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ENHANCEMENT OF KINETIC INHIBITOR (PVP) WITH ADDITION OF POLYETHYLENE OXIDE (PEO)

by

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

MAY 2011

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CERTIFICATION OF ORIGINALITY

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

Naila Qistina binti Mohammed

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfillment of the requirement for the
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ABSTRACT

Plugging of pipelines and processing equipment has severe economical consequences and poses safety concerns. It is therefore of great interest to prevent the formation of gas hydrates. There are a variety of methods of hydrate prevention which are classified either as thermodynamic or kinetic inhibition methods.This study aims to shed some light on **Enhancement of kinetic Inhibitor (PVP) with addition of Polyethylene Oxide (PEO)**. This study is an experimental study, which the objective is to demonstrate the impact of polyethylene oxide (PEO) on the performance of known kinetic hydrate inhibitor (KHI). Comparison will be conducted on the induction time for crystallization of gas hydrate containing various concentrations of PEO together with the known KHI which in this study is PVP. The experiment is being conducted using Pyris 1 DSC which use is to measure the heat flow into or from the samples as it is heated, cooled or held under isothermal conditions. The outcome of this study is mainly to find the most favorable concentration of the mixture of KHI and PEO that will exhibit the strongest inhibition by highest time delayed in gas hydrate formation. The study expects to find that as the concentration of the mixture of PEO and PVP increases, the induction time for gas hydrate crystallization increases, but after a certain point, the induction time would be constant. From the results of this study, the knowledge of how PEO and PVP mixture affects the performance of gas hydrate inhibition, may help oil and gas industry to solve problems in flow assurance.

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1.0 INTRODUCTION

1.1 Background of Study

Natural gas hydrates creates problems in the production, transportation, and processing of natural gases. It becomes critical as producers drill in deeper waters and in cooler waters. The past decade has seen the gas and oil industry moving towards deep-water exploration and production currently over 10,000 feet of water depth, where pressures and temperatures are ideal for hydrate formation (Huoa et al., 2001). The hydrates can form in a wellbore while the fluids go through pressure and temperature induced phase changes near the mud line. The hydrates also form in the flow lines from subsea completions to the separation facilities (Talaghat, 2011). This has brought new challenges for hydrate prevention in transportation.

Due to the value of the infrastructures involved, safety considerations and production requirements, oil and gas companies are necessarily cautious about new technologies, particularly where data for their effectiveness are scarce. There have been many field trials to assess the performance of thermodynamic hydrate inhibitors (THI), kinetic hydrate inhibitors (KHIs), and anti-agglomerates (AAs), and there are fields where they are now routinely used as part of the hydrate mitigation strategy (Kozielski et al., 2007). However, the target is always moving, and in order to make new fields viable the technology must also improve without significant increases in cost.

Several methods are known to prevent hydrate formation and subsequent problems in pipeline and other processing equipments. Physical methods have been used such as increasing gas temperature in the pipeline, drying the gas before introduction into the pipeline, and lowering the gas pressure in the system. However, these techniques are either costly or are undesirable due to the loss of efficiency, and production. Chemical procedures have also been used. Alternatively, the addition of methanol or glycols may be used. Today, attempts are therefore being made to replace thermodynamic inhibitors by adding, at temperature and pressure ranges in which gas hydrates can form, additives in amounts of less than 2% which either delay the gas hydrate formation (Talaghat, 2011).

As for this study, it focuses on the additive PEO mixed with known kinetic hydrate inhibitor which is PVP. This study will contribute to the knowledge of the use of PVP with the addition of PEO of various concentrations, in terms of its effectiveness in altering the induction time of gas hydrate crystallization.

1.2 Problem Statement

Formation of hydrates in production pipeline must be inhibited and dissolved for gas production to occur. The operator must maintain the well and production lines free of hydrates at all times for efficiency of production and transportation. The difficulty of finding effective hydrate control method in a system at hydrate conditions is complicated in offshore environments due to the absence control over the fluid composition, bottom hole pressure, and temperature. Moreover, the well operator has only a limited control over the wellhead pressure. In order to handle the problems, hydrate inhibitor are used. Hydrate inhibitors are classified into three groups; thermodynamic inhibitors (THI), kinetic inhibitors (KHI) and anti-agglomerates (AA). The effectiveness of THI is well known, but large concentrations are needed, which sometimes impact project economics. KHIs are effective at lower concentrations than THIs, but they do not perform well at pipeline or well shut-in conditions, or at higher subcooling. Therefore, this project aims to find the most effective ratio of PEO and known KHI which is PVP, as hydrate inhibitors that will exhibit the strongest inhibition by highest time delayed in gas hydrate formation.

1.3 Objective and Scope of Study

The objectives of this study are:

- To compare the induction time for crystallization of the hydrate system with the addition of PEO at different concentration.
- To determine the effective ratio of PEO and PVP as hydrate inhibitors.

The scope of this study is to find the most effective ratio of PEO and PVP as hydrate inhibitors that will exhibit the strongest inhibition by highest time delayed in gas hydrate formation.

1.4 Relevancy of the Project

This study will produce a general relationship between an independent variable (concentration of the mixture of PEO and PVP) and a dependant variable (induction time for crystallization of the gas hydrate system containing the mixture). This relationship will give an idea on how the independent variable will increase or decrease the induction time for crystallization in gas hydrate system.

1.5 Feasibility of the Project within the Scope and Time frame

Strategies have been investigated to combat hydrate plugs and to ensure regular flow in oil and gas operations which includes mechanical, thermal, hydraulic and chemical methods. The chemical method involves the injection of thermodynamic inhibitors such as alcohols, glycols, aqueous electrolytes or a combination of these and others. The injections of these chemicals shift the equilibrium temperature and thus prevent gas hydrate crystallisation/formation at the pipeline working conditions.

Although the methods have proved to be effective in preventing gas hydrate formation and are currently the most commonly used in the oil and gas industry the usage of glycol or methanol is usually associated with high operating capital costs. Large volumes of the inhibitors are required and the cost associated with the operation and recovery of the inhibitors is very high.

Driven by the need to cut operating cost and reduce the environmental impact of operating oil and gas facilities, many recent research and development activities have been focused on the design and development of novel, cheap and environmentally friendly low dosage hydrate inhibitors (LDHIs) (Ding et al., 2009). KHI and AA are categorized in LDHIs. As for this project, PVP is one type of KHIs.

From the results of this study, the knowledge of how PEO and PVP mixture affects the performance of gas hydrate inhibition, may help petroleum engineers to optimize production and transportation of reservoir to the refineries.

The study is expected to be feasible after much deliberation based on below:

- All equipments, tools and materials are readily available at the university labs, and thus there is no wastage of time in ordering and waiting for their arrival.
- The scope consists of varying an independent variable to see the effect on a dependant variable. The form of this study is a straight forward experimental research, and thus should be simple to conduct.
- A limited amount of formulations will be prepared, in order to fit within the time frame, hence proper research must be done into the formulation calculations beforehand. Result collected from experiments will be analyzed and discussed.

The literature review will be covered in the next section, followed by the description of the research methodology in the following part, as well as the current progress. The results will be then discussed. The conclusions of the study are summarized in the last section.

2.0 LITERATURE REVIEW

2.1 Gas Hydrate

Gas clathrate hydrates were first identified in 1810 by Sir Humphrey Davy in the chlorine and water system which later in 1934, clathrate hydrates were extensively studied when Hammerschmidt found that natural gas transport lines could be blocked by the formation of clathrate hydrates (Talaghat, 2011). The occurrence of natural gas hydrates in subsea gas pipelines should be highly noted because these solids causes high economic loss and ecological risks, as well as potential safety hazards to exploration and transmission personnel. Besides that, they also have technological importance in separation processes, fuel transportation and storage (Koh, 2001).

The prevention of gas hydrate plugging of flow lines is considered one of the main production issues to deal with in deepwater field developments as it is most commonly encountered in subsea, cold climate wet gas, and multiphase pipelines. Gas hydrates are formed during drilling, completion, and workover operations as well as in gas-processing facilities, gas injection lines, and aqueous chemical injection in gas lift lines by right pressure and temperature conditions (Taylor and Francis Group, 2009).

