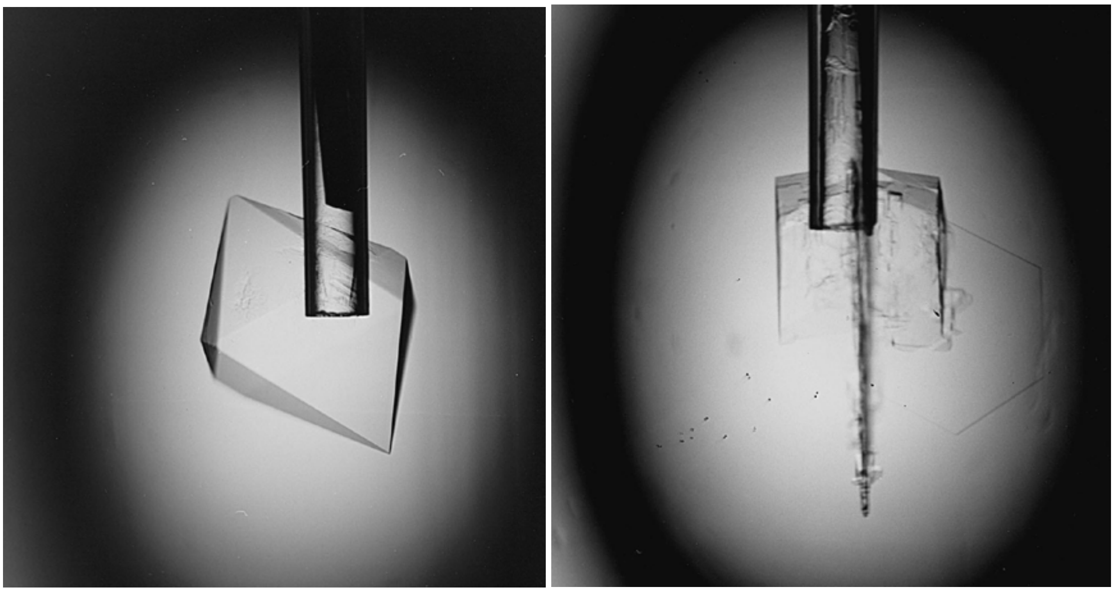


Figure 10: (left) *Octahedral sII -1114 crystal of THF hydrate grown in a stoichiometric solution without any additives at a supercooling of DTs1.4 K,* ***(right),*** *THF hydrate crystal having been transferred to a stoichiometric solution with 0.025 wt.% PVP in the water phase at a supercooling of* $\Delta T=1.4$ *K (Larsen et al 1998)*.

In year Kalbus et al. (1995) from Colorado School of Mines has carried out an experiment to identify inhibitors of hydrate formation rate using viscometer. In this experiment, viscometer is used in order to show the development of hydrate formation in water-THF solutions and water-gas solutions at conditions that favouring hydrate formation in the presence of PVP. The obtained result gives a curve of viscosity versus temperature versus elapsed time. The curve indicate that when PVP concentration increasing, the time of hydrate crystals to form will also increase. As an example, at 0.1% of PVP, hydrate growth is stopped for about 1000 seconds and at 0.5% of PVP, hydrate growth is stopped for about 19,000 seconds.

Abay (2011) from University of Stavanger, Norway have recently used Autoclave cell to study about the effect of PVP on methane hydrate nucleation and growth. Abay proposed the use of derived real gas equation to calculate the effect of PVP towards to methane hydrate formation.

In this study, the cylindrical cell (145ml inner volume; in each experiment 50ml of the cell was filled with the actual aqueous solution and 95ml for pressurized methane gas) was charged with test solution (PVP in DIW at concentrations of 0, 20, 50, 100, 500, 1000, and2000 ppm) and methane to the desired pressure and the system was cooled from an initial temperature of 13.7 °C down to 4 °C with a cooling rate of 10 °C/h. At 4 °C and 90 bar the sub-cooling, ΔT, with reference to hydrate equilibrium is approximately 8 °C. From gas consumption plot and the temperature pulse they measured and obtained 28.12min is the induction time of methane hydrate to growth in the sample.

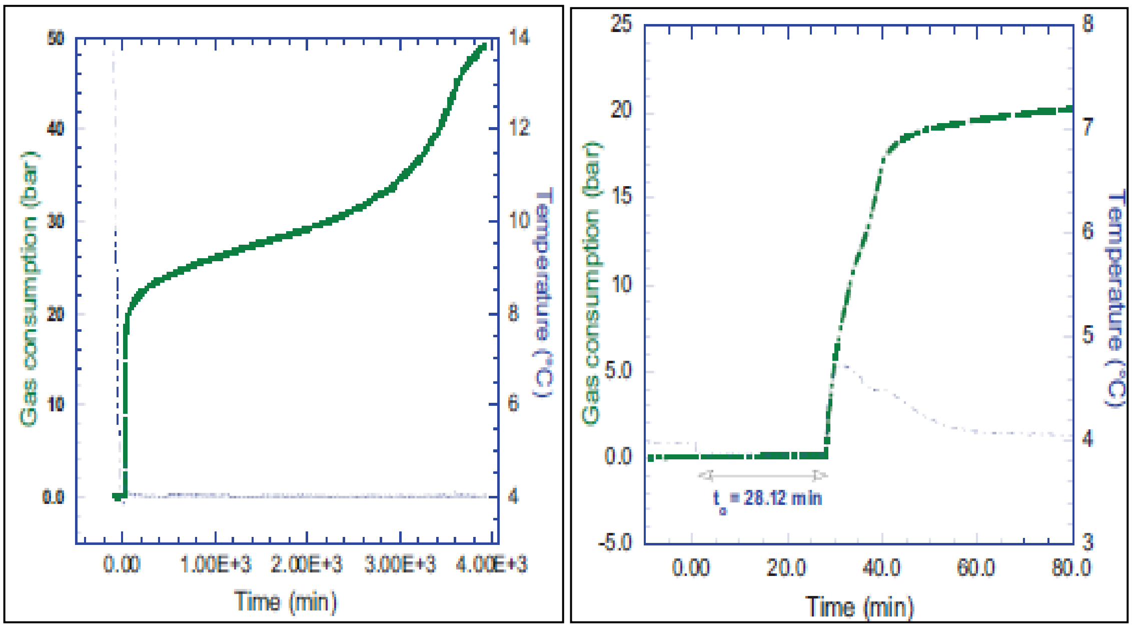


Figure 11: (left)*, gas consumption and temperature plots from the start of the experiment to the end illustrating onset and growth of sI hydrates and* ***(right)****, measurement of induction time from gas consumption curve and temperature pulse at onset of hydrate formation is 28.12min at 0.02% wt of PVP.*

Another experiment that ran by Dalmazzone et al. was performed at atmospheric pressure and they used DSC to study dissociation of methane hydrate equilibrium. During the experiment, methane hydrate was studied in various aqueous media including pure water, high concentration of calcium chloride solutions and water-in-oil emulsions at pressure from 5 to 10MPa and temperature ranging from -20 to +5°C. They obtained DSC curves of heat flow versus temperature at various methane pressures and they suggested that under sufficient methane pressure and at a temperature that is strongly pressure dependent a second peak will occur. They have concluded that at this point hydrate dissociation happen because dissociation equilibrium between temperature and pressure were obtained. Dalmazzone et al. also stated that DSC equipment is suitable to use for the study of kinetics of hydrate formation because DSC is rapid and versatile equipment that can efficiently used for analytical, thermodynamic and kinetic studies.

