Effect of Natural Polymer as Kinetic Hydrate Inhibitor Using Micro Differential Scanning Calorimetry (µDSC)

by

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12207

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the requirements for the
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CERTIFICATION OF APPROVAL

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(PETROLEUM ENGINEERING)

Approved by,

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(MRS.MAZUIN JASAMAI)

CERTIFICATION OF ORIGINALITY

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

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(SYAZWANI BT. MOHD SARIFFUDDIN)

ABSTRACT

Gas hydrate is a one of the major concerns in flow assurance industry. Formation of gas hydrate would cause the plugging of the pipeline, interruption in drilling operations and damage of rig equipment. This will increase the OPEX of the field development which later reduces the revenue of oil and gas production.

One of the ways to overcome this problem is by adding kinetic inhibitor which inhibits the formation of gas hydrate. Nowadays, there has been a trend in the use of kinetic hydrate inhibitors as substitutes for thermodynamic inhibitors like methanol.

This project aims to study the effectiveness of using natural polymers as kinetic inhibitors. To achieve the main objective, firstly, a thorough research was done to fully understand the formation of hydrate and kinetic inhibitors. Next, the experiment starts with preparation of samples in the lab and later testing the samples using Micro-Differential Scanning Calorimetry equipment which measures the heat flux of a sample versus time or temperature, while the temperature of the sample is programmed, in a controlled environment.

From the experimental works of this project, it was found that both of chitosan and starch shows a kinetic inhibiting effect whereby the addition of each natural polymer were able to prolong the induction time of hydrate formation. The induction time for the natural polymers are; 1.0 wt% of chitosan (98.4 min) , 1.0 wt% of starch (96.7 min), 0.1 wt% chitosan (98.4 min) and 0.1 wt% starch (91.5 min). Comparing the induction time of each natural polymers with the blank sample (distilled water, 92.2 min), all of the samples tested were able to delay the hydrate formation, except for 0.1 wt% starch.

By studying the effectiveness of natural polymers as kinetic hydrate inhibitor, the environmental effect of using kinetic inhibitor can be reduced as the natural polymers are known to be biodegradable, as well producing a more cost-effective way of solving hydrate problems.

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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITRATURE REVIEW

CHAPTER 3: METHODOLOGY

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Clathrate hydrates, or commonly known as gas hydrates are solid ice-like substance consists of natural gas molecules trapped in cages of water molecules.[1] Hydrates generally are formed under a high pressure and low temperature conditions.

The formation of gas hydrates in the facilities and transportation pipelines will result in the blockage, and therefore shutdown. The impacts of gas hydrate will affect the cost and safety of a field development. The solution for gas hydrate problem can be achieved in several ways, for example, by removing the hydrate blockage or heating the exposed pipeline with a torch. However, removing the blockage could be a high risk operation [2] and pipeline heating is very expensive. Moreover, according to Sloan, the cost to prevent the formation of hydrates and aggregation in the oil and gas industry is estimated to be over USD 200 million annually.

Traditionally, thermodynamic inhibitor was used to prevent the formation of hydrates. Thermodynamic inhibitor acts by shifting the hydrate equilibrium curve to the left, which decrease the hydrate equilibrium temperature, out of the hydrate formation region. An example of commonly used thermodynamic inhibitors is methanol. Methanol is used to absorb the water molecules form thus preventing the formation of hydrate. However, methanol requires a large treatment amount, approximately 10-50 wt% of the water phase. This contributes to the high of of using methanol, as the estimated worldwide methanol expense for hydrate prevention was $150MM per year [3]. Methanol is also known to be very toxic, and therefore a regeneration system is required to remove the chemical before the oil product reaches the market.

Nowadays, more technologies are developed to control the formation effectively, and this includes Low Dosage Hydrate Inhibitor (LHDIs). LHDIs requires much less concentrations as compared to thermodynamic inhibitors, hence LHDIs are more favorable nowadays. Apart from that, LHDIs also helps to reduce the project expenditure and saves million of dollars each year because LHDIs requires fewer deliveries and smaller pump and storage requirements offshore.

There are two broad classes of LHDIs, which are Kinetic Inhibitor (KI) and Anti Agglomerant (AA). AA allows the formation of hydrate, but maintaining them as small particles and well dispersed, which prevents the formation of blockage and allows the hydrate to be transported along with the produced fluids

On the other hand, KI works by delaying the time for nucleation or crystal growth [4]. The kinetic inhibitors for gas hydrate formation are mostly made up from synthetic polymers, namely poly (vinylpryrrolidone) (PVP), poly (vinylcaprolactam) (PVCap), poly(N-methyl-N-vinylacetamide) (VIMA), poly(N-vinylvalerolactam) (PVVam), poly(acryoyl pyrro- lidine) (PAPYD), and poly(acryloylmorpholine) (PAMOR), Luvi- cap (40 wt% PVCap in EG), and a terpolymer combination VC- 713 (a 37 wt% solution of the terpolymer of N-vinylpyrrolidone, N-vinylcaprolactam, and dimethylamino–ethyl–methacrylate in ethanol) (Arjmandi et al., 2005; Freer and Sloan, 2000; Lederhos et al., 1996; Karaaslan and Parlaktuna, 2002).

In contrary, there are also KIs which applies the natural polymer, such as chitosan, starch and antifreeze proteins (AFP).

Chitosan is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (such as crabs and shrimp) and cell walls of fungi.

On the other hand, starch is a polysaccharide produced by all green plants as an energy store.

Antifreeze protein, are variable class of proteins that can be found in fish and cold-adaptive bacteria, plants and insects.

The usage of these natural polymers has been proven to delay the onset of nucleation [6][7][8]. Hence, there is a future for the use of these natural polymers as kinetic inhibitors, which are not only environmental friendly, but could also be a more cost efficient solution for hydrate formation problem.

1.2 Problem Statement

The formation of gas hydrate will result in the pipeline blockage, which contributes to the increase in cost to remediate the situation and also leads to safety hazard. Thus, it is very important for us to prevent the hydrate formation, which can be achieved by using the gas hydrate inhibitors.

Thermodynamic inhibitor, kinetic inhibitor and anti-agglomerant are the three types of inhibitors commonly utilized by the petroleum industry to prevent hydrate formation.