Clathrate hydrates or gas hydrates are crystalline solid compounds that are formed in mixtures of water and non- or slightly polar low molecular weight gases or volatile liquids and when subjected to appropriate temperature and pressure conditions (Khalik, 2009). Sloan (1998) concluded that the ice-like clathrate solids are formed at elevated pressures and at lower temperatures. However, Frostman et al. (2003) stated that the temperature below which hydrates can form increases with increasing pressure and can sometimes be as high as 30 °C.

Gas hydrates are formed when hydrogen bonded water molecules form cage-like structures, known as cavities in the crystalline lattice. These cavities have to be at least partially filled with the hydrate-forming molecules, also known as the 'guest molecules', in order to stabilize the structure. Different gas hydrate structures can be formed, depending on the type and the size of guest molecule presents. Clathrate hydrate structures are distinguished by the types of cavities that are formed and the distribution of those cavities in a unit cell (Khalik, 2009).

Gas hydrate formation can be divided into gas dissolution, hydrate nucleation and agglomeration stages as shown in *Figure 1*. Under the condition of gas hydrate formation, water molecules form quasi-cavities by hydrogen bonds. When gases dissolve, gas molecules are entrapped into these quasi-cavities to 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 (Tang et al., 2010).

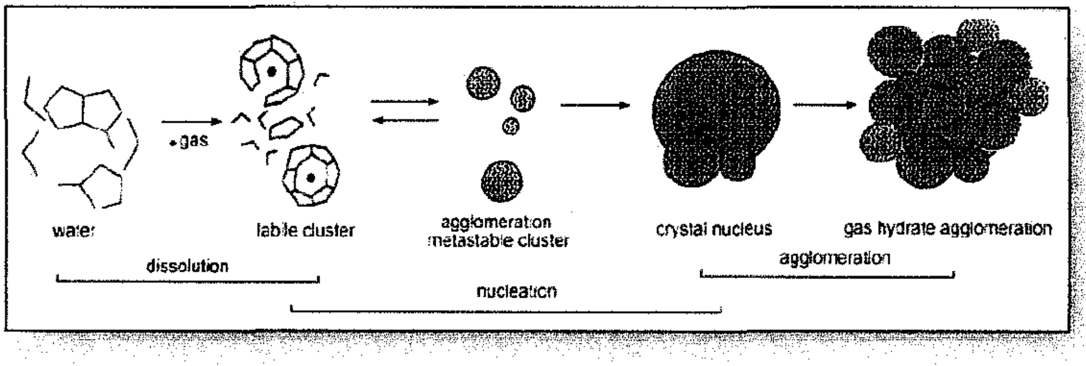


Figure 1: Gas hydrate formation process (Tang et al., 2010)

Hydrate structures are classified into three categories based on the geometries of their constituent water cages: cubic structures I and II and hexagonal structure H, as shown in *Figure 2*. Each crystalline structure contains geometrically distinct water cages with different size cavities which typically accommodate only one guest molecule ranging in diameter from 0.40 - 0.90 nm. Structure I (SI) hydrates are the most commonly encountered naturally occurring hydrate structure which encases small diameter molecules (0.40 - 0.55 nm) such as methane or ethane gas. Structures II (SII) and H (SH) hydrates accommodate larger guest molecules, typically propane or iso-butane for SII or combinations of methane gas and nexohexane or cycloheptane for SH, but are less prevalent in nature.

For SI hydrates, the unit cell consists of 46 water molecules arranged into two small dodecahedral cages (each with twelve pentagonal faces) and six large tetradecahedral cages (each with two hexagonal and twelve pentagonal faces). Assuming full occupancy, the ideal molar guest to water ratio for an SI hydrate is 1: 5.75 (Harrison, 2010).

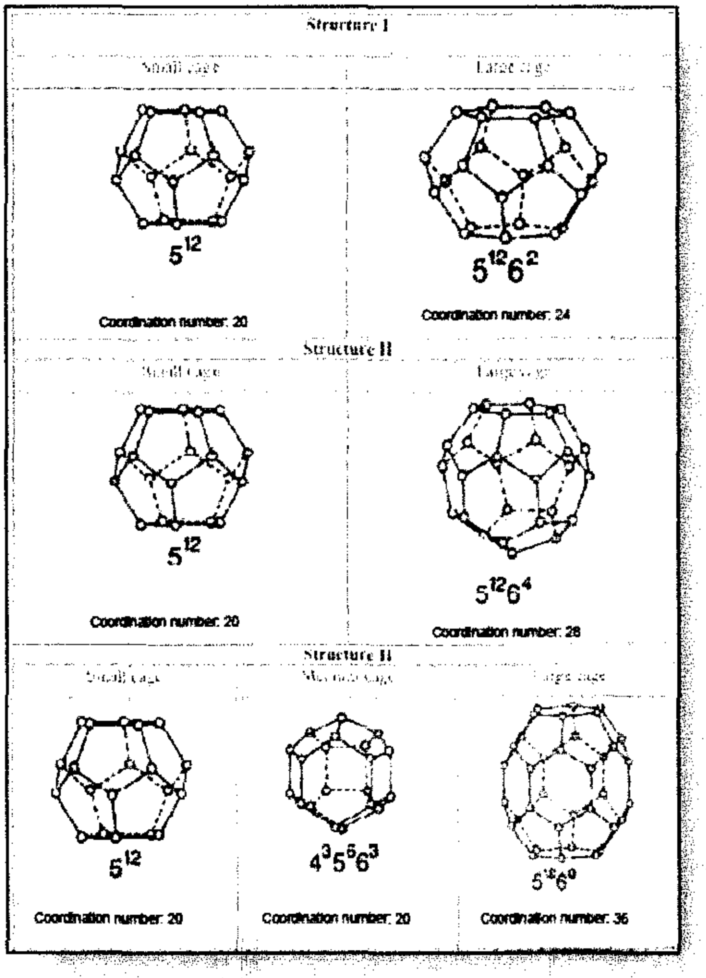


Figure 2: Cages and their coordination number in clathrate structures I, II and H (Khalik, 2009)

2.2 Hydrate Inhibitors

Chemical treatment to prevent hydrate plugging can be accomplished with three different classes of chemical, all of which are now used in the field; thermodynamic hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHIs), and anti-agglomerants (AAs).

The last two categories are known collectively as low-dosage hydrate inhibitors (LDHIs), reflecting the much lower dosage requirements compared with THIs; THIs are used at high concentrations (10-60 wt %), KHIs and AAs are added at low concentrations (<1 wt %). Both KHIs and AAs are usually polymers with surfactant properties (Karaaslan and Parlaktuna, 2002 and Sloan and Koh, 2008).

Deepwater reservoirs require the use of kinetic inhibitors or anti-agglomerants, which inhibit the crystals' growth, both by preventing agglomeration of the nuclei and by creation of many crystallization centers, leading to a suspension of hydrates that can be transported through pipes. These inhibitors are surfactant polymers such as PVP and acrylic polymers, among others (Lucas et al., 2009).

2.2.1 Kinetic Hydrate Inhibitors

In the 1990s there was substantial research into compounds found to delay the hydrate formation rate, known as kinetic hydrate inhibitors (Kozielski et al., 2007). The key components in all known KHI formulations are water-soluble polymers often with other smaller organic molecules added as performance enhancers, also known as synergists (E. Dendy Sloan and Carolyn A. Koh, 2008).

KHIs do not shift the hydrate equilibrium conditions; rather, they decrease the rate at which hydrates form, preventing plugs for a period longer than the free water residence time in a gas line. KHIs are effective at lower concentrations than THIs, but they do not perform well at pipeline/well shut-in conditions or at higher subcooling (i.e. ΔT, the difference between hydrate equilibrium temperature and operating temperature at a given pressure). As hydrocarbon exploration moves to deeper water, inhibitors effective at larger ΔT are necessary (Huoa et al., 2001).

Generally, the polymers show little partitioning to liquid hydrocarbon phases, yet these phases often affect KHI performance. In subsea multiphase transportation, this enables produced fluids to be transported to the process facilities before gas hydrate formation and deposition occurs in the line. Thus, any need for long shut-ins will be critical in determining the field applicability of a KHI.