On the other hand, one of the problems that may affect the effectiveness of PVP on controlling methane hydrate formation is the occurrence of emulsion in the pure water/ NaCl – methane – PVP sample. Due to emulsion, PVP in molecules will coalesce and the required percentage of PVP molecules to absorb on hydrate interface reduced. This situation resulted in unwanted trend of DSC plot of methane hydrate formation. So, the occurrence of emulsion must be avoided during the experiment by setting the right temperature range for the sample. According to experiment that performed by K. P. McNamee (2011) the occurrence of emulsion caused multiple crystallization formation peaks as shown below;

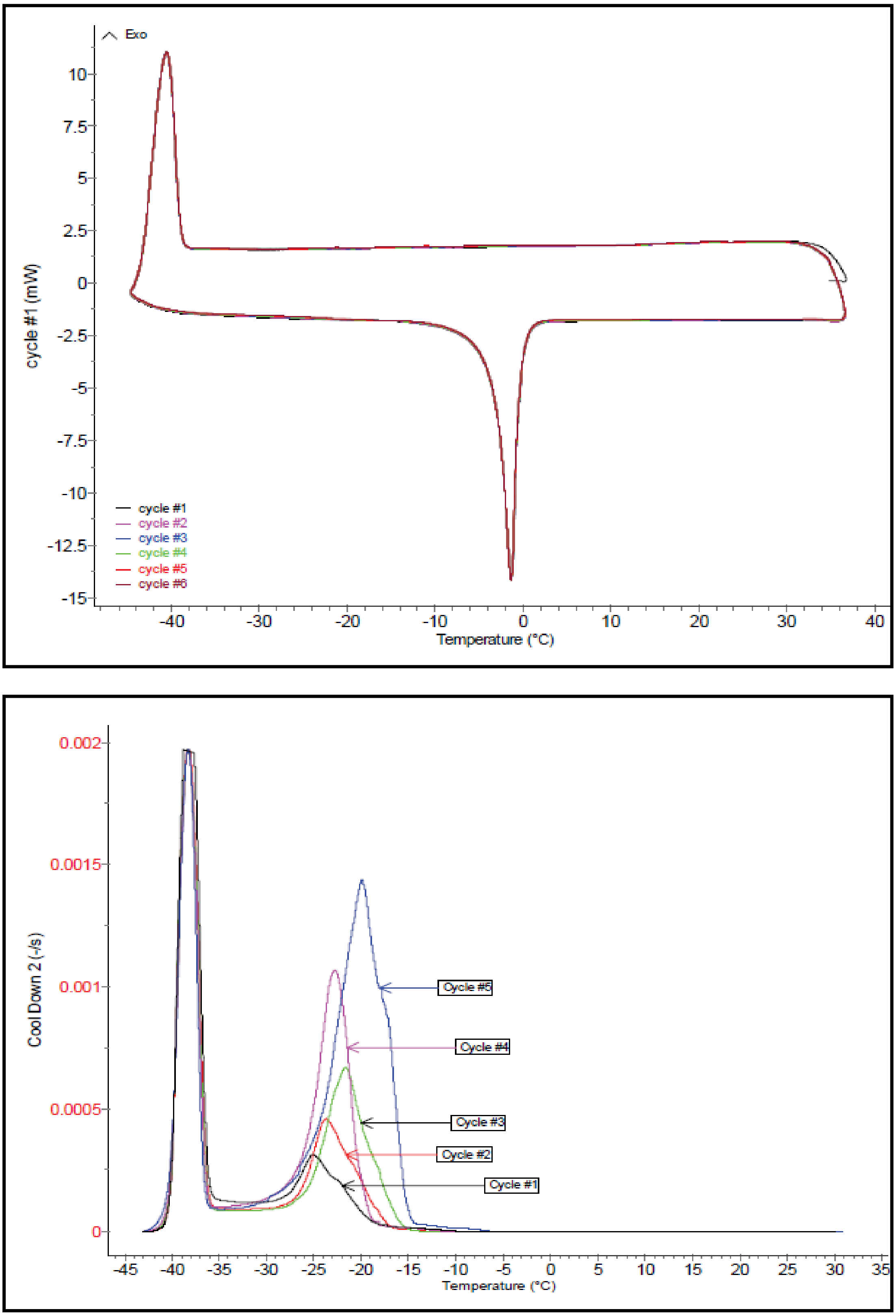


Figure 12: (top), *hydrate growth formation without emulsion of KHI's and* ***(bottom)****, with emulsion of KHI's in pure water-KHI's-methane gas system.*

In this experiment, concentration of (0.2, 0.6, 1.4 and 2) wt% PVP were used and the effect of PVP emulsion towards rate of methane hydrate formation growth is measured where hydrate nucleation occurrence times is indicate by hold time that recorded by DSC as an endothermic event while hydrate dissociation is indicate by exothermic event. The study was done in collaboration with Natco Company and Center for Hydrate Research at Colorado School of Mines.

DSC is the suitable equipment to be use because it enables us to determine physico –transformation such as phase transition that undergo by sample. According to the Mettler-Toledo, one of the DSC manufacturer company, through this technique, we can determine whether the sample experienced exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crytallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions.

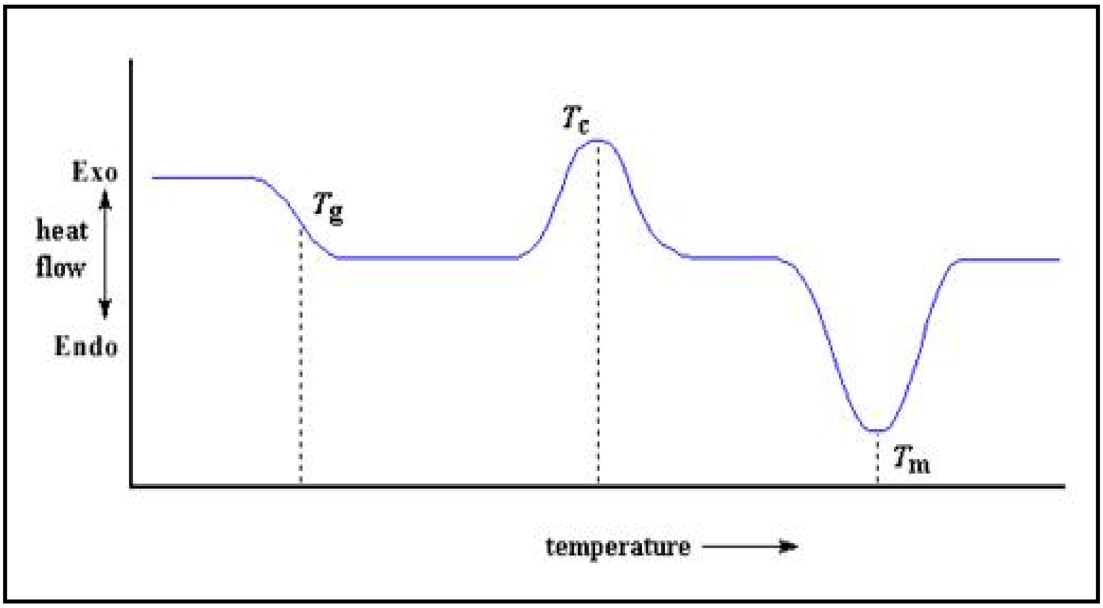


Figure 13: *A schematic DSC curve demonstrating the appearance of several common features where Tg indicate glass transition point, Tc indicate crystallization occurrence and Tm indicate melting point of a sample.*

CHAPTER 3

METHODOLOGY

This project is conducted based on experiment and laboratory work basis. The experiment is divided into two parts as shown below;