However, the use of thermodynamic inhibitor, for example, methanol, could be costly to be applied in offshore and remote facilities because the huge treatment amount, which required about 10-50 wt% of the water phase.

Apart from that, methanol also leads to unexpected corrosion problems when in use with alcohol-based corrosion inhibitor chemicals [9] because the presence of dissolve oxygen in the chemical, and the presence of methanol may decrease the efficiency of some corrosion inhibitors (Hagen, 2010).

Kinetic inhibitor had been use commercially the industry for 17 years [10]. The kinetic inhibitor prevents hydrates formation by delaying the nucleation and growth.

Despite the fact that the use of kinetic inhibitor offers certain advantages over thermodynamic inhibitor, such as low concentration usage and reduced OPEX and CAPEX, the application in field operation has been limited, and some countries banned the use of commercial KI such as PVP, due to the environment restrictions because of their poor biodegradability [11].

1.3 Significance of Project

By studying the effect of natural polymers as kinetic inhibitor, it will contribute to the development of a more economical and less hazardous alternative for hydrate formation treatment. The use of naturally polymers as kinetic inhibitor in the real oil and gas production has not been perform, however by having more research on this potential KI, it might create the awareness for developing more types of green kinetic inhibitor in the future.

1.4 Objectives

The aims of this project are as follows:

a) To study and understand the gas hydrate formation

b) To investigate the effect of chitosan and starch as gas hydrate inhibitor to the induction time of hydrate.

c) To determine the optimum concentration for the two types of natural polymer.

1.5 Scope of Study

This scope of study in this project was divided in two phases.

The first phase involves in the research for understanding the nature of gas hydrate including the properties and the mechanism of hydrate formation. Besides that, the problems that rises due to hydrate, and also the preventive method introduced in the industry were also studied during the research.

The research continues with the understanding of natural polymer as kinetic inhibitor in the Structure I Hydrate, which is carbon dioxide, CO_2. The identification of the types of natural polymer and the method of studying and evaluating effectiveness of these natural polymers in avoiding hydrate formation in carbon dioxide were also investigated from the research. From this phase, the identified natural polymers to be used in this project were chitosan and starch, because of their ability to delay the induction time of hydrates (Xu, 2010) (Lee, 2007).

The second stage will focus on experimental work in the lab, using the Micro Differential Scanning Calorimetry (µDSC) equipment to study on the gas hydrate phase equilibrium, kinetic and thermal properties. Blank sample, 0.1 wt% of chitosan, 0.1 wt% starch solution, 1.0 wt% chitosan and 1.0 wt% of starch were evaluated in this experiment to study the effect of these natural polymers on the induction time of hydrate formation. Distilled water was used as a blank sample to prove that the addition of natural polymers will have a positive effect on inhibiting formation of hydrate.

Lastly, the analysis and comparisons with the commercial KI will be done based on the information gathered from experimental results and research studies.

1.6 Relevancy of Project

Apart from being potentially harmful to the environment, polymeric compounds of common KIs such as PVCap and PVP are also being banned in several locations [12] namely Danish and Norwegian sector of North Sea [13].

Therefore, there is a need to develop a more eco-friendly kinetic inhibitor for this sector particularly. By identifying the potential of applying natural polymer as kinetic hydrate inhibitor will contribute in long-term solution for hydrate prevention and also promotes green engineering practices as well as conserving environmental sustainability. [14]

1.7 Feasibility of Project

This project involved research and also experiments conduction in the lab. The experiments were conducted in the lab in Block 15, and also by using Micro DSC in Block 17 in Universiti Teknologi PETRONAS. The works in this project were done within the time frame, which is 8 months.

CHAPTER 2

LITERATURE REVIEW

2.1 Gas Hydrates

One of the problems faced in the production of oil and gas is hydrates. Hydrates are formed when natural gas molecules are combined with water molecules in a low temperature and high pressure condition. In the early era of the gas business, the importance of natural gas hydrates was not apparent, because the gas was produced and delivered at relatively low pressure.

With the expansion of the natural gas industry in the 20th century, the production, processing and distribution of gas became high pressure operations. This condition later was found out to cause plugging with an ice-like substance. Later, in 1930s, Hammerschmidt clearly demonstrated that the ice-like substance was actually gas hydrates. Apart from gas, liquids may also form hydrates. One example of the liquid that forms hydrate is dichlorodifluoromethane (Freaon 12) [13].

Gas hydrates, or also termed as “clathrates” or inclusion compounds are water molecules network of cages that can trap small guest molecule, such as ethane, propane, isobutene, normal butane, nitrogen, carbon dioxide and hydrogen sulphide. Gas hydrates can also form without the presence of water where non-water molecules made up the molecular structural array, because there is no chemical bonding between the host and guest molecule.

There are three common structures of hydrates as shown in Figure I, Structure I (sI), Structure II (sII) and structure H (sH), with only Structure I and II are typically found in the oil and gas operation.

Structure I of the lattice has cavities of the size to accept small molecules such as methane of ethane. These “guest” gas molecules are called “hydrate formers”.In general, the compounds that form Structure I hydrates are light components such as C_1,C_2, and CO_2.

Structure II of the lattice has bigger cavities that allow the entrapment of heavier alkanes with medium-sized molecules, such as C_3, i-C_4 and n-C_4, in addition to methane and ethane, to form Structure II hydrates.

On the other hand, Structure H,are formed by three types of cages. The formation of Structure H is assisted by two other guest molecules (large and small) to be stable. It has large cavities to contain molecules the size of common components of naptha and gasoline. Structure H mainly exists in the Gulf of Mexico.

The unit cell of each of the hydrate structures can be found in Table 1.