Normally field applications of most of the commercial KHIs are limited to a maximum of 9-10°C (16-18°F) subcooling in the production line because the required delay time before hydrate formation is most often in the regions of days. Higher subcoolings (driving forces) would give shorter delay times before hydrate formation occurred. Thus, KHIs are not applicable for most deepwater fields where the subcooling and pressure are both high. Of course, if the residence time of the produced fluids is small, it may be possible to use KHIs at higher subcoolings than 9-10°C (16-18°F).

KHIs have been used commercially in the field since about 1995. They are added at low concentrations, less than 1 wt.% of the water phase and often around 0.3-0.5 wt.%. This can be contrasted with the 20-60 wt.% needed for THIs such as methanol or glycols. In one field application, CAPEX savings of U.S.$40 million were realized by choosing KHI technology instead of methanol injection and regeneration. Many water-soluble polymers have been shown to work as KHIs (Sloan and Koh, 2008).

2.2.2 Polyvinylpyrrolidone

The first KHI to be discovered is polyvinylpyrrolidone (PVP). The performance of KHIs is sometimes quoted as the subcooling at which a multiphase fluid can be transported without hydrate formation for a period (hold time) of 48 h at a given pressure. For PVP, without any synergists, that subcooling is only 3-4° C (5.4-7.2°F) at 70-90 bar.

The mechanism by which PVP and other improved KHIs work is the subject of debate. Two major mechanisms have been proposed. The first suggests that KHI polymers perturb the water structure to such a degree that gas hydrate particles cannot grow to the critical nuclear size, at which point growth becomes spontaneous. Molecular modeling studies indicate that this happens for some KHIs including PVP. However, a neutron diffraction study showed that PVP does not affect the water structure in propane-water systems before and during gas hydrate formation.

The second mechanism suggests that KHI polymers adsorb onto the surfaces of growing hydrate particles limiting their growth, and possibly deforming the hydrate cavities. This can occur before or after the particles reach the critical nuclear size so they can act as nucleation and crystal growth inhibitors (Sloan and Koh, 2008).

Jensen *et al.* found addition of PVP to the aqueous phase could slightly reduce the gas dissolution rate, but the induction times were substantially prolonged upon addition of PVP. Tang et al. (2010) concluded that the prolongation of induction times according to the model was regarded to be due to a change in the nuclei-substrate contact angle.

2.3 Polyethylene oxide

Polyethylene oxide (PEO) is a non-ionic, water-soluble, linear polymer. It has a general chemical formula of $-(-CH_2-CH_2-O-)_n-$, where *n* indicates the number of repeating units. PEO has relatively high melting point, good structural integrity, low glass transition temperature, which permits ion transport at ambient temperatures, low toxicity and biocompatibility (Saboormaleki et al., 2004).

It is a white to off-white powder obtainable in several grades, varying in viscosity profile in an aqueous isopropyl alcohol solution (Talaghat, 2011). It may contain a suitable antioxidant (Costello et al., 1999).

Phase separation of a dilute aqueous PEO solution occurs at a temperature close to 100 °C. The phase separation temperature is often known as the cloud point temperature (CPT). It is defined as the temperature at which a homogenous aqueous PEO solution starts to turn cloudy. It signifies the phase separation of the PEO–H_2O system into two phases; a polymer-rich and a polymer-lean phase.

PEO in water exhibits an inverse solubility–temperature relationship. As the temperature increases, the PEO–water system separates into two phases; a polymer-rich phase and a polymer-lean phase. However, under certain conditions, the PEO–water system exhibits a closed solubility gap (Talaghat, 2010). Previous work has shown that PEO is a weak thermodynamic inhibitor (Englezos and Ngan, 1994; Englezos and Hall, 1994). Furthermore, it has been considered to be unable to exhibit kinetic inhibition by itself (King et al., 2000).

PEO has been characterized as having a moderate tensile modulus, high elongation and ability to orient when stressed. Its solubility in various solvents is a function of its molecular weight and temperature (Mohd Nasir et al., 2005). The PEO products found to be most effective in various papermaking applications are those having very high molecular mass, much in excess of one million grams per mole. Polyethylene oxide is usually received as dry granules. These need to be dispersed with care, using a dilution ratio of at least 100 and avoidance of excessive shear (Lee and Englezos, 2005).

PEO is also highly hydrophilic and characterized with flocculent, thickening, sustained-release, lubrication, dispersing, and water-retention properties. Grades of PEO differ according to their molecular weight, which range from 200 to 7310. Products with molecular weights below 25,000 are viscous liquids or waxy solids and are commonly referred to as polyethylene glycols (PEGs). PEO resins are made commercially by the catalytic polymerization of ethylene oxide in the presence of metallic catalyst systems. Uses of PEO include mucoadhesives, water-soluble films, rheology control agents and thickeners, and additives in pharmaceutical products (Dhawan et al., 2005).

3.0 RESEARCH METHODOLOGY

The main objective of this project is to experimentally study the effect of the mixture of PEO and PVP towards hydrate inhibition, in order to find the most effective ratio of PEO and PVP as hydrate inhibitors that will exhibit the strongest inhibition by highest time delayed in gas hydrate formation.

3.1 Project Activities

The experimental work is divided into two parts which are the preparation of PEO and PVP mixtures and the use of the mixture into DSC. Below are the details of each part.

Preparation of PEO and PVP Mixtures

There are four samples for this experiment, labelled as 0.1wt%, 0.3wt%, 0.5wt% and 0.7wt%. All of the samples are the mixture of 100ml Dulang crude oil, 30ml distilled water, 0.112g PVP, and calculated mass of PEO based on the weight percentage.

Mass of PEO, x is calculated using the formula below;

$$\text{wt\%} = \frac{x}{\text{Mass of Crude Oil} + \text{Mass of Distilled Water} + \text{Mass of PVP} + x} \times 100\%$$

The mass of PEO used for the samples in this experiment is calculated and tabulated in *Table 1*.

Table 1: Mass of PEO corresponds to weight percentage.

Weight percentage (%)	PEO (g)
0.1	0.130
0.3	0.392
0.5	0.654
0.7	0.920

For the preparation of 0.1wt% sample, the experimental procedures are given as follows;

1. At the beginning of the operation, in the presence of kinetic inhibitors and PEO as an additive, the typical kinetic inhibitor (PVP) and additive (PEO) are added to the distilled water in a beaker to produce the desired weight percent concentration of inhibitor and additive in the aqueous solution. Mass measurement of 0.112g PVP and 0.130g PEO were done using a digital weighing machine.

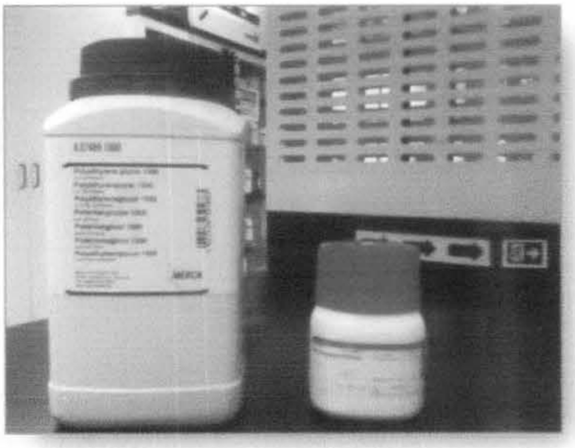


Figure 3: PEO (left) and PVP (right) that were used in the experiment.

2. Later the solution is poured into a beaker that contained 100ml crude oil. The mixture was stirred again before inserted into a sample container and proceed to the experiment using DSC.

3. Step 1 and 2 were repeated for 0.3wt%, 0.5wt% and 0.7wt%.

Experiment using DSC

1. In this experiment, the DSC uses Nitrogen as the supply gas for hydrate formation.

2. The mixture is first stirred due to the separation of two layers which is crude oil layer and PEO-PVP mixture layer before being operated into DSC.