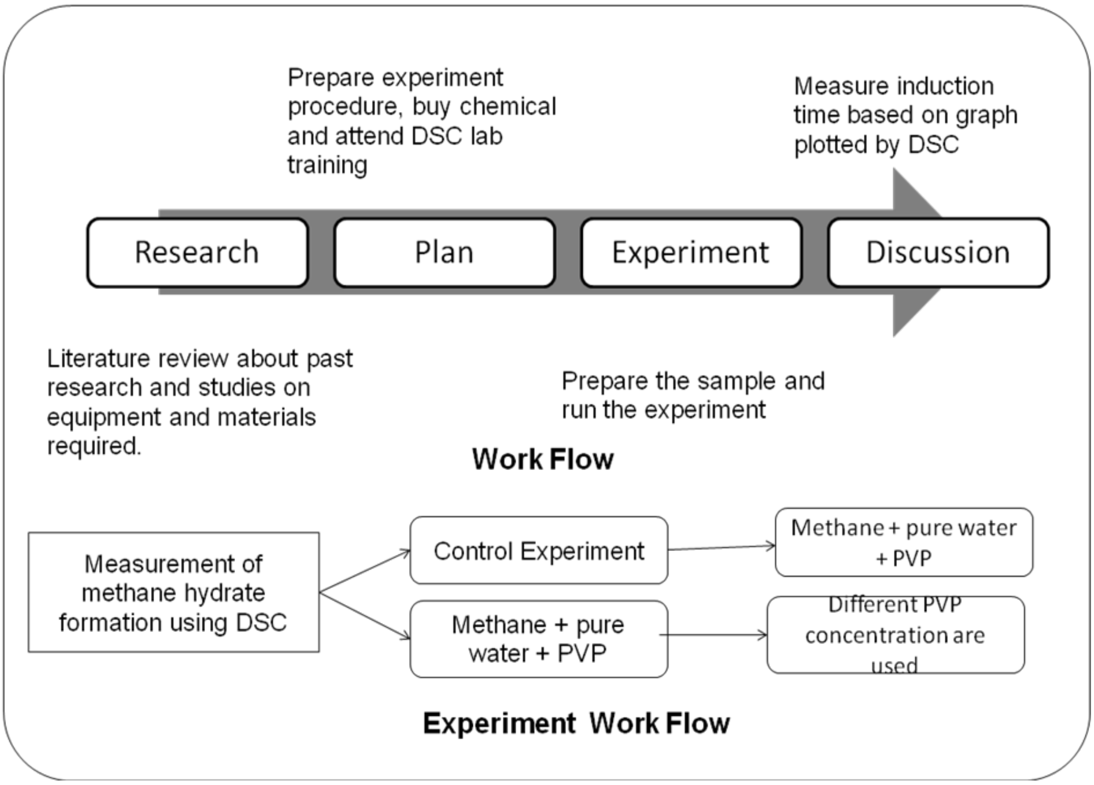


Figure 14: *work flow and experiment work flow that use in the project*

3.1 Materials (Experimental Liquids, Gases and Inhibitor)

Chemical that used in this project is polyvinylpyrrolidone (PVP) that purchased from Merck with 99.95% purity and also available in powder form. PVP is also soluble in water and other polar solvents. Kinetic (PVP) Inhibitor is chosen because it has the strongest polar charge than polyvinylcaprolactam (PVP), N,N-dimethylaminoethyl methacrylate (VC-713) and co-polymer of N-vinylpyrrolidone-co-N-vinylcaprolactam (VP/VC). In controlling methane hydrate, PVP has good stabilizing effect on partial cavities due to the large pendant group of PVP and provide strong enough adsorption on aqueous-methane hydrate interface (Larsen et al, 1998).

On the other hand, nitrogen gas that was purged into the DSC furnace was supplied by MOX gas with 99.99% purity. Nitrogen is used instead of methane because nitrogen is an inert gas, thus able to avoid fire to happen in the furnace while methane is highly flammable. Distilled water is water that has many of its impurities removed through distillation. Distillation involves boiling the water and then condensing the steam into a clean container. It is used as a solvent and already available in the lab.

To obtain different concentration, in term of weigh percentage, wt% PVP powder was diluted with distilled water. Then the samples were tested to determine its rheology properties before ran in the DSC.

All chemicals that were used in this experiment as the following;

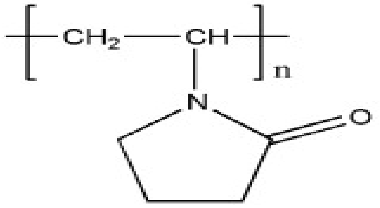
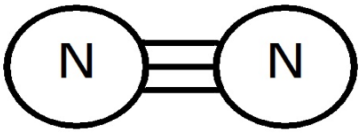
Symbol	Chemical Name	Chemical Structure
PVP	Polyvinylpyrrolidone, Povidone, Polyvidone Poly[1-(2-oxo-1-pyrrolidinyl)ethylen]	
N_2	Nitrogen	

__Table 3:__ Chemical and Gas used in this project

3.2 Experimental Apparatus

The apparatus that will be used to measure methane hydrate formations consist of a Density Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and a computer use to record the data from of the project. TGA will be use to observes changes in sample weight in relation to change in temperature. While, DSC that will be use is Pyris 1 DSC system and manufactured by Perkin Almer. The desirable specifications that have by this equipment are its ability to measure physico –transformation such as phase transition that undergo by sample whether the sample experienced exothermic (indicate methane hydrate formation) or endothermic (indicate methane hydrate dissociation) condition.

Besides, it can operate at temperature range -20 C to 500 C with a scan rate of 0.1 to 200 C/min and sample to be run is put in the sample pan. There are three types of pan which made from available in aluminium, copper or gold and aluminium pan is used during the experiment.

For accurate analysis, 2 mg of samples are needed. DSC also has calorimetry precision better than ±0.01°C and accuracy better than ±1%. In addition is provided with sensitivity as low as 0.2μW and this feature enable the Pyris 1 DSC easily to measured the phase transitions that undergo by the sample as a function of time and temperature.

Figure 15: *DSC equipment that will be used to investigate methane hydrate formation growth*

Figure 16: *DSC calorimetry cell*

Figure 17: *Sample Pan that used to placed PVP solution and pure water before it was put into DSC calorimetry cell*

As for rheology test, was used to determine single or multi-point viscosities. It has fixed speeds of 3 (GEL), 100, 200, 300 and 600 RPM that are switch selectable with the RPM knob.

Figure 18: *Rheometer that is used to studied PVP solution rheology*

3.3 Procedures

3.3.1 Sample Preparation

To make PVP solutions, 10 grams of PVP powder was weighted carefully and dissolved in 990ml of distilled water to produce 1wt% (10,000ppm) concentration. Solution is prepared at room temperature which is 25°C. The beaker is placed on magnetic stirrer and magnetic bar is used to stir the solution. In order to avoid fish eye formation and to ensure polymer is dissolved thoroughly in the water PVP was added slowly at the outer side of vortex water during the mixing process and solution is stirred for two hours.

There are three PVP liquid concentrations that will be used in this study which are at 1 wt%, 0.5 wt% and 0.7 and 0.3 wt%. Then, 1 wt% aqueous was diluted according to calculated distilled water in order to produce 0.7 wt%, 0.5 wt% and 0.3 wt% concentration. Equation below is used to calculate the required 1wt% of PVP liquid concentration to produce 0.7 wt%, 0.5 wt% and 0.3 wt% PVP liquid concentration.

Solution wt %	Amount of V_1	Amount of V_2	Remarks
0.3	150	350	Stirred for 2 hours and no fish eye
0.5	250	250	
0.7	350	150	

Table 4: *The summary of the PVP solutions dilute-process made*

$M_1V_1 = M_2V_2$

Where, M_1 and M_2 are the concentration of first solution and desired concentration. Meanwhile, V_1 is the volume of initial solution to produce desired concentration with

V_2 volume

3.3.2 Experiment Procedure

PVP solutions were prepared and tested for it rheology properties. Rheology refers to the deformation and flow behaviour of all forms of matter. By doing this, viscosity, gel strength, yields point and plastic viscosity of each concentration can be studied. From viscosity information, types of fluid can be determined either PVP solution is Newtonian (viscosity is constant) or Non-Newtonian (viscosity not constant) fluid.

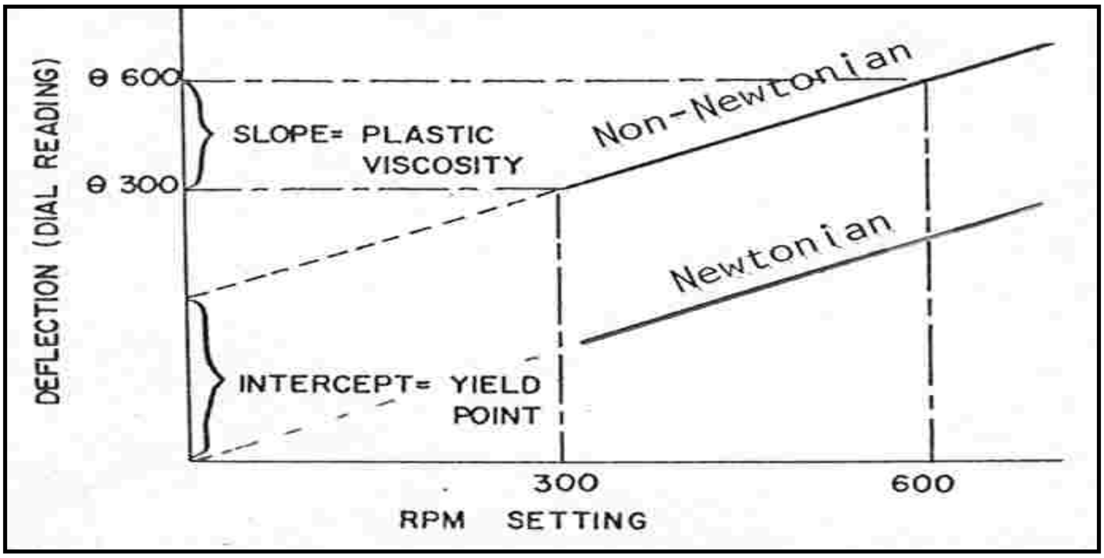


Figure 19: *Flow Curves of Newtonian and non-Newtonian Fluids*

Then, all PVP concentration will be bring to DSC equipment and purged with methane gas in order to obtain the rate of growth of methane hydrate.