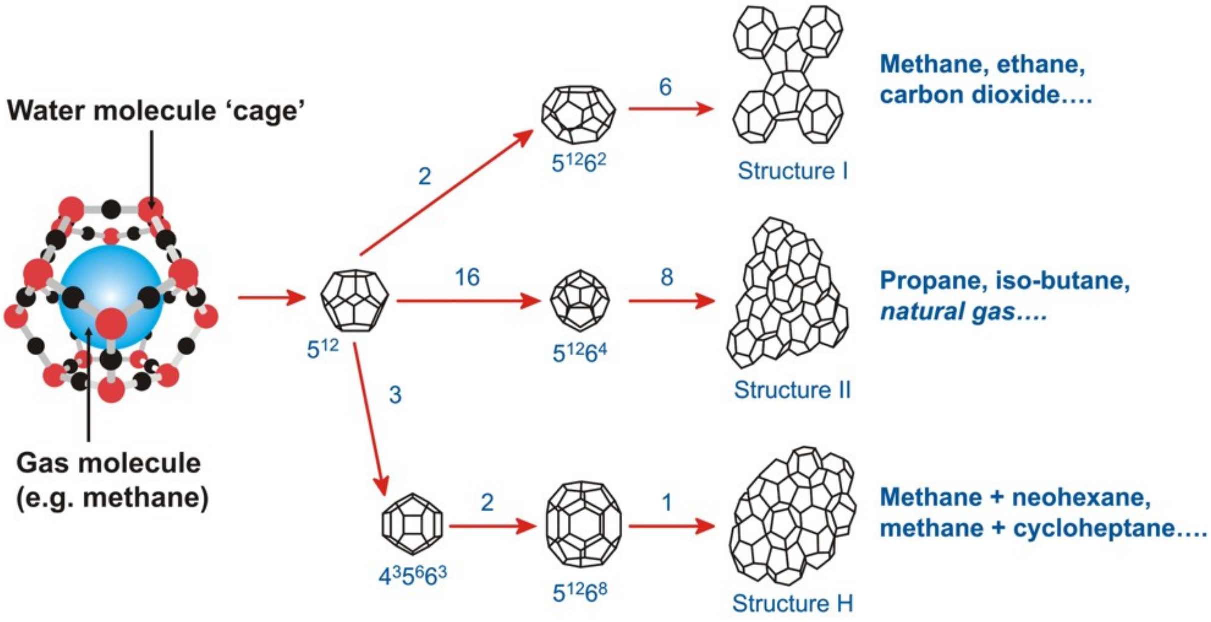


FIGURE 1: Hydrate structures (Sloan, 1998)

TABLE 1: Unit cell structure of hydrates

Structure	**Number of Cages**					
	5^{12}	$5^{12}6^2$	$5^{12}6^4$	$5^{12}6^8$	$4^55^36^3$	H_2O
I	**2**	**6**	**-**	**-**	**-**	**46**
II	**15**	**-**	**8**	**-**	**-**	**136**
H	**3**	**-**	**-**	**1**	**2**	**34**

2.2 Hydrates Formation

There are four elements that contribute to the formation of hydrates:

1) High pressure condition
2) Low temperature condition
3) Presence of water molecule
4) Presence of hydrate forming guest molecules

According to Sloan (2000), there are several conditions that could enhance the formation of gas hydrates. These are:

- The presence of free water and gas molecules with size range from methane to butane;
- The presence of H_2S or CO_2 as a substantial factor contributing to the formation of hydrate due to their solubility in water
- Temperature below the “hydrate formation temperature” for the pressure and gas composition considered;
- High operating pressures that increase the “hydrate formation temperature”;
- High velocity or agitation through piping or equipment;
- The presence of small “seed” crystal of hydrate;
- Natural gas at or below its water dew point with liquid present.

The gas hydrates formation can be interpreted in the form of the diagram (Figure 2). The white region are where the pressures and temperatures of the hydrates are set thermodynamically unstable and hence ‘hydrate free’ as indicated.

The dark grey (V-I-H) region represents ‘hydrate risk’, where stable carbon dioxide hydrate can exist, despite that in practice they may not form because of the failure to nucleate or slow formation kinetics. The CO_2 (S) region represents the ‘hydrate zone’, the degree of supercooling is sufficient such that hydrates can form instantaneously (Alseme, 1993). The hydrate formation curve indicates the region whereby the temperature and pressure are suitable for formation of hydrates, whereas the hydrate dissociation curve is the temperature and pressure at which hydrates start to dissociate.