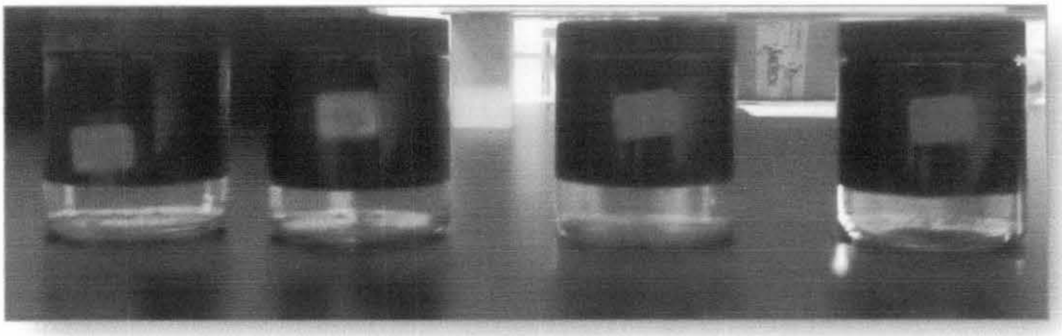


Figure 4: Samples of the mixture. From left to right: 0.1wt%, 0.3wt%, 0.5wt% and 0.7wt%.

3. The operating conditions for DSC in this experiment mentioned below;
   i) COOLING

      From room temperature to -25°C at rate 1°C/min

   ii) HEATING

      Heating back from -25°C to room temperature at rate 1°C/min

   iii) ISOTHERMAL

      Cooling to -25°C then hold it for 2 hours

4. The induction time and heat flow are recorded for both Cooling-Heating Mode and Isothermal Mode.

3.2 Key Milestone

Figure 5 below describes the overall milestones and general flow of this project.

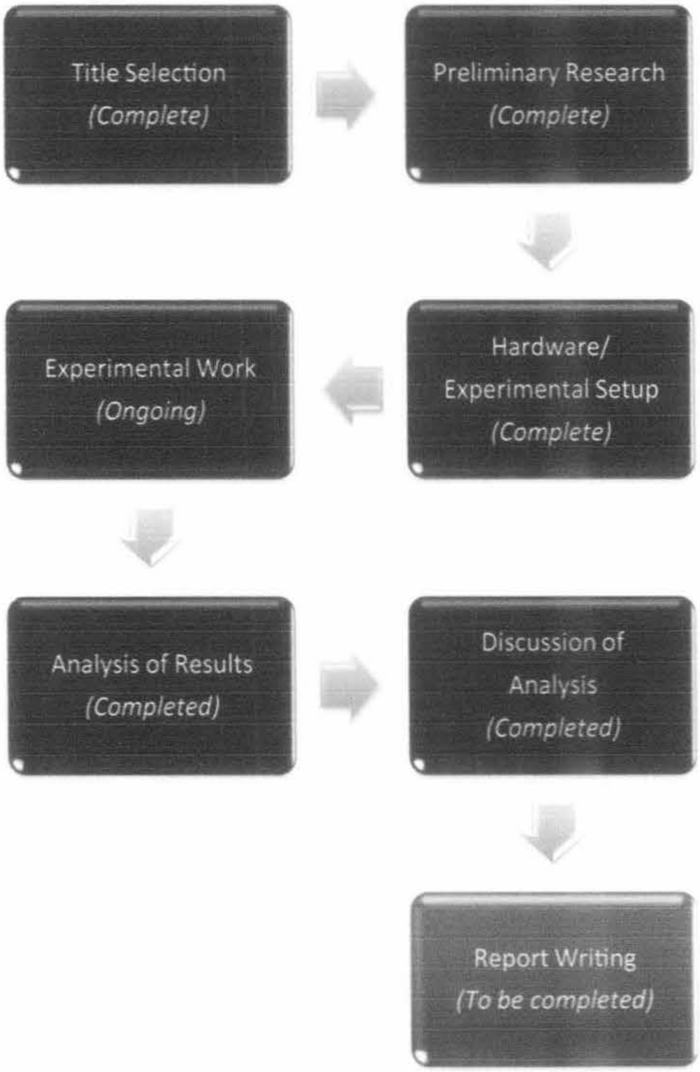


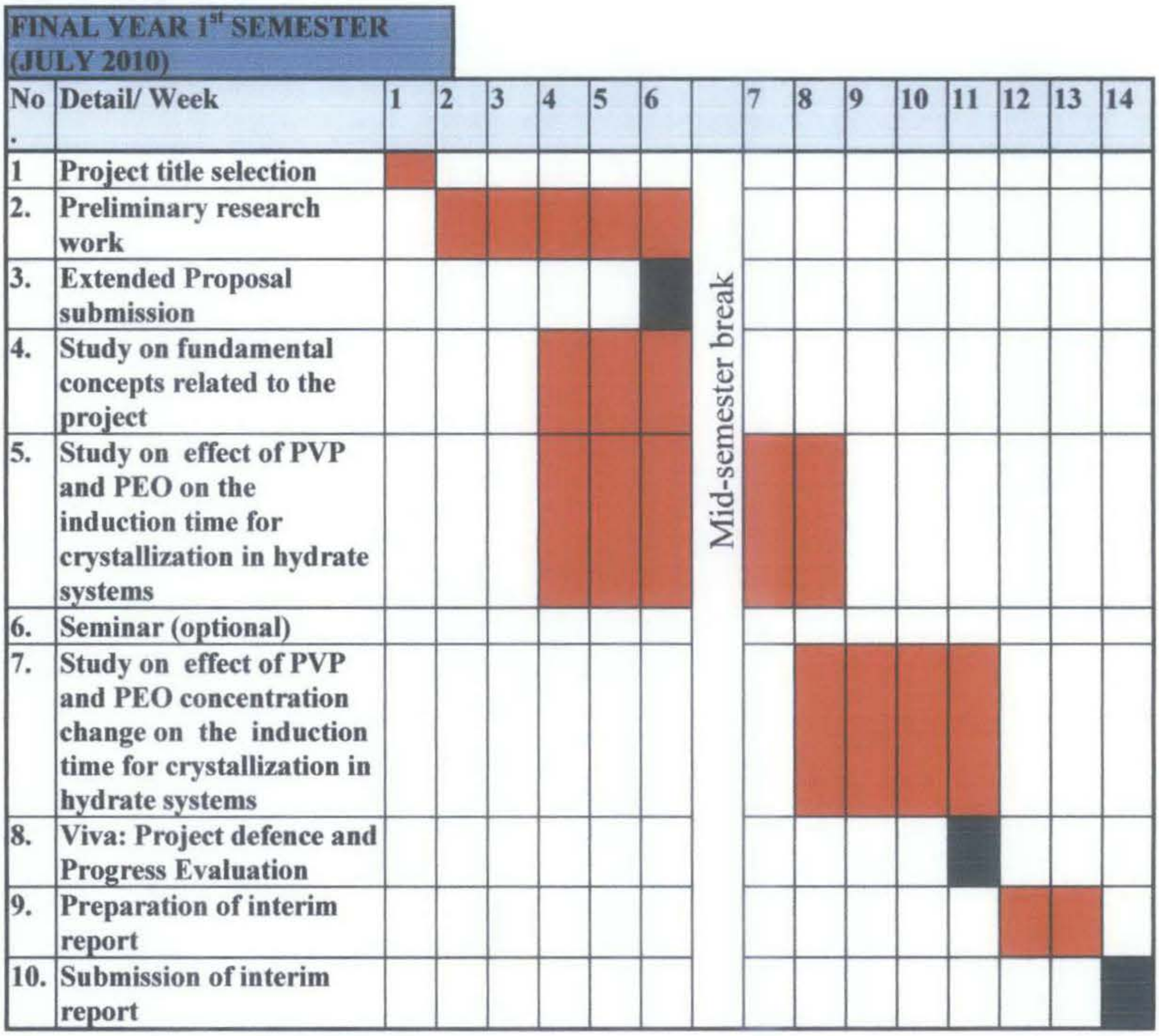
Figure 5: Flowchart Representation of Project Key Milestones

Table 2: Elaboration on the Key Milestones

Steps	Activity
Title Selection ***(Complete)***	Selection of the most appropriate final year project title.
Preliminary Research ***(Complete)***	Performing initial ground work in obtaining information regarding the project and its elements like fundamental theories and concepts, hardware, software and other verifications. Also includes critical literature survey to enhance knowledge about advances and previous studies regarding gas hydrate, and kinetic inhibitors, among others. Initial tools/equipments that are required are identified.
Hardware / Experimental Setup ***(Complete)***	Selection and design of experimental apparatus, materials, and procedures and learn how to operate hardware. Involves booking for the use of hardware in the lab. If necessary, it involves also the purchasing of surfactants (or other items, if necessary). Cable termination, instrument setup and PC/Laptop initializations are done.
Experimental Work ***(Ongoing)***	A mixture of crude oil and solution of PVP-PEO will be produced for this experiment to create the simulation of gas hydrate system. The independent variable which is the concentration of the mixture PEO-PVP will be manipulated. Their changing effect on the induction time of the gas hydrate system will be monitored and measured using the DSC. Results are then recorded and tabulated.
Analysis of Results ***(To be completed)***	The data from the experiment for both induction time of hydrate crystallization and heat flow in the system is used to plot graphs. The curves will provide an illustration of their relationships.
Discussion of Analysis ***(To be completed)***	Discussion of the findings from the results obtained. The results are studied to conclude which concentration of the mixture PEO-PVP is the most optimal in inhibiting the occurrence of gas hydrate. Determination if the objectives are met.
Report Writing ***(To be completed)***	Compilation of all research findings, literature reviews, experimental works and outcomes into a final report.