Experiment is conducted as shown below:

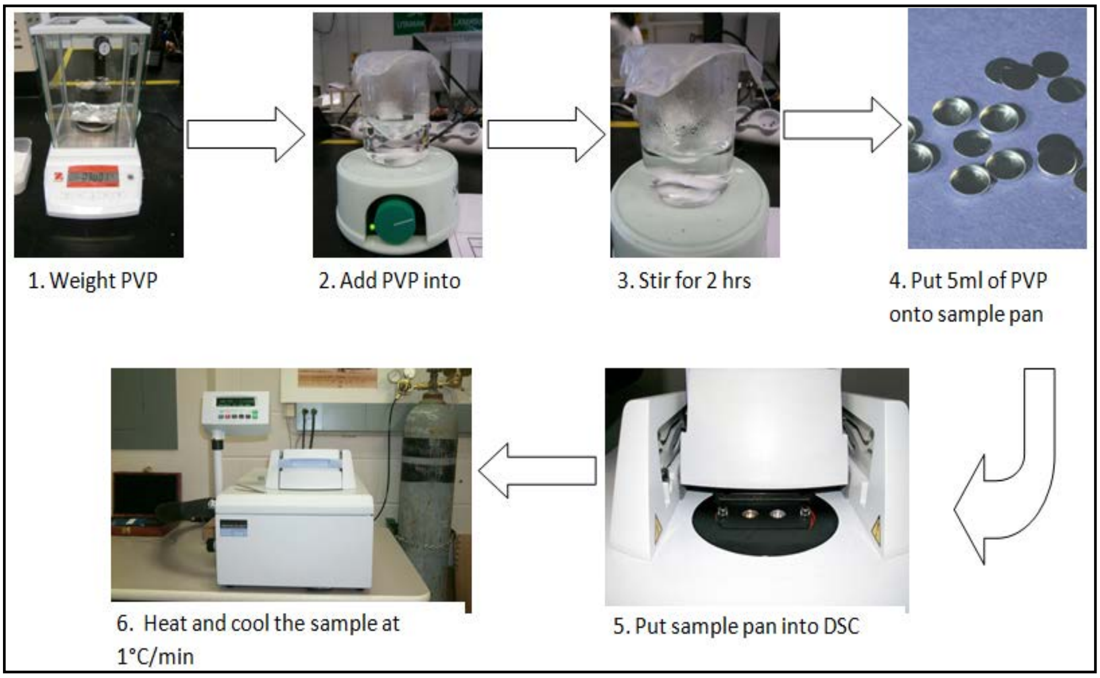


Figure 20: *Picture showed process to carried out the experiment*

3.3.2.1 Rheology Test

For viscosity measurement, 450ml of 1.0 wt% of PVP solution is poured in the cup. Then, the cup is placed on the rheometer plate and the plate is adjusted until the solution is immersed at the designated line of rotor sleeve. Later, solution is stirred for about 5 to 10 seconds at 600RPM and 300RPM and the dial reading is recorded when dial reading is stabilized.

As for gel strength, solution is stirred for about 10 to 15 seconds. Then, rotor is turned off for 10 minutes. Then, rotor is turned on and the highest reading at dial reading is recorded as gel strength in lb/100 ft2. The same procedure is repeated for (0.3, 0.5 and 0.7) wt% PVP solutions. Afterwards, the rheology properties of each solution towards the rate of hydrate formation will be studied.

3.3.2.2 DSC Test

5mg of 1.0wt% solution was placed in the aluminium sample pan. Then, that pan is put into the sample cell (DSC furnace) and throughout the experiment; nitrogen is purged into DSC cell. Two different mode were used which are ramp and isothermal mode. For ramped mode, sample is heat to 30° and then cooled to -30°C. After that, sample is heat up again to 30°C. This step is held in order to study the effect of ice/hydrate towards stability of the PVP solutions.

While isothermal mode heat the sample to 30°C and cooled to -30°C. At -30°C the sample is held for about 5 minutes. After that, the sample is heat up again to 30°C. Both modes are run with cooling and heating rate at 1°C/min.

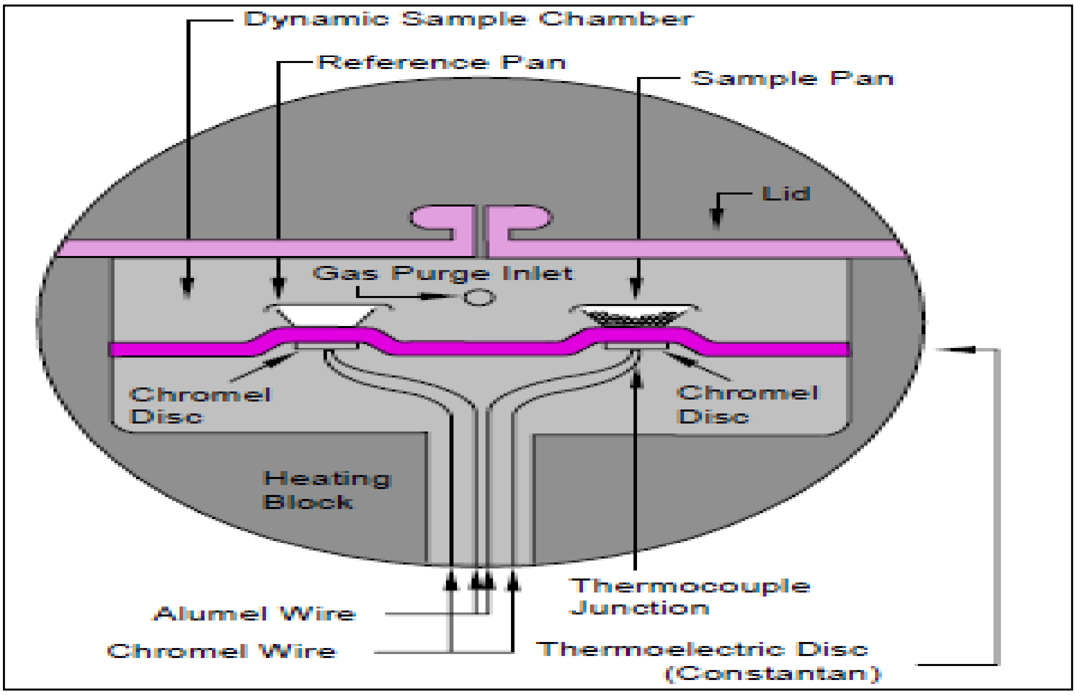


Figure 21: *Cell Schematic Diagram of DSC show the gas inlet, gas outlet, sample cell and reference cell.*

3.4 Hydrate/ Ice Induction Time Measurement

Once the experiment is complete, the induction time of hydrate/ice at different concentration of PVP will be studied as DSC gives a curve of heat flux versus temperature or versus time and crystallization and dissociation of hydrate/ice can be observed from the peak point as shown in the graph. The exothermic point indicates crystallization of hydrate/ice is where water and gas hydrate release its heat to the surrounding to form ice/hydrate. While, endothermic point indicates hydrate dissociation occurs and because solid formation absorb heat in order to change from solid to liquid and gas phase. Leveling of heat or time indicate hydrate/ice growth is stopped and when the temperature start to decreasing again, growth of hydrate/ice continue again as PVP only prevent hydrate formation by delaying its formation process

CHAPTER 4

RESULT AND DISCUSSION

4.1 Rheology Test

PVP wt%	600rpm (θ600)	300rpm (θ300)	Plastic Viscosity, cp	Yield Point lb/ 100ft	10min gel strength, lb/ 100ft^2	Density, ρ (g/mL)
0.3	6	4.5	1.5	1	1.0	1.0003
0.5	8	7	1	2	1.0	1.0007
0.7	9	8	1	5	1.0	1.0012
1.0	10	9	1	8	1.0	1.0019
*PV= θ600 - θ300 * YP= θ300 - PV						

Table 5: *rheology test for each PVP solution concentration*

Based on the result, 1.0 wt% of PVP has the highest density followed by 0.7wt%, 0.5wt% and 0.3%. In terms of plastic viscosity most all PVP concentration has 1.0cp. While gel strength which has tested after PVP solutions set quiescently for a period of time (10 seconds and 10 minutes) showed 1.0 lb/100ft. These fluid properties indicate that PVP will not affect flow assurance of the system that injected with PVP is capable to flow at its designated flow rate because of the low viscosity of the PVP concentration.