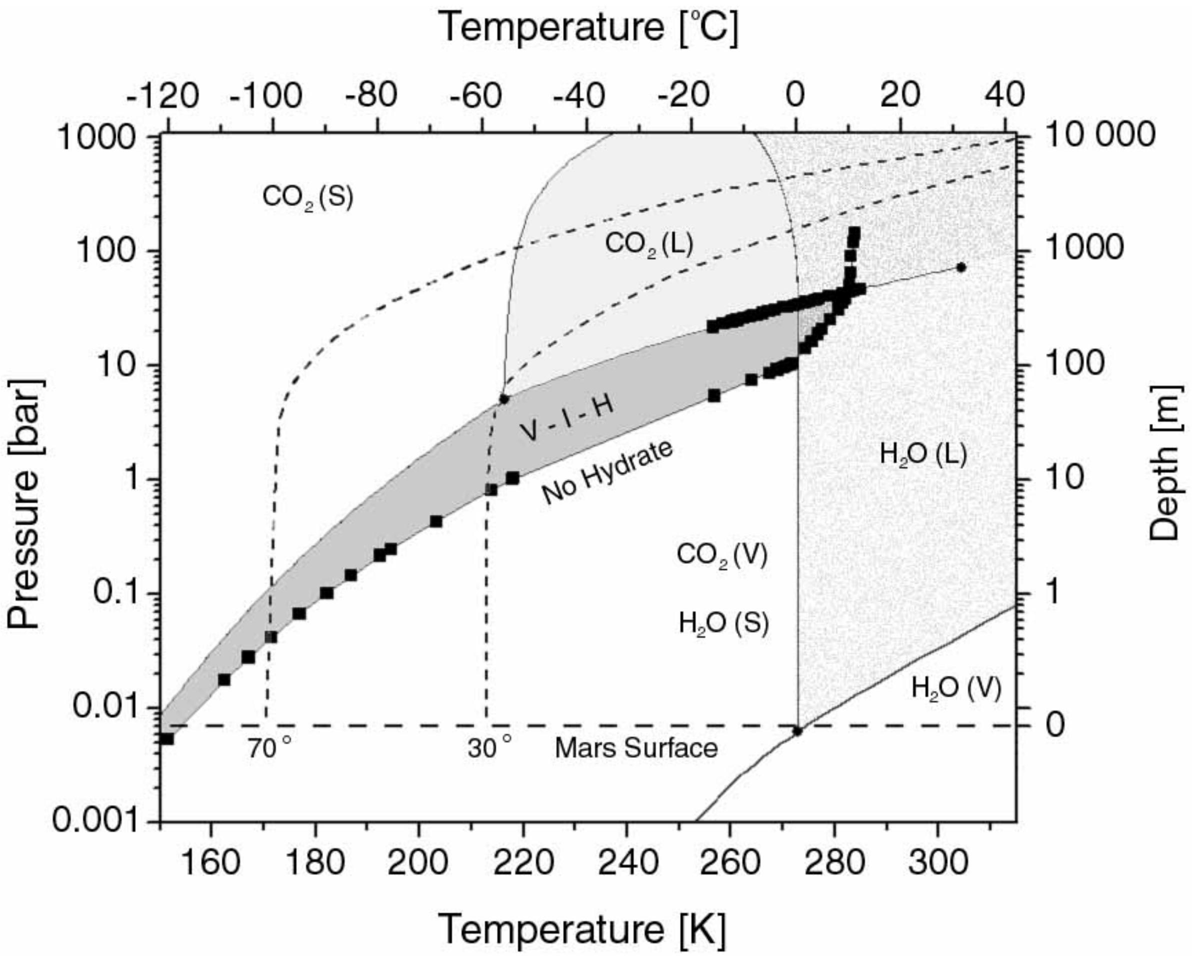


FIGURE 2: Hydrate diagram for pure CO_2

Hydrates are normally found in the permafrost region of deepwater, usually at the water-hydrocarbon interface in a pipeline that has the highest availability of hydrate forming molecules.

Whereas hydrate plugs occur during transient and abnormal operations such as on start-up, or operational shutdown when free water is present due to dehydrator failure or inhibitor injection failure, or during cooling occurs with flow across a valve or restriction (Sloan, 2003).

Figure 3 shows the illustration of an offshore system where formation of hydrate takes place.

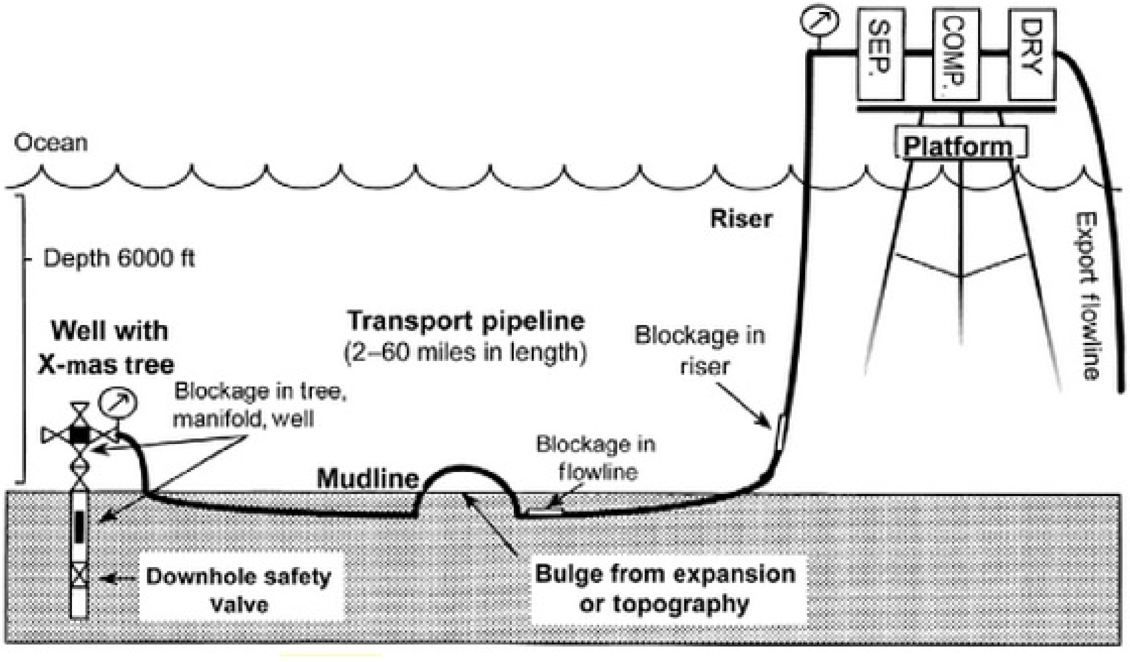


FIGURE 3: Points of hydrate plug formation in offshore system

2.3 Hydrate induction time

Induction time of hydrate is the time elapsed until the end of hydrate former gas consumption, or the time elapsed until the presence of detectable volume of hydrate phase. During this period, pressure and temperature conditions are in the range of the hydrate stable region.

The growth of hydrate begins in region 2. During the growth, the gases are trapped inside the ice cages, resulting in the densely packed of molecules compared to those in vapor. As the hydrate formation consumes water, the consumption of the gas slope eventually decreases with time.

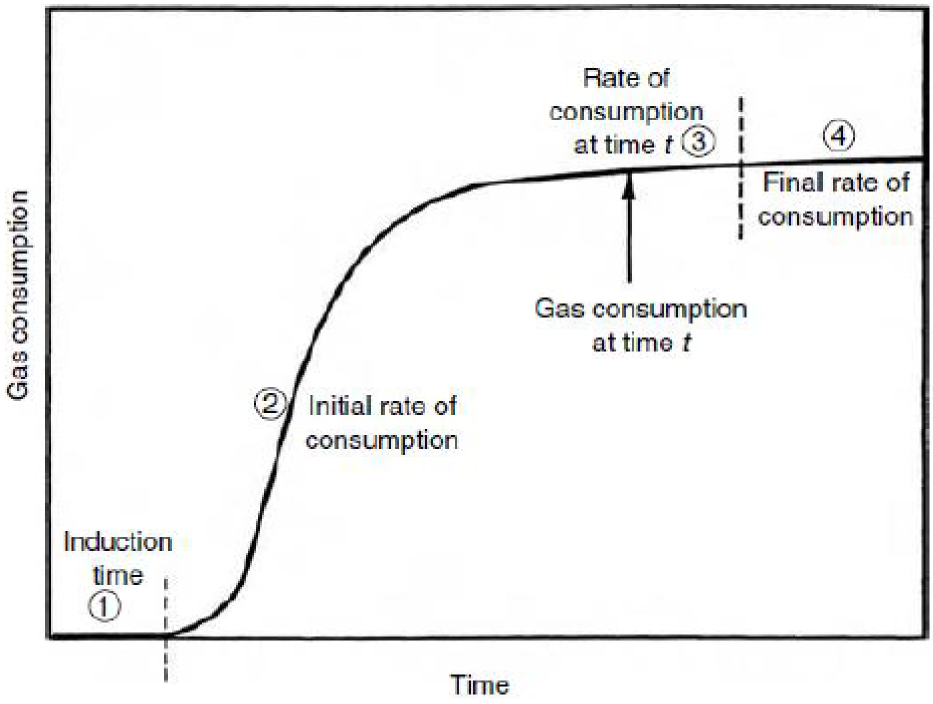


FIGURE 4: Gas consumption vs. time for hydrate formation.