3.3 Gantt Chart

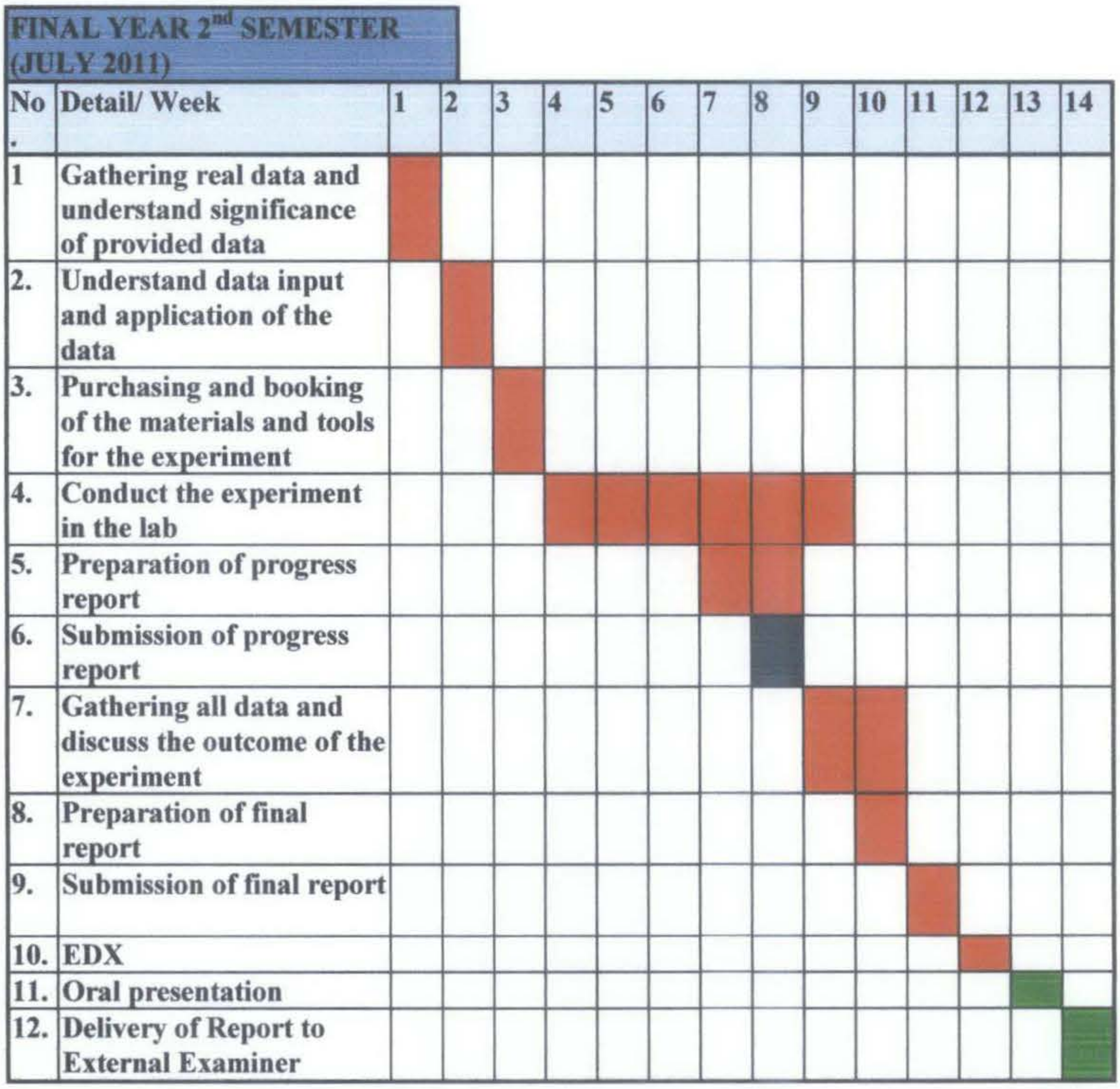
There are two semesters in the completion of this project. The research semester and the experimental work semester. There are two Gantt Charts below for each of the semesters:



FINAL YEAR 1^{st} SEMESTER (JULY 2010)

No.	Detail/ Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
1	Project title selection	🟥						Mid-semester break								
2.	Preliminary research work		🟥	🟥	🟥	🟥	🟥									
3.	Extended Proposal submission						⬛									
4.	Study on fundamental concepts related to the project				🟥	🟥	🟥									
5.	Study on effect of PVP and PEO on the induction time for crystallization in hydrate systems				🟥	🟥	🟥		🟥	🟥						
6.	Seminar (optional)															
7.	Study on effect of PVP and PEO concentration change on the induction time for crystallization in hydrate systems									🟥	🟥	🟥	🟥			
8.	Viva: Project defence and Progress Evaluation												⬛			
9.	Preparation of interim report													🟥	🟥	
10.	Submission of interim report															⬛

Figure 6: The Gantt Chart for the Research Semester



FINAL YEAR 2nd SEMESTER (JULY 2011)

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Gathering real data and understand significance of provided data	🟥													
2.	Understand data input and application of the data		🟥												
3.	Purchasing and booking of the materials and tools for the experiment			🟥											
4.	Conduct the experiment in the lab				🟥	🟥	🟥	🟥	🟥	🟥					
5.	Preparation of progress report							🟥	🟥						
6.	Submission of progress report								⬛						
7.	Gathering all data and discuss the outcome of the experiment									🟥	🟥				
8.	Preparation of final report										🟥				
9.	Submission of final report											🟥			
10.	EDX												🟥		
11.	Oral presentation													🟩	
12.	Delivery of Report to External Examiner														🟩

Figure 7: The Gantt Chart for Experimental Work Semester

(Legend: Completed: 🟥 Ongoing : 🟩)

3.4 Tool

There equipment needed in this project to conduct the experiment in order to investigate the effect of PVP and PEO concentration to the induction time for crystallization in gas hydrate system is the Pyris 1 DSC manufactured by PerkinElmer Instruments, shown in *Figure 8* below.

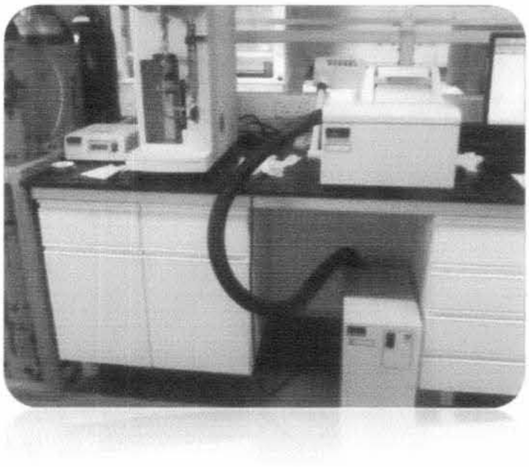


Figure 8: Pyris 1 DSC at Block 17, UTP

Differential Scanning Calorimetry (DSC) measures the heat flow into or from a sample as it is heated, cooled or held under isothermal conditions (Sichina, 2000).

DSC provides valuable and important information for this project which are;

- Crystallization times and temperatures
- Heats of melting and crystallization

Gas supply that is used for the hydrate formation in this project is Nitrogen.