In addition, PVP also act as drag reducing agent (DRA) as it can reduce the frictional pressure drop along the pipeline’s length. This phenomenon occurred because PVP molecules will interact with the pipe wall and functioning as shock absorbers and energy loss due to friction between fluid and pipe wall were reduced. As a result, energy used to transport the fluid in the throughout the pipe system will decreased and enhance flow rate of the liquid.

4.2 Transition Phase of the Sample

Results that obtained from DSC showed in **figure 22, 23, 24, 25, 26, 27, 28, 29 and 30.**

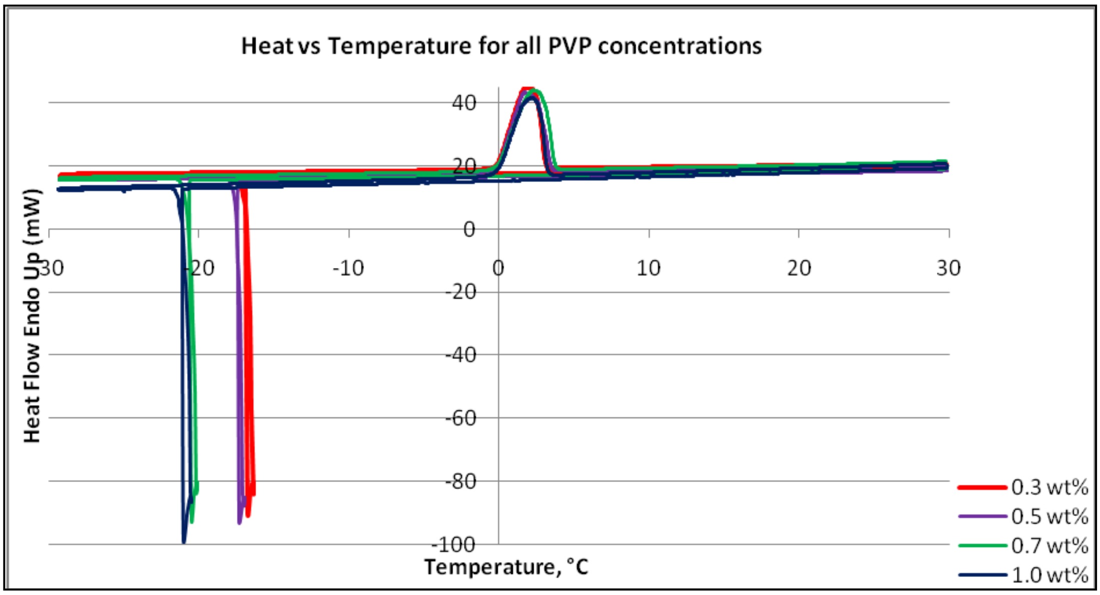


Figure 22: *DSC curves (heat flow vs temperature) for all PVP solution concentration showing the crystallization and melting peak*

There four types of line that can be observed in all DSC results which are baseline, peak, initial peak temperature and final peak temperature. Baseline is a line that connects the measured curve before and after curve. Peak is a deviation from the baseline that indicates disruption of steady state due to production (exothermic) and consumption (endothermic) of heat by the sample. Initial peak temperature is a point where the curve begins to deviate from the baseline and final peak temperature is a point of temperature where the curve returns to the baseline. Positive peak that read by DSC indicate endothermic process where melting of occurred and negative peak indicate endothermic process where crystallization of the substance occurred.

In **figure 22**, concentration with 1.0wt% has the highest crystallization peak, followed by 0.7wt%, 0.5wt% and 0.3wt%. There are two types of results that obtained from the DSC where temperature vs heat flow (mW) and heat flow vs time where will be used to investigate induction time of the phase transition that undergo by the samples.

However, during the melting phase, sample with 0.5 wt% of PVP melt at the highest temperature compare to all PVP concentration. From the graph above, the temperature of the sample is increased at constant rate which at 1°C/min in order to avoid o reduce stochastic of hydrate or ice formation (Sloan and Koh, 2008). At first, sample is heated to 30°C as the temperature rise then it cooled to -30°C. During this process, heat flow is constant until the crystallization process start to occur where sudden drop of heat flow occur. This situation happens as energy in term of heat from the sample is released to the surrounding and detect by DSC as exothermic event where liquid change it phase to solid. After reached its peaks, the heat flow undergo sudden rise and then it start to increased in constant rate.

When melting phase start to occur, the sample experienced sudden rise of heat where a large amount of heat is absorbed within the DSC furnace into sample as heat is added for melting process and DSC detect this situation as endothermic event.

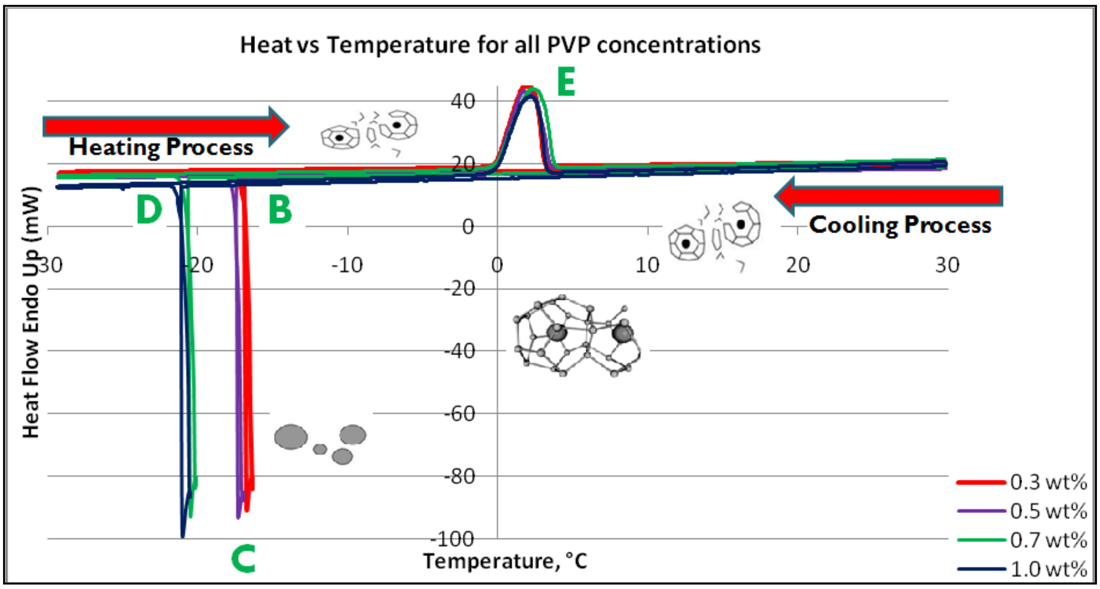


Figure 23: *DSC curves (heat flow vs temperature) showed process and phases transition of the samples.*

From A to B, nitrogen is dissolved in the water and water molecules start to form cages to trap nitrogen molecules. The linking of cluster to each other occurs at this stage. Then, from B to C a rapid nucleation and growth of occurs where critical radius of cluster form at C which at the peak of the curve. After that, from point C to D complete crystallization and solidification were achieved. After point D to E, the reaction is drive to dissociate the ice/hydrate. Then, at point E and afterwards sample is back to its liquid state.

This experiment is conducted at constant pressure where;

$$dH = TdS = dq$$

$$\Delta H = \int dH = q$$

From the above equation, change in the enthalpy value is directly proportional to the heat flow in the system as the obtained results.