(Taken from Lederhos et al.,1996).

2.4 Kinetic Inhibitor

In solving the hydrate formation issue, there were many preventive measures that were applied in the field. Inhibitors were then introduced, where thermodynamic inhibitor was commonly used in the industry. However, thermodynamic inhibitor posed many threats to the production, i.e. the use of methanol, has proven to be toxic and high costs since that it requires up to 60% wt of application. Since then, the industry has been shifting towards another alternative of inhibitor, which is the kinetic inhibitor.

Kinetic inhibitor is a class of Low Dosage Hydrate Inhibitor (LHDI, work by delaying the nucleation time and growth of hydrate. The "first successful commercial deployment" of kinetic inhibitor that replaced both methanol and glycol for a North Sea application involved both BP and TR Oil Services (now Clariant) was recorded in 1996.Kinetic inhibitors cab be effective at a low concentration (<1 wt%).

Compared to the conventional thermodynamic inhibitor, kinetic inhibitors do not change the thermodynamic condition of hydrate formation but instead it delays the hydrate nucleation and growth. The kinetic inhibitor retards crystal growth of hydrate by adhering to the surface of hydrate particles at the start of nucleation process. This will prevent the particle from achieving its critical size where if achieved, it will become thermodynamically in favor of hydrate formation.

Various polymeric chemistries have been applied as kinetic hydrate inhibitors. One of the first, basic patents was filed by Professor Dendy Sloan of the Colorado School of Mines in 1992. The patents cover polyvinylpyrrolidone (PVP) alone or in combination with hydroxylcellulose (HEC) to prevent the agglomeration of clathrate hydrate masses. According to Long et al, PVP is found to be a good kinetic hydrate inhibitor as compared to the others.

2.4 Natural Polymer as Kinetic Inhibitor

Despite the commercial use of synthetic polymers as kinetic inhibitors, there is also a trend towards a nature friendly inhibitors or also known as Green Hydrate Inhibitor (Kelland,2006).

Chitosan

Among the type of Green Hydrate Inhibitor is chitosan. Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit).

Known for its eco-friendly properties as it is biodegradable and biocompactible, chitosan is produced by deacetylation of chitin,which is the structural element in the exoskeleton of crustaceans, such as crab and shrimp shells.

The production of chitosan is currently based on crabs and shrimp shells discarded by the canning industries in Oregon, Washington, Virginia and Japan and by other finishing fleets in the Antartic (Kumar, 2000). The production of chitosan gained from the food industry waste is economically efficient.

From the industry, the production of 1kg of deacetylated chitosan from shrimp shells requires 6.3 kg of hydrochloric acid and 1.8 kg of sodium hydroxide in addition to nitrogen, process water (0.5 t) and cooling water (0.9 t) (Majeti N.V.,2000).

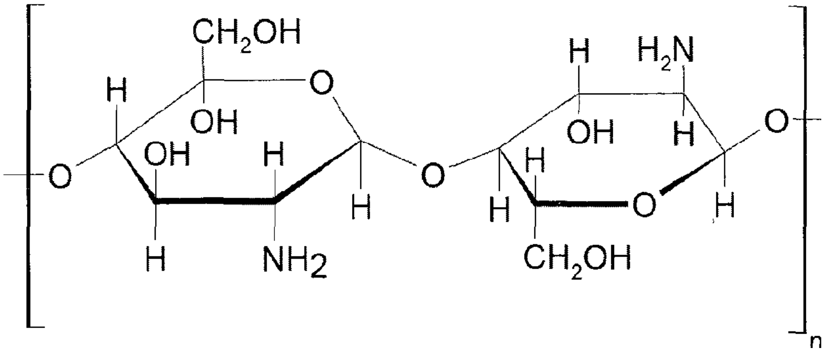


FIGURE 5: Chemical structure of chitosan

Starch

Starch is the most abundant polysaccharide and a mix of two polymers of anyhydroglucose units, amylase and amylopectin. It is produced by green plants as an energy store. Usually the starch will be cationized and then used in industrial application, such as in the papermaking industry [7].

Starch is a non-toxic and biodegradable, hence this provides a more advantage of using natural polymer compared to the conventional ones.

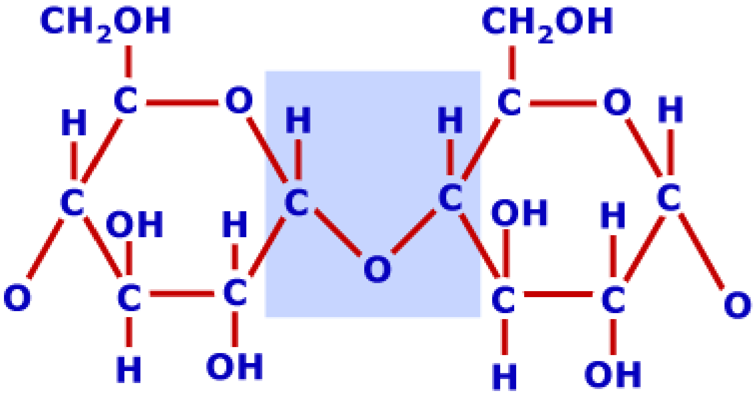


FIGURE 6: Chemical structure of simple starch

2.6 Chitosan and starch as kinetic inhibitor

The industry has now aware on the importance of producing a greener kinetic inhibitor, due to the increasing awareness on the environment.