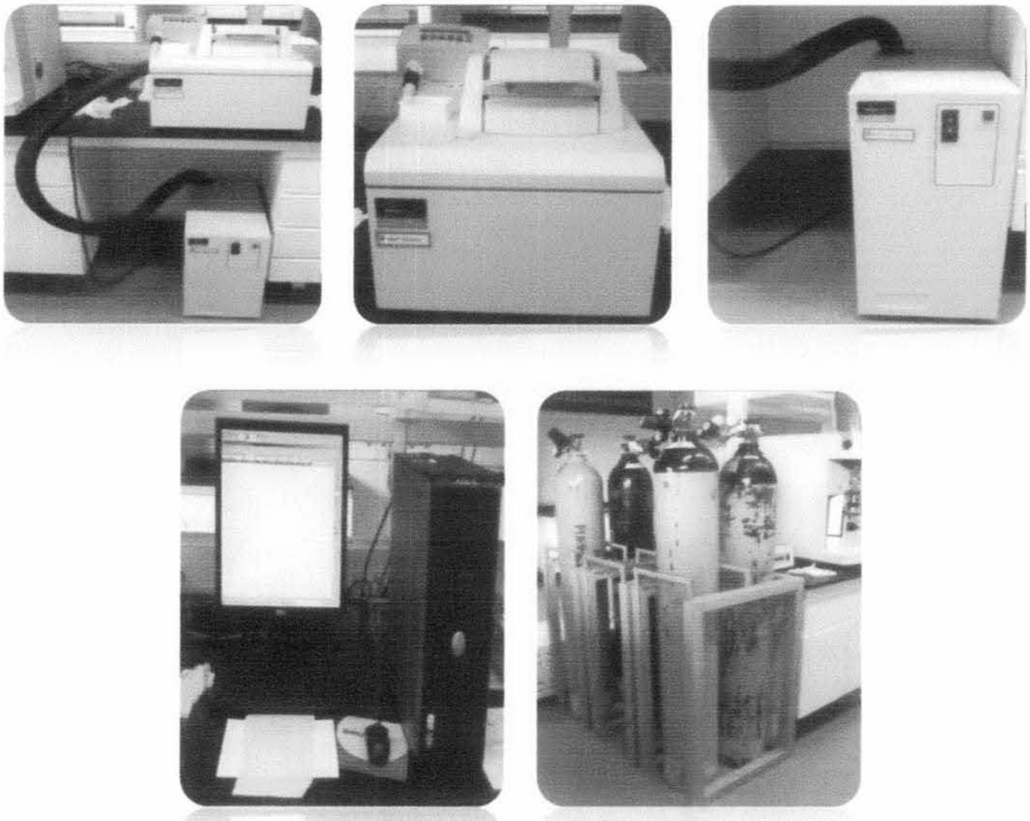


Figure 9: From left to right: (above) DSC system, DSC Machine, DSC Cooling Unit, (below) Data Gathering, Gas Supply

Other materials used in this experiment are digital weighing machine, magnetic stirrer, and laboratory apparatus such as beaker and spatula.

4.0 RESULT AND DISCUSSION

4.1 Results and Discussion

This experiment expects the results on the influence of concentration of the mixture of PEO and PVP on the point of view, decrease water accessibility for guest, hence, decreased induction time for crystallization of the gas hydrate system, which are done based on the literature review.

The induction time of gas hydrate nucleation is an important characteristic in evaluating the inhibition effect of kinetic hydrate inhibitors. The induction time is defined as the time taken for hydrates to be detected macroscopically, after nucleation and onset of growth have occurred (Khalik, 2010).

The study expects to find that as the concentration increases, the induction is delayed, but after a certain point, the induction time would be constant.

Talaghat (2011) concluded that addition of high molecular weight PEO to a kinetic hydrate inhibitor solution was found to enhance the performance of the kinetic hydrate inhibitor by an order of magnitude in some cases. The rate of gas consumption during gas hydrate formation in the absence of the kinetic hydrate inhibitor (fresh water) is seen to be faster.

As for the inclusion of PEO in the solution, from the macroscopic point of view, increase subcooling and from the microscopic for detecting the first appearance of stable hydrate crystal or induction time increases (Talaghat, 2009). The result of PEO on the performance of KHI (PVP) is remarkable. The kinetic hydrate inhibitor causes only a small reduction in the hydrate crystal growth rate. This indicates that the inclusion of PEO in the inhibitor solution impacts the induction time for nucleation and not the growth of the hydrate crystals (Talaghat, 2010).

Sloan and Koh (2008) stated that hydrate nucleation is a process during which small cluster of hydrate nuclei grow and disperse in an attempt to achieve critical size for continuous growth. This nucleation step is a microscopic phenomenon involving tens of thousands of molecules.

Lee and Englezos (2005) concluded that the mixture of PVP and PEO extended the induction time for a period less than one hour, which is classified as very weak inhibitors. In comparison for PVP solution with PVP-PEO solution as hydrate inhibitor, the induction time for PVP is 6.6min while for PVP-PEO solution, the induction time is 7.3min. Thus the addition of PEO prolongs the hydrate formation.

Two types of graphs are obtained based on the experiment using DSC, which are Ramped Mode graph and Isothermal Mode graph.

4.1.1 Ramped Mode

The operation condition undergone by the samples using DSC to obtain Ramped Mode graph is cooling from room temperature to -25°C at rate 1°C/min followed by heating back from -25°C to room temperature at rate 1°C/min.

Talaghat (2011) explains that when hydrate crystallisation occurs by progressive nucleation (hydrate crystallisation proceeds by progressive nucleation when the hydrate crystallites are continuously nucleated during the process), inclusion the kinetic hydrate inhibitors into solution, from the macroscopic point of view, they delay the first appearance of stable hydrate crystal, and from the microscopic point of view, they adsorb on hydrate crystal faces to block crystal growth.

This causes hydrate to remain as small crystals and sterically block guest diffusion. Hence, the required time for detectable volume of hydrate phase or induction time delay.

As for this experiment, the responsiveness of the mixture PVP and PEO can be observed from DSC results by its transitions in both heating and cooling runs shown in *Figure 10*.

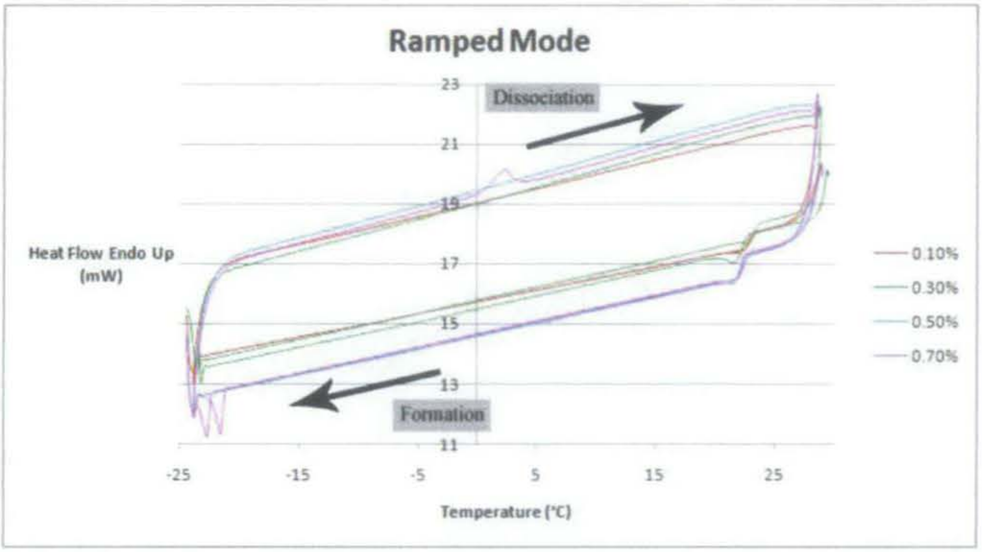


Figure 10: Ramped Mode graph.

Interestingly, the slope of the curves is similar which indicates same crystal growth rates. However, the point which rapid drop occurs is different with respect to the concentration. This can be seen by the temperatures of hydrate formation and hydrate dissociation at *Figure 10*, summarized in numerical value in *Table 3* and *4*.