Summary of melting and crystallization peak of each PVP concentration as shown below;

Concentration wt %	**Temperature Peak**		**Heat Flow Peak**	
	Crystal	**Melt**	**Crystal**	**Melt**
0.3	-16.74	2.12	-90.1795	44.6329
0.5	-17.29	1.86	-92.6853	42.9312
0.7	-20.52	2.68	-92.1085	43.6478
1.0	-21.04	2.47	-98.6191	40.6411

Table 6: *temperature peak and heat flow peak that recorded by DSC*

4.2.2 Stability of PVP and Cluster Size

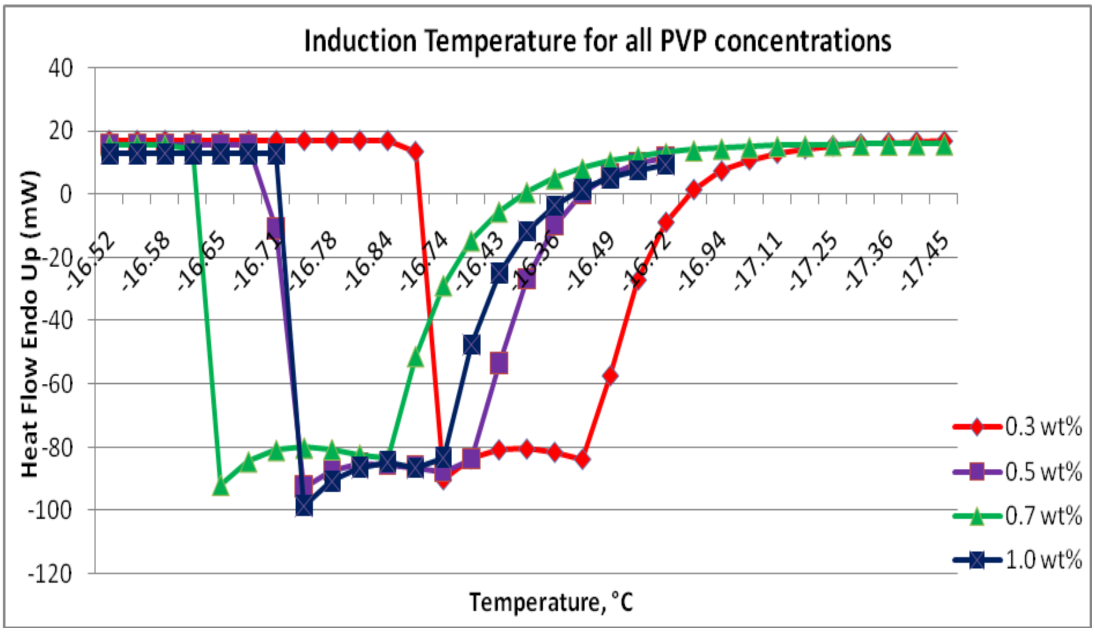


Figure 24: *DSC curves for induction of heat flow vs temperature for all PVP solution concentration*

From the above graph, **figure 24**, the longest induction temperature obtained by 0.3 wt% of PVP, followed by 1.0 wt%, 0.5 wt% and 0.7 wt%. By using DSC, heat flow signals during the heating and cooling rate can be indicator to show size of hydrate/ice because at temperature where crystallization took placed is a function of sample size. At the maximum peak of temperature droplets size can be determined; the lower the crystallization temperature the thinner the droplets are (Dalmazzone, 2001).

Besides, temperature also reflects the stability of the solution for every PVP concentration. This phenomena can be determined through trend of curve that recorded by DSC during heating programme. If the melting peak can be easily tracked from the graph it shows that the PVP solution is stable. If the graph consists of two or more peaks during the heating programme, merged and difficult to distinguish it shows that PVP solution is not stable because eutectic that not crystallize (Rolley, 1994) and (Dalmazzone 2001).

This situation suggest that 1.0 wt% of PVP disrupt the water-gas interface and prevent clusters to join and grow on the vapour side of the surface, thus cause the droplet to obtained the thinnest size. This followed by 0.7 wt%, 0.5 wt% and 0.3 wt% of PVP. In addition, trend of curves which are smooth and continuous suggest that homogenous nucleation occurs within the samples due to the absence of impurities which enable water and gas molecules to collide simultaneously. This suggests that the solution with high concentration can reduce the size of ice/hydrate formation. PVP stability can be observed during crystallization and melting process. From the result, it is clear that during the crystallization and melting phase all curve were not merged and all peaks can be easily read from the graph. It can be concluded that all PVP solutions (0.3, 0.5, 0.7 and 1.0) wt% were stable in the presence of ice/hydrate.

4.2.3 Kinetic Process and Induction Time for Solidification Process

On the other hand, **figure 25** showed the heat flow vs time that plotted by DSC where the highest peak of time obtained by 1.0 wt% of PVP, followed by 0.7 wt%, 0.5 wt% and 0.3 wt%. Time taken to form solid and liquid state will be investigated closely in order to obtain induction time to undergo crystallization process, to evaluate performance of PVP and also to get the sufficient concentration of PVP to prevent ice or hydrate formation.

Concentration wt %	**Time Peak**		**Heat Flow Peak**	
	Crystal	**Melt**	**Crystal**	**Melt**
0.3	24.817	48.75	-90.1795	44.6329
0.5	25.067	48.75	-92.6853	42.9312
0.7	26.683	48.95	-92.1085	43.6478
1.0	-26.9	39.29	-98.6191	40.6411

Table 7**:** *time peak and heat flow peak plotted by DSC indicate phase transition of sample*

In addition, time where initial peak and final peak time of crystallization is very important because it shows the kinetics of the process. Induction time that occurs between these two period reflect the appearance of the very first cluster of ice or hydrate at supernucleus size (D. Kashchiev, 2002). At this point, cluster wills growth from microscopic to macroscopic size.

Based on result in **figure 26,** crystallization process that contains 1.0 wt% of PVP was highly inhibited compared to the other concentration. This situation indicates interaction between nucleation at the interface and interfacial forces, which affect by concentration of inhibitor and also driving force. Generally, PVP contains surface-active agents and small amount of PVP can disrupt the crystallization process. At microscopic level of crystallization process the interface of water and gas are covered by PVP and destroys the liquid water molecule grid generated by the hydrogen bond. Thus cause low driving forces interfacial phenomena.

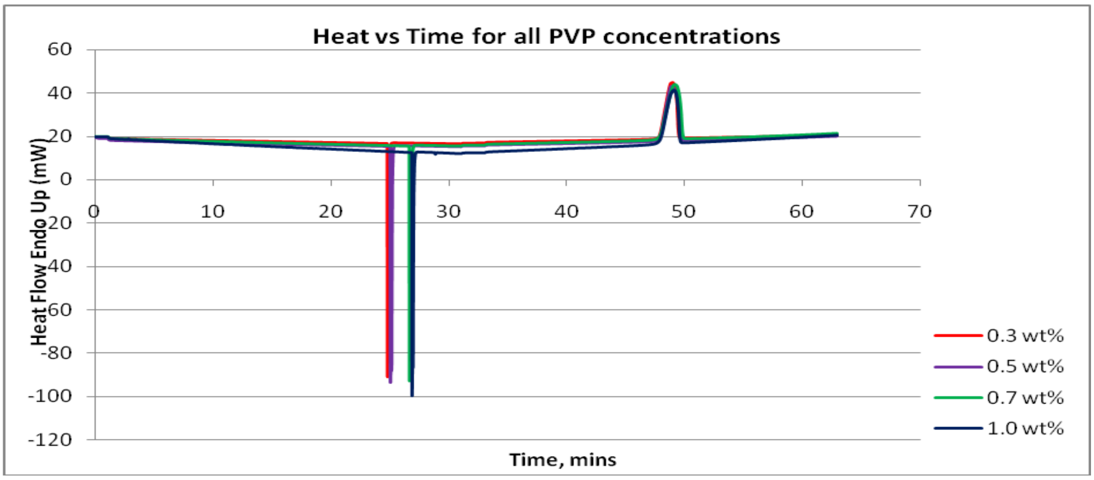


Figure 25: *DSC curves (heat flow vs time) for all PVP solution concentration showing the crystallization and melting peak*