Chitosan and starch are known to be highly hydrophilic. The hydrophilic pendant lactam ring of chitosan and starch is the key role to its kinetic inhibiting effect. The characteristic of these natural polymers allow them to create hydrogen bonds with other entities in the solution.

There is a probability that the anyhydroglucose unit of chitosan and starch fits within the hydrate structure in the same way as the hydrophilic lactam group.

Thus, the adsorption of the green inhibitor assists in delaying the induction time of the hydrate by altering the growth pattern. Apart from that, the inhibitors also block the contact between hydrate forming substance and the hydrate structure, which disrupts the formation of hydrate crystal.

Therefore, chitosan and starch should have good inhibition effects for gas hydrate formation.

2.5 Detection of Hydrate Dissociation by using µDSC

Introduced by the French Institute of Petroleum (IFP), Micro-Differential Scanning Calorimetry (µDSC) is used to characterize hydrate formation in drilling fluids up to 100 bar (Dalmazzone, 2001). µDSC is also an easy tool for gas hydrate stability condition measuring in complex emulsions and suspensions such as drilling fluids in a high pressure.

µDSC measures the amount of energy (heat) absorbed or released by a sample as it is heated, cooled or held at an isothermal temperature versus time. From Figure 4, the different pressure curves decline shows the dissociation of methane hydrate due to the absorption of heat energy.

Besides that, µDSC also been used to measure emulsion characteristics such as droplet size distribution, which allows the interfacial tension of each droplet to modify the critical nuclei size for hydrate formation in each droplet (Sloan, 1990), and later causes a difference in nucleation time of hydrate in the droplets. Hence, the isothermal hydrate formation peak can be used as a statistical analysis of droplet nucleation over time.

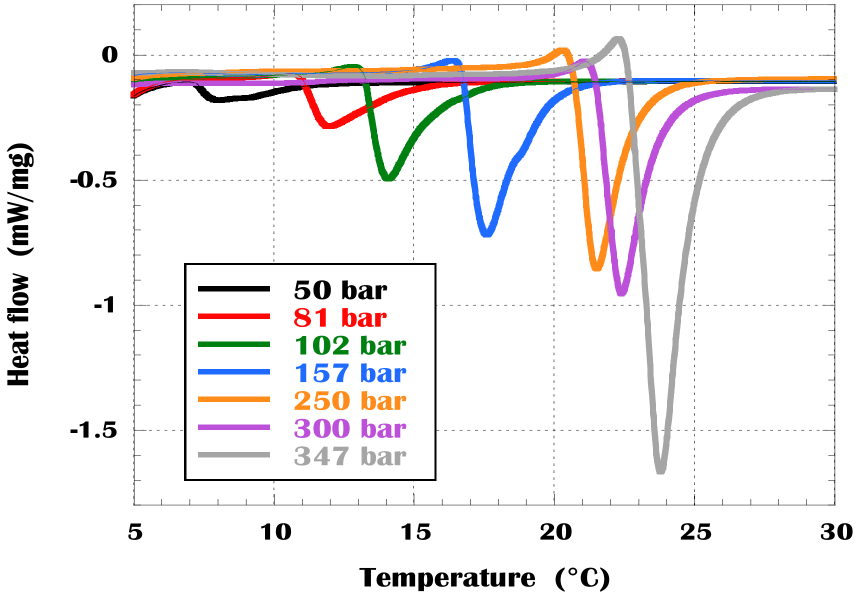


FIGURE 7: Thermal Curves of Methane Hydrate Dissociation by Using µDSC

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Before executing the project, a thorough research had been conducted to expose self to the knowledge of hydrate and natural polymers as kinetic hydrate inhibitors. After that, experiments will be conducted to test the theory of effectiveness of the natural polymers. The experiment will mostly involve in the laboratory in Block 17 using the Micro Differential Scanning Calorimetry (DSC).

3.2 Project Gantt Chart & Activities

TABLE 2: Gantt Chart for FYP I

No.	Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1.	Selection of Project Topic	🟩	🟩						MID SEMESTER BREAK							
2.	Study on Hydrates Formation and Kinetic Inhibitors			🟩	🟩	🟩	🟩									
3.	Submission of Extended Proposal							●								
4.	Proposal Defence									🟩	🟩					
5.	Further study on natural polymers as KI											🟩	🟩	🟩		
6.	Submission of Interim Draft Report														●	
7.	Submission of Interim Report															●

TABLE 3 : Gantt Chart for FYPII

No.	**Activities**	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**
1.	Lab work	🟩	🟩	🟩	🟩	🟩	🟩	🟩	**MID SEMESTER BREAK**							
2.	Submission of Progress Report							🟡								
3.	Lab work continues									🟩	🟩	🟩	🟩	🟩		
4.	Pre-Sedex											🟡				
5.	Submission of Draft Report												🟡			
6.	Submission of Dissertation													🟡		
7.	Submission of Technical Paper													🟡		
8.	Oral Presentation															🟡

Legend:

🟩 Process 🟡 Milestone

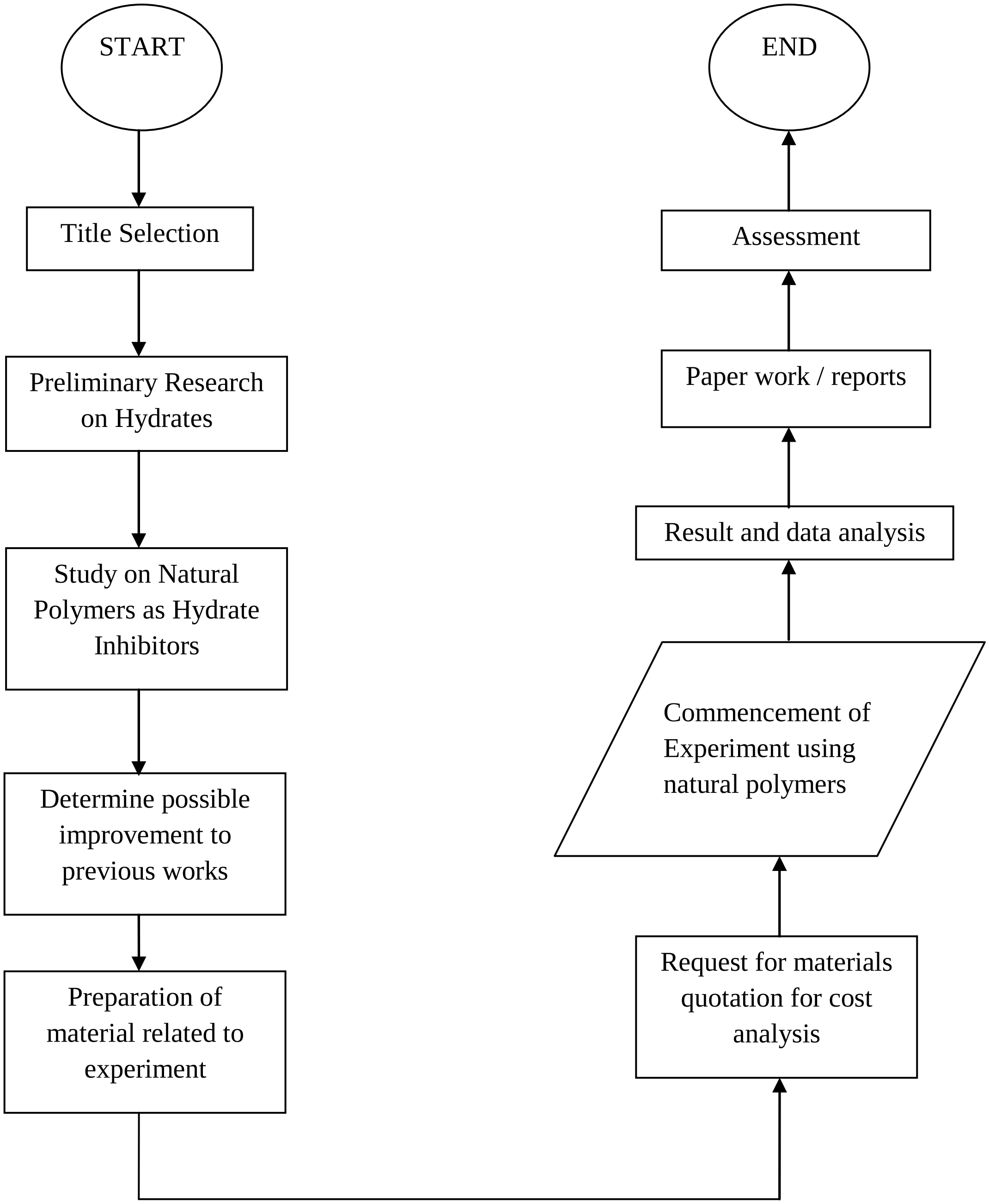


FIGURE 8: Flow Chart of Project Activities

3.3 Experimental Methodology

3.3.1 Apparatus

Magnetic stirrer, glass rod, 1000ml beaker, Fume hood, Electronic Balance, Micro-Differential Scanning Calorimetry (µ-DSC VIIa, Setaram Inc).

FIGURE 9: Micro DSC

3.3.2 Materials

The materials that were used in this study are listed in Table 3.

TABLE 3: Materials used in this study

General Name	Description
Chitosan,Poly-(1-4)-2-Amino-2-deoxy-β-D-Glucan	Chitosan flakes with 70 – 97 % DD was provided by UTP and purchased from R & M Chemicals.
Tapioca Starch	Purchased from local market.
Acetic Acid, Ethanoic acid (CH_3COOH)	Glacial acetic acid was purchased from Avantis Lab, Ipoh,Perak.
Distilled water, H_2O	Obtained from the UTP Block 15 lab.

3.3.3 Procedure

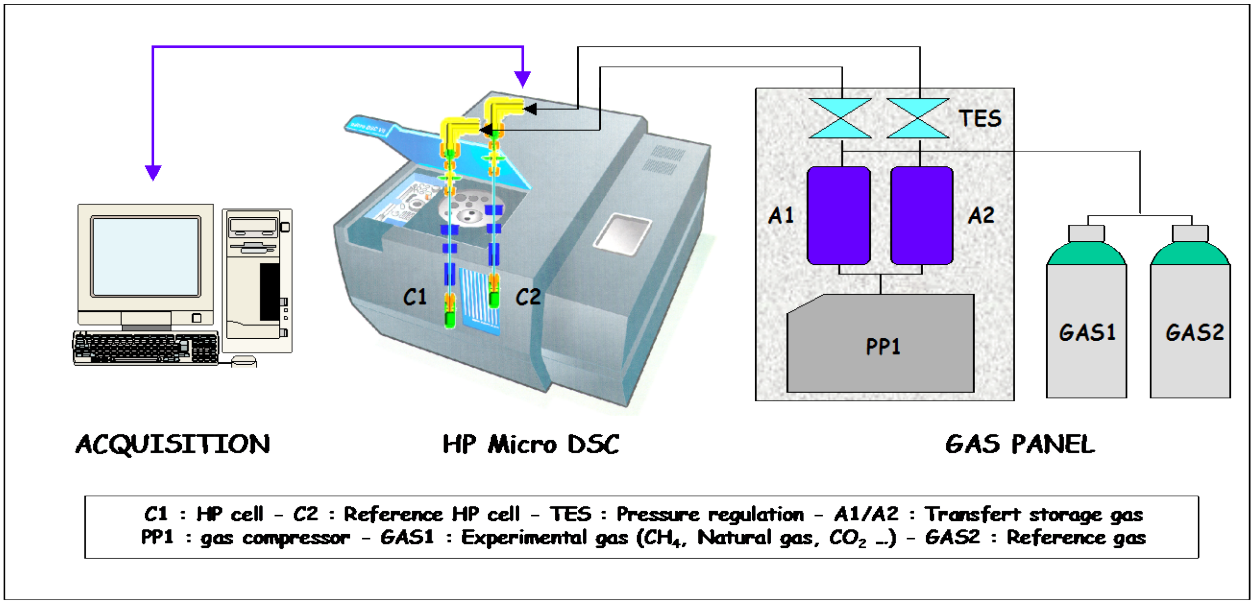


FIGURE 9: Experiment setup using Micro DSC

The experimental works will be carried out in two parts for this project. The first part, is to prepare the samples needed for experiment. There are 2 types of natural polymers used for this purpose; chitosan and starch. A blank sample is used for the purpose of indicator in investigating the formation carbon dioxide hydrate. There are five samples obtained in this experiment:

- Blank Sample (distilled water)
- 0.1 and 1.0 wt% Chitosan solution
- 0.1 and 1.0 wt% Starch solution

- **Preparation of Chitosan Solution**

1. A stock solution of 0.1 wt% chitosan was prepared by adding 0.1 g of chitosan flakes into 100 ml of 5 % acetic acid solution and continuous stirring for 1 hour.
2. The procedure above is repeated by adding 1 g of chitosan flakes into the acetic acid solution to obtain 1.0 wt% of chitosan solution.