Table 3: Hydrate Formation

Concentration (wt%)	Temperature (°C)
0.1	-23.9
0.3	-23.4
0.5	-23.7
0.7	-23.8

Table 4: Hydrate Dissociation

Concentration (wt%)	Temperature (°C)
0.1	28.6
0.3	28.8
0.5	28.5
0.7	28.6

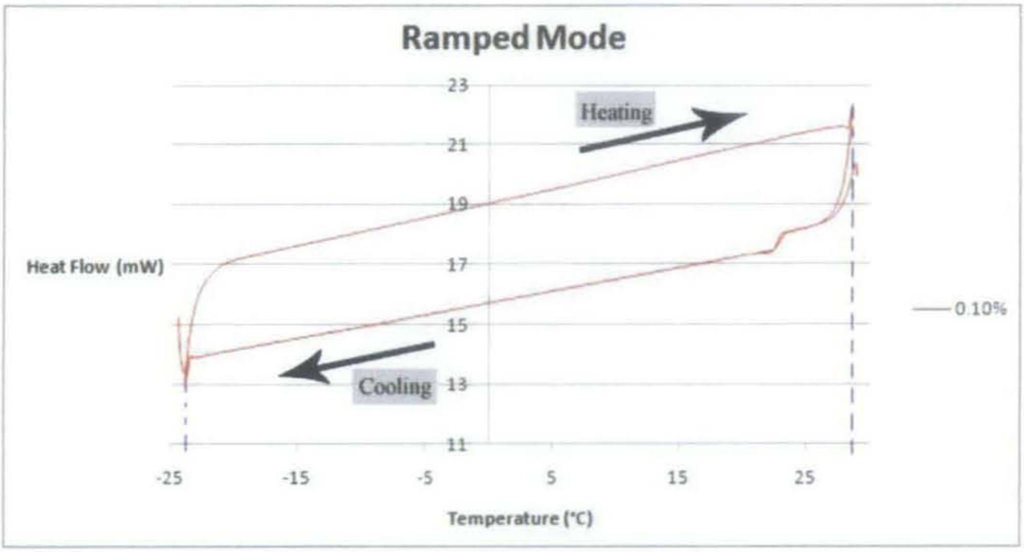


Figure 11: Ramped Mode graph for 0.1wt%

Hydrate formation is an exothermic process. Based on *Figure 11*, during heating, an endothermic peak is observed at 28°C while a corresponding exothermic peak appears at -23°C during cooling. The observed endothermic peak in the DSC scan is an indication of a phase transition.

A shoulder peak is observed during the cooling cycle. This means the polymer solution behaves differently during cooling from its behaviour during heating, due to different kinetics of association and dissociation of gas hydrate.

The temperatures are almost the same for all the concentrations both for hydrate formation and hydrate dissociation. This is due to the small margin of PEO weight difference used for each concentration.

4.1.2 Isothermal Mode

For Isothermal Mode, the samples undergo cooling to -25°C and then being hold for 2 hours. This mode will show the highest time delayed for the crystallization of hydrate to occur.

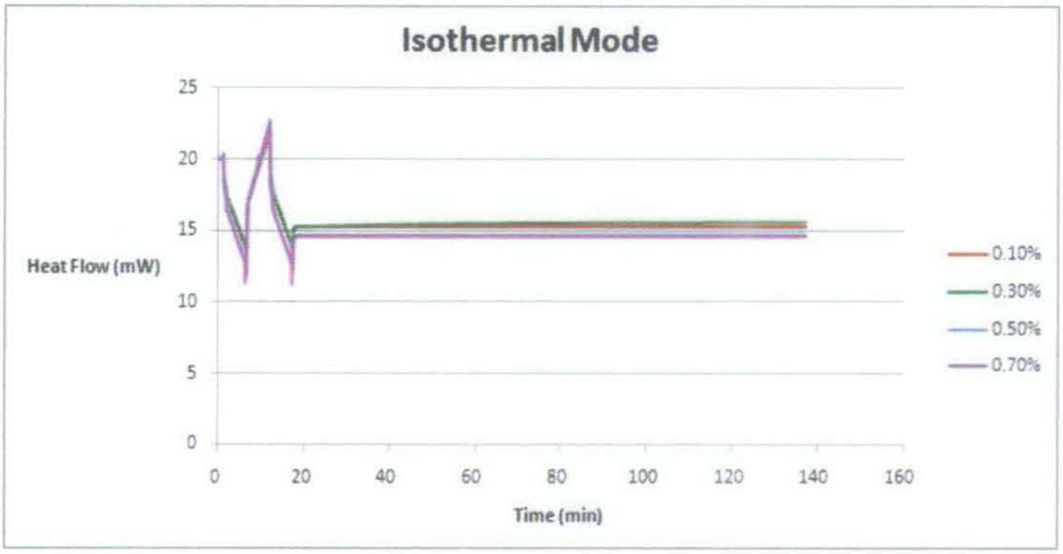


Figure 12: Isothermal Mode graph

As shown in *Figure 12*, the pattern of the graphs is the same. The peak indicates that the hydrate is started to be dissociated which the inhibition using PVP with the addition of PEO is beginning to work.

As discussed before, the DSC measurements of PVP-PEO solutions give rise to a large endothermic transformation peak with increasing temperature.

Figure 13 portrays a clearer image of the curves which differ by the position of the peak, with respect to the concentration. The curves differ by either being shifted upward or downward, left or right, depending on the concentration of the mixture of PVP and PEO.

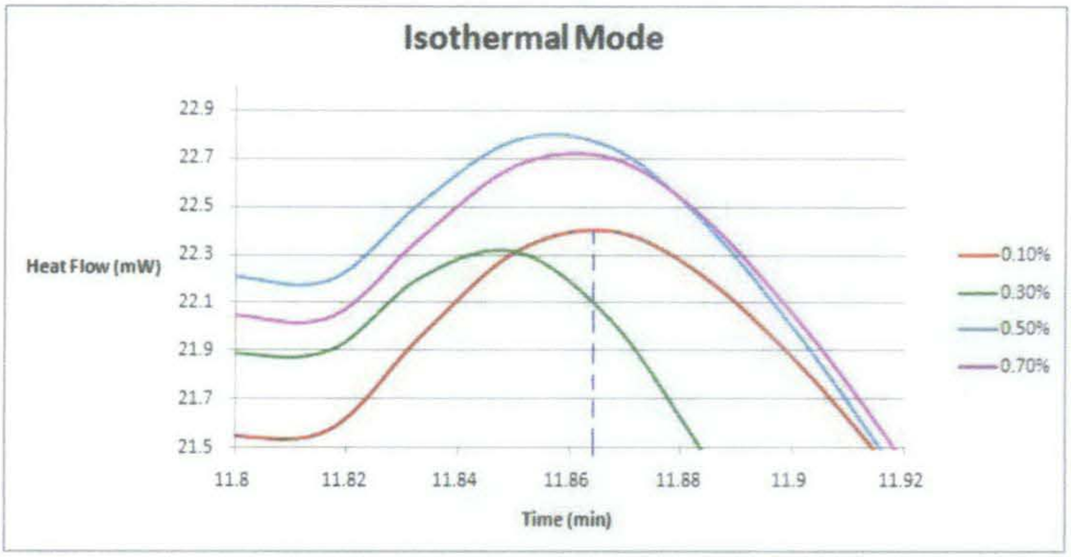


Figure 13: The peak of the curves in Isothermal Mode graph

For this experiment, the curve that is shifted to the right indicates highest time delayed, shown by the mixture of PVP and PEO at 0.1 wt% concentration, indicated by the blue line. The time delayed in minute for each concentration is shown in *Table 5*.

Table 5: Highest time delayed with respect to concentration of PVP-PEO mixture

Concentration (wt%)	Highest Heat Flow Endo Up (mW)	Highest Time Delayed (min)
0.1	22.4	11.87
0.3	22.3	11.85
0.5	22.8	11.86
0.7	22.7	11.86

It is expected that 0.7 wt% would be the optimum concentration, based on the expected hypothesis which is as the concentration increases, the time delayed for hydrate formation also increases. However, due to the uncertainties which will be discussed later, 0.1 wt% is the optimum concentration for this experiment.

4.2 Uncertainties

The results obtained do not follow the hypothesis made which is as the concentration of PVP-PEO increases, the time delayed for hydrate formation also increases. Below are the explanations of the situation.

Ugur Karaaslan and Mahmut Parlaktuna (2002) concluded that, from their experiment, although 0.01 wt% PVP solution retarded the hydrate formation for a period of 40-45 minutes, after that time the hydrate formation accelerated, indicating that the inhibitor lost its efficiency.