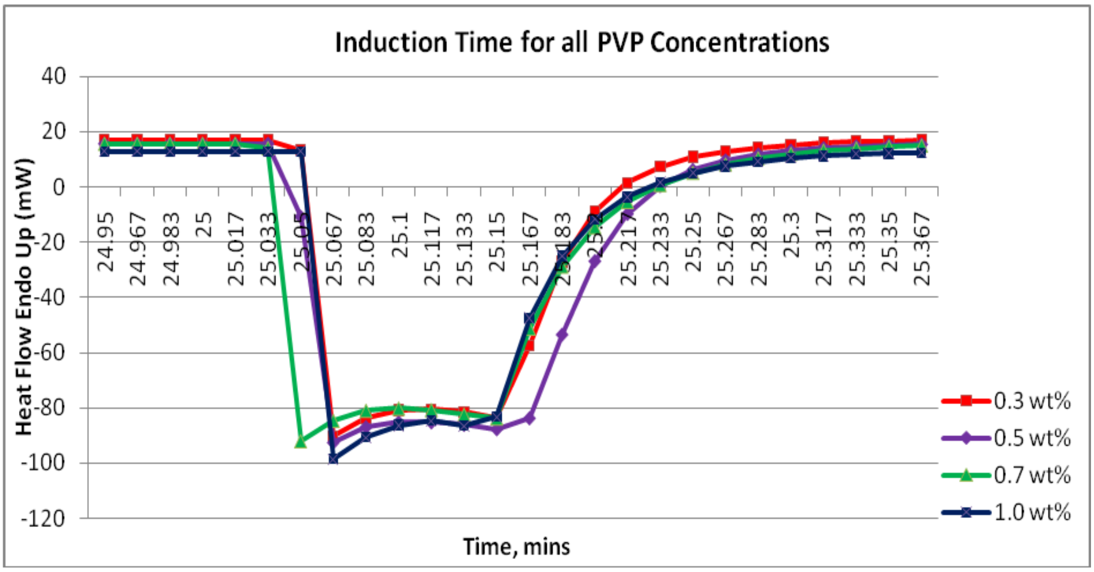


***Figure 26:** DSC curves for induction of heat flow vs time for all PVP solution concentration*

However, at 0.3 wt% of PVP the induction time of sample to undergo crystallization process is rapid due to high driving force at water-gas interface. At 0.3 wt%, PVP molecules that adsorb and destroy the hydrogen bonding at the gas-water interface not much as 1.0 wt% of PVP. For 0.3wt% PVP ice/hydrate formation is indicated at approximately 51.4 minutes. That means the induction time for ice/hydrate to occur is about 7.2 seconds.

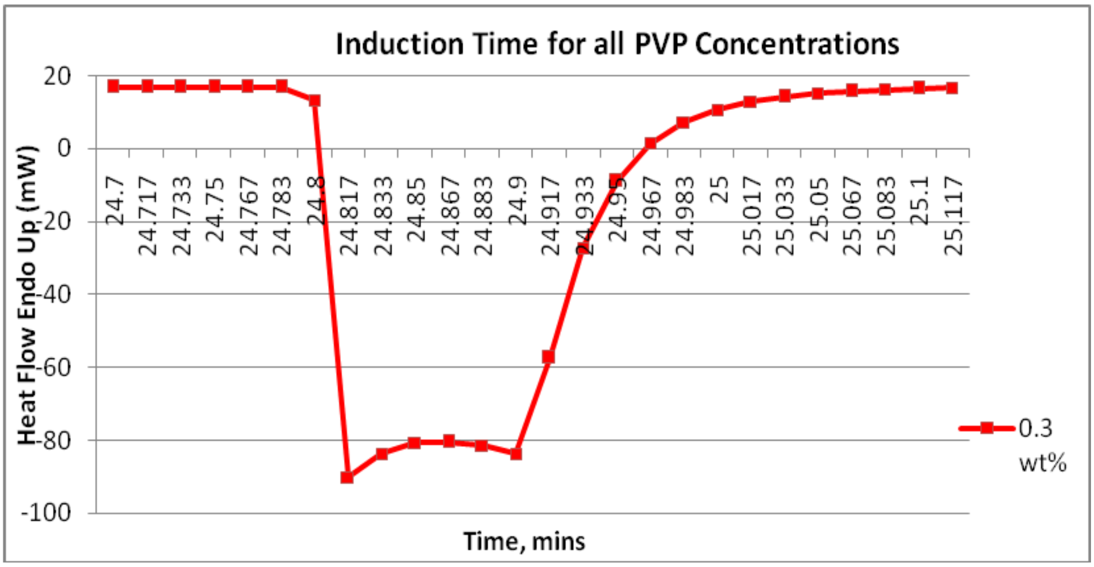


***Figure 27**: DSC curve (heat flow vs time) shows induction time for PVP solution containing 0.3wt%*

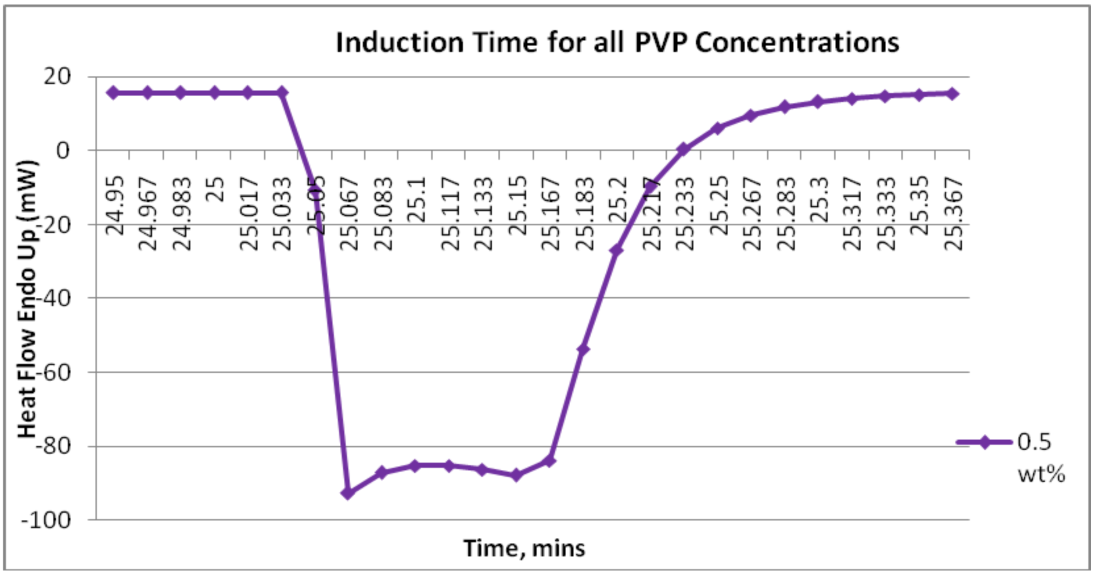


Figure 28: *DSC curve (heat flow vs time) shows induction time for PVP solution containing 0.5wt%*

For 0.5wt% PVP, ice/hydrate formation is indicated at approximately 46.2minutes where ice/hydrate induction time is about 12.6 seconds. While 0.7wt% PVP induction time is about 13 seconds as ice/hydrate is indicated to form at 45.83 minutes.

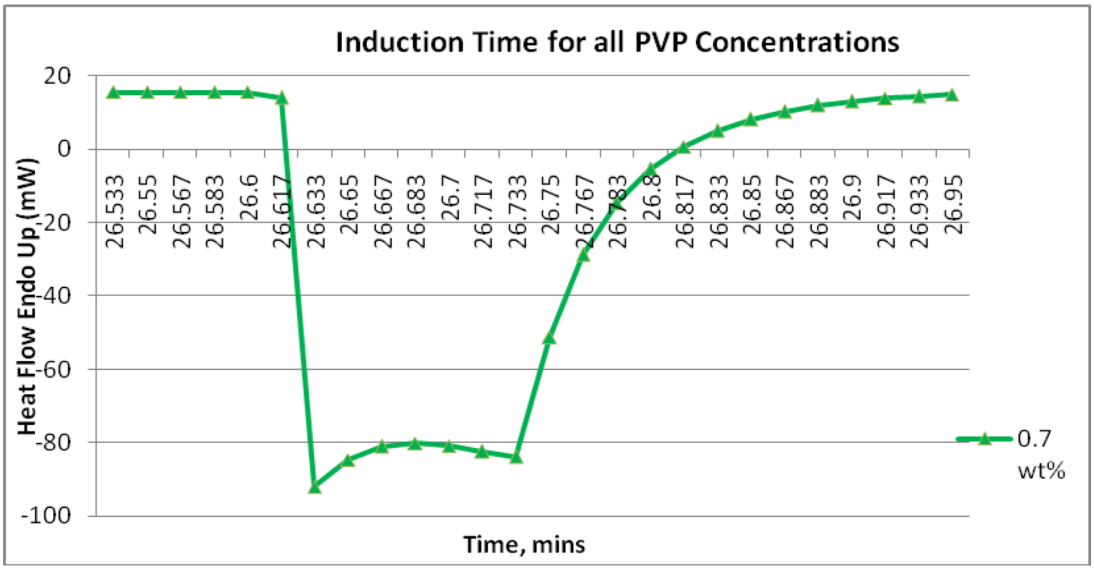


Figure 29: *DSC curve (heat flow vs time) shows induction time for PVP solution containing 0.7wt%*

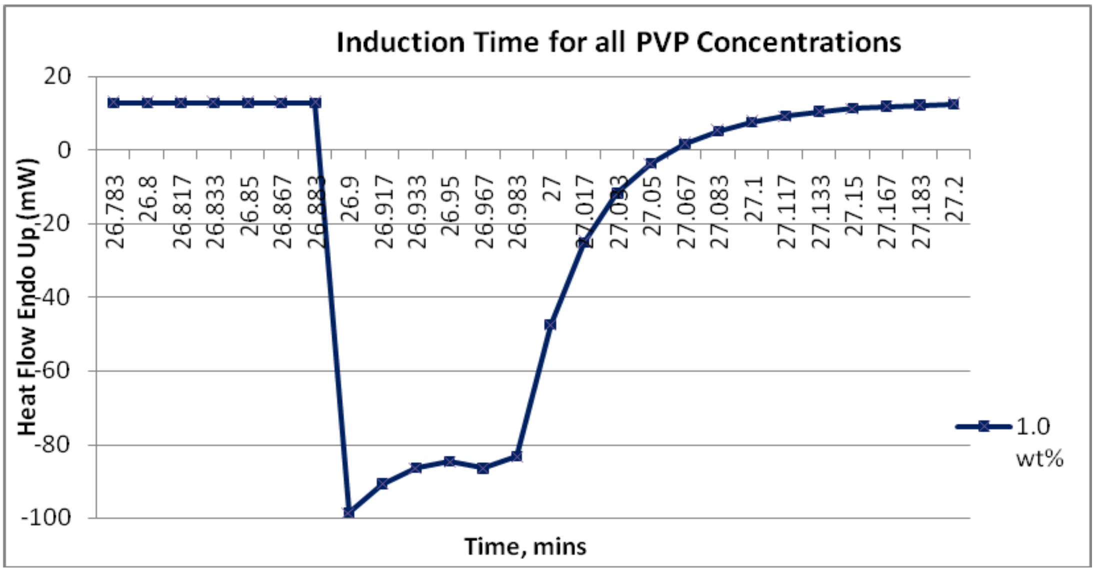


Figure 30: *DSC curve (heat flow vs time) shows induction time for PVP solution containing 1.0wt%*

Lastly, 1.0wt% delayed the ice/hydrate formation for about 15 seconds due to formation of ice/hydrate at approximately 51.52 minutes. This suggest that the use of (0.3, 0.5, 0.7 and 1.0) wt% of PVP increases the induction time of ice/hydrate to occur by addition of 3seconds for each PVP solution. This is also indicate PVP slow down the initial nucleation of ice/ hydrate due to PVP monomer adsorption on the interface of pure water through strong surface interactions. As the PVP concentration increase, the adsorption of PVP on the water surface will also increase and prevent ice/hydrate clusters to join and grow to achieve it critical size in a temporary period.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The experiment is conducted to study the rate of methane hydrate growth in the presence of difference concentration PVP by using DSC. For kinetic of ice/hydrate formation, two graph are plotted by DSC are heat flow vs temperature and heat flow vs time. Heat flow graph vs temperature curve help to determine the droplet size that occur during the crystallization process and also indicate the stability of PVP throughout the experiment. PVP with the lowest concentration, 0.3 wt%, is less effective as the droplet size is bigger compare to the rest of PVP concentrations. However, it has been found that the higher concentration of PVP that exist in the system reduce the size of the droplet.

On the other hand, heat flow vs time indicate the induction time to obtain critical size of droplet and this situation indicates interaction between nucleation at the interface and interfacial forces, which affect by concentration of inhibitor and also driving force. Generally, PVP contains surface-active agents and small amount of PVP can disrupt the crystallization process. At microscopic level of crystallization process the interface of water and gas are covered by PVP and destroys the liquid water molecule grid generated by the hydrogen bond. Thus cause low driving forces interfacial phenomena. In has been found that, the higher concentration of PVP result in longer induction time for the system to form hydrate/ ice. Presence of PVP in the system has shown effect toward ice/hydrate formation inhibition. Even though at low concentration of PVP showed less significant effect towards formation inhibition but it still showed potential to inhibit the crystallization process. Based on the obtained result, 0.5 wt% of PVP concentration is the minimum and sufficient to inhibit hydrate/ice formation.

One of the major limitations of this project come from the DSC Pyris 1as DSC in UTP laboratory does not have ability to run experiment at high pressure condition. In the real situation, pressure in the pipeline is high as 70-120Bar.It is recommended to conduct this study using high pressure and high temperature DSC such as DSC 111(SETARAM) because it is found that, the solid that formed in the system is not hydrate but ice as hydrate cannot exist at ambient pressure and the gas that use in the project is not methane but nitrogen. This happen due to equipment limitation as pressure can’t be manipulated and methane gas can’t be use as it can cause fire in the DSC furnace. Besides that, it is recommend to conduct experiment lower than 1°C/min in order to reduce stochastic effect on the data accuracy by getting more data points.

REFERENCES

1. AGI Summary on the Methane Hydrate Research and Development Act
2. Dr. Ram Sivaraman,Understanding and Controlling Natural Gas Hydrate,2002
3. Kathy Marvin 2010, “Understanding the Clathrate Hydrate”
4. http://chem.ps.uci.edu/~kcjanda/Group/index.html
5. Sloan, E.D, Clathrate Hydrate of Natural Gas, 2nd ed., Marcel Dekker, New York, NY, (1997)
6. Rachel O'Reilly, Nga Sze Ieong, Pei Cheng Chua, Pei Cheng Chua, (2011)“Crystal growth inhibition of tetrahydrofuran hydrate with poly(N-vinyl piperidone) and other poly(N-vinyl lactam) homopolymers”
7. Archana Parmar, 2009, “ PVP as Kinetic Hydrate Inhibitor in Gas-Water Systems”
8. University of Southern Mississippi, Department of Polymer Sciences, http://pslc.ws/macrog/dsc.htm
9. Sloan, E.D. and Koh, C.A., “Clathrate Hydrates of Natural Gases”, 3rd Edition, Taylor & Francis/CRC Press (2008)
10. Mehta, A. P.; Sloan, E. D., "Structure H Hydrates: Implications for the Petroleum Industry" SPE Journal, 1999.
11. Larsen, R.; Knight, C. A.; Rider, K. T.; Sloan, E. D., "Melt growth and inhibition of ethylene oxide Clathrate hydrate" Journal of Crystal Growth, 1999.
12. Kelkar, S. K.; Selim, M. S.; Sloan, E. D., "Hydrate dissociation rates in pipelines" Fluid Phase Equilibria, 1998
13. Larsen, R.; Knight, C. A.; Sloan, E. D., "Clathrate hydrate growth and inhibition" Fluid Phase Equilibria, 1998
14. Christiansen, R. L.; Sloan, E. D., "Mechanisms and kinetics of hydrate formation" International Conference on Natural Gas Hydrates, 1994,
15. Sanggono Adisasmit0, Robert J. Frank, 111, and E. Dendy Sloan, Jr.',” Hydrates of Carbon Dioxide and Methane Mixtures”, *Colorado School of Mines, Golden, 1991*

16. K. P. McNamee SPE/Nalco, “Evaluation of Kinetic Hydrate Inhibitor Performance by High-Pressure Differential Scanning Calorimetry”, Offshore Technology Conference, 2011,

17. Kalbus, James S., Intera Information Technologies, Inc.; Christiansen, Richard L., Sloan, Jr., E. Dendy, “Identifying Inhibitors of Hydrate Formation Rate with Viscometric Experiments”, 1995.
18. Didier Dalmazzone, ENSTA; Christine Dalmazzone, Benjamin Herzhaft, Institut Français du Petrole” Differential Scanning Calorimetry: A New Technique to Characterize Hydrate Formation in Drilling Muds”, SPE Journal, 2002.
19. Hailu K. Abay1!, Jonas Hovland 1 and Thor M. Svartas, “The Effect of PVP on Methane Hydrate Nucleation and Growth”, *7th International Conference on Gas Hydrates, 2011*
20. E. Dendy Sloan Jr, “Fundamental principles and applications of natural gas hydrate”, Journal of Nature p.353-359, 2003.
21. API 1163 In Line Inspection System Qualification Standard
22. Carigali Inspection and Maintenance Guidelines (CIMG)