- **Preparation of Starch Solution**

1. 0.1 wt% of starch solution is prepared by adding 0.1 g of starch powder into 100 ml of distilled water and stirred vigorously.
2. The procedure above is repeated again by adding 1.0 g of starch powder into the distilled water to obtain 1.0 wt% of starch solution.

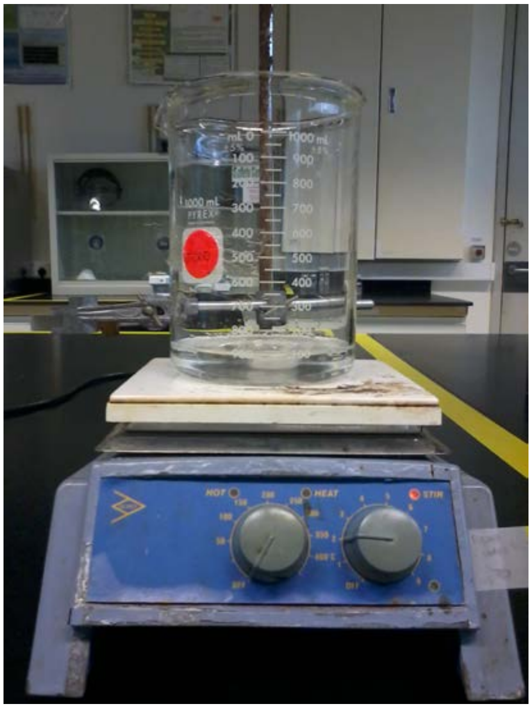


FIGURE 11: Preparation of chitosan solution using magnetic stirrer

- **Mode of Operation**

Experimental tests were conducted using Micro-Differential Scanning Calorimetry (μ-DSC). Approximately 60 mg of the prepared samples were placed in the sample cell. Carbon dioxide gas was later introduced into the sample cell at 298 K (25^oC).

All of the samples were run in ramped mode. Initially, the samples were cooled from 298 K (25^oC) to 248 K (-25^oC) to form the gas hydrate and stabilize at this temperature. Later, the temperature was reheated to the initial temperature, 298 K (25^oC) to detect the dissociation of gas hydrate.

From this experiment, thermogram analysis of the parameters of heat flow (mW), temperature and time for all samples tested were obtained.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Determination of phases based on thermogram

The objective of this experiment is to study the effect of natural polymers on hydrate formation time.

Induction time is defined as the time elapsing until the second which onset of precipitation detected, which is the total of tome for critical nucleus growth and formation to detectable size (Behar, 1994).To compare the performance of different inhibitors, the induction time of each inhibitors must be measured in the same experimental procedure and apparatus.

There are five samples involved in this experiment, (1) Blank sample, (2) 0.1 wt% of Chitosan solution, (3) 1.0 wt% of Chitosan solution, (4) 0.1 wt% of Starch solution and (5) 1.0 wt% of Starch solution. All of these samples were run in ramped mode.The thermogram of the samples are as in the following figures (Figure 7, 8 & 9).

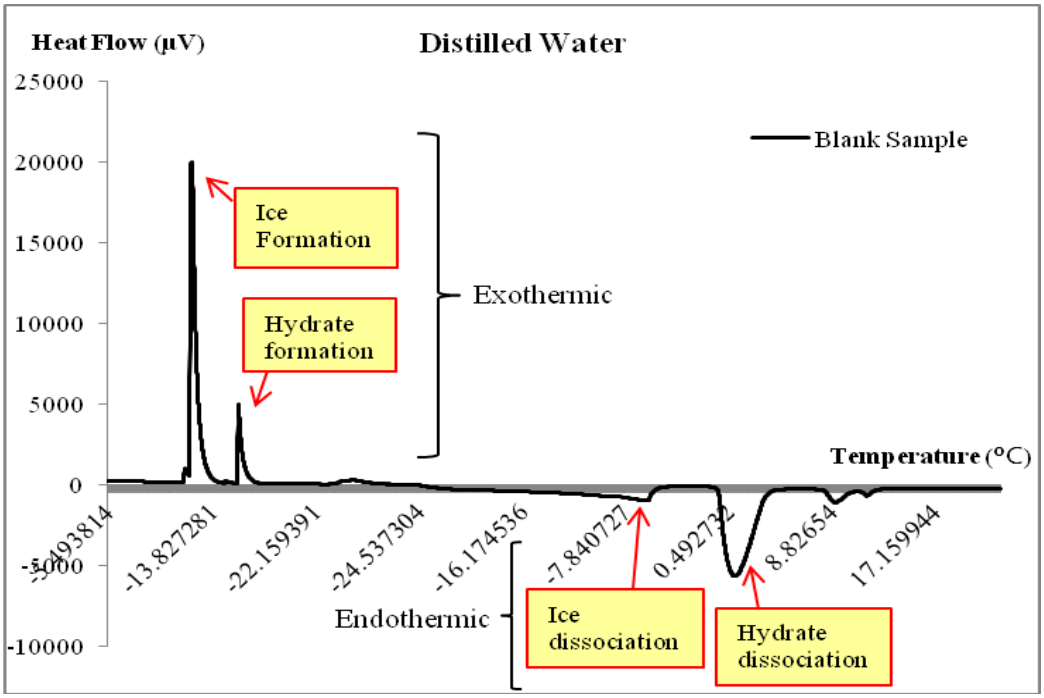


FIGURE 12: Hydrate/Ice formation and dissociation trend in blank sample

Initially, the blank sample was cooled from 25ºC to -25ºC.During the cooling stage, an exothermic reaction occurs, where by heat is released from system. From Figure 3, the exorthermic reaction can be represented by the first two peaks that in the graph. The first peak was identified as ice formation, whereas the second peak was hydrate formation.

According to Hester, contact between the water and guest phase, in this