As for this experiment, the samples are tested only after three weeks since the preparation of the samples are made. This is due to the long queue for the students to use the equipment which is DSC. Unknown reaction in sample may occur hence change the properties of the inhibitor. This contributes to the uncertainties in the result of the experiment.

Besides that, separate layers between the crude oil and the solution of PVP-PEO are formed due to density difference. When the samples are to be tested using DSC, it needs to be shaken for it to be mixed well. However, this process does not use proper stirrer. This also contributes to the uncertainties of mixing the sample.

The use of Nitrogen gives different result than the normally experimented for hydrate inhibition researches. Nitrogen has different composition with methane and carbon dioxide thus the temperature given is much higher than the expected temperatures.

For the inhibition to take place effectively, the concentration of 0.7 wt% PVP should be used. However, 0.1 wt% PVP was used thus the hydrate inhibition does not really give much difference. In order to see a bigger impact, the research should be continued with 0.7 wt% PVP which is 0.787g PVP instead of 0.112g.

Lastly, due to time constraint, experiments were not repeated thus error of accuracy is possible.

5.0 CONCLUSION, FUTURE WORK AND RECOMMENDATIONS

This study has able to achieve the objectives which is to compare the induction time for crystallization of the hydrate system with the addition of PEO at different concentrations which are 0.1, 0.3, 0.5, and 0.7 wt%. Based on the Ramped Mode graph and Isothermal Mode graph, the effective ratio of PVP with the addition of PEO as hydrate inhibitor is 0.1 wt% with time delayed 11.87min.

Due to the uncertainties as well as for the improvement of this study, below are the recommendations for future work;

- Carry out the experiment as soon as the preparation of the samples is completed.
- Conduct the experiment at reservoir condition.
- Use methane as the carrier gas for hydrate formation.
- Use the 0.7 wt% concentration which gives optimum hydrate inhibition compared to the experimented 0.1 wt% in this study.

This study will contribute to the knowledge of the use of kinetic inhibitors in gas hydrate inhibition, in terms of how its effectiveness in inhibiting gas hydrate formation is influenced by the concentration of the mixture containing PEO and PVP.

6.0 REFERENCES

1. Ailin Ding, Shuo Wang, Tina Pelemis, Carmelo Crisafio and Xia Lou, 2009, *Specific Critical Concentrations of Low Dosage Hydrate Inhibitors in a THF–NaCl Hydrate Formation Solution,* ASIA-PACIFIC JOURNAL OF CHEMICAL ENGINEERING; 5: 577–584

2. C. Dalmazzone, B. Herzhaft, L. Rousseau, P. Le Parlouer, D. Dalmazzone, 2003, *Prediction of Gas Hydrates Formation with DSC Technique*, SPE 84315

3. Carolyn A. Koh, 2001, *Towards a Fundamental Understanding of Natural Gas Hydrate,* The Royal Society of Chemistry, Chem. Soc. Rev., 2002, 31, 157–167

4. Dimo Kashchiev, Abbas Firoozabadi, 2003, *Induction Time in Crystallization of Gas Hydrates,* Journal of Crystal Growth 250 (2003) 499–515

5. E . Dendy Sloan and Carolyn A . Koh, 2008, *Clathrate Hydrates of Natural Gases,* Third Edition, CRC Press 2008

6. Elizabete F. Lucas, Claudia R. E. Mansur, Luciana Spinelli, and Yure G. C. Queirós, 2009, *Polymer Science Applied to Petroleum Production,* Pure Appl. Chem., Vol. 81, No. 3, pp. 473–494

7. Englezos, P., Ngan,Y.T., 1994. *Effect of Polyethylene Oxide on Gas Hydrate Phase Equilibria,* FluidPhase Equilibria 92, 271–288

8. Englezos, P., Lee, J.D., 2004. *A New Additive Chemical Mixture to Reduce the Speedof Gas Hydrate Crystal Formation,*UnitedStates Provisional Patent Application

9. Frostman, L. M.; Thieu, V.; Crosby, D. L.; Downs, H. H., 2003, *Proceedings of the SPE International Symposium on Oilfield Chemistry,* Houston, TX, February 5-8, SPE 80269

10. Ju Dong Lee, Peter Englezos, 2005, *Enhancement of the Performance of Gas Hydrate Kinetic Inhibitors with Polyethylene Oxide*, Chemical Engineering Science 60 (2005) 5323 – 5330

11. Karen Kozielski, Edson Nakagawa and Gerardo Sanchez. 2007, *Unplugging Pipelines*. Report Commonwealth Scientific and Industrial Research Organisation (CSIRO), TOUCH BRIEFINGS 2007

12. Khalik M. Sabil, 2009, *Phase Behaviour, Thermodynamics and Kinetics of Clathrate Hydrate Systems of Carbon Dioxide in Presence of Tetrahydrofuran and Electrolyte*, International Journal of Greenhouse Gas Control 4 798–805

13. Khalik M. Sabil, Geert-Jan Witkamp, Cor J. Peters, 2010, *Estimations of Enthalpies of Dissociation of Simple and Mixed Carbon Dioxide Hydrates from Phase Equilibrium Data*, Fluid Phase Equilibria 290 109–114

14. King, H.E., Hutter, J.L., Lin, M.Y., Sun, T., 2000. *Polymer conformations of gas-hydrate kinetic inhibitors: a small-angle neutron scattering study*. Journal of Chemical Physics 112 (5), 2523–2532

15. Mahnaz Saboormaleki, Andrew R. Barnes and Walkiria S. Schlindwein, 2004, "*Characterization of Polyethylene Oxide (PEO) Based Polymer Electrolytes,*" The Electrochemical Society, Inc. Abs. 726, 205th Meeting

16. Malcolm A. Kelland, 2006, *History of the Development of Low Dosage Hydrate Inhibitors*, American Chemical Society

17. Mohammad Reza Talaghat, 2011, *Enhancement of the Performance of Kinetic Inhibitors in the Presence of Polyethylene Oxide and Polypropylene Oxide for Binary Mixtures during Gas Hydrate Formation in a Flow Mini-Loop Apparatu*, THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING VOLUME 9999

18. N.F.Mohd Nasir, N.Mohd Zain, M. G. Raha, N.A. Kadri, 2005, *Characterization of Chitosan-poly (Ethylene Oxide) Blends as Haemodialysis Membrane,* American Journal of Applied Sciences 2 (12): 1578-1583

19. Praveen Linga, Rajnish Kumar, Peter Englezos, 2007, *Gas Hydrate Formation from Hydrogen/Carbon Dioxide and Nitrogen/Carbon Dioxide Gas Mixture*, Chemical Engineering Science 62 (2007) 4268 – 4276

20. S.Dhawan, K.Dhawan, M.Varma, and V.R. Sinha, 2005, *"Applications of Poly(ethylene oxide) in Drug Delivery Systems Part II,"* Pharmaceutical Technology

21. Sara E. Harrison, 2010, *Natural Gas Hydrates*, <http://large.stanford.edu/courses/2010/ph240/harrison1/>

22. Sloan E. D., 1998, *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York

23. Tang Cuiping, Dai Xingxue, Du Jianwei, Li Dongliang, Zang Xiaoya, Yang Xiangyang & Liang Deqing, 2010, *Kinetic Studies of Gas Hydrate Formation with Low-Dosage Hydrate Inhibitor*, Science China Chemistry Vol.53 No.12: 2622–2627

24. Ugur Karaaslan and Mahmut Parlaktuna, 2002, *Kinetic Inhibition of Methane Hydrate By Polymers,* Fuel Chemistry Division Preprints 2002, 47(1), 355

25. W.J. Sichina, 2000, *Benefits and Applications of the Power Compensated Pyris 1 DSC,* PerkinElmer, Inc.

26. Y. Zhang, Y.M. Lam, W.S. Tan, 2005, *Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)-g-poly(vinylpyrrolidone): Association behavior in aqueous solution and interaction with anionic surfactant*, Journal of Colloid and Interface Science 285 (2005) 74–79

27. Z. Huoa, E. Freera, M. Lamara, B. Sannigrahib, D. M. Knaussc, E. D. Sloan Jr., 2001, *"Hydrate plug prevention by anti-agglomeration"* Chemical Engineering Science 56 (2001) 4979–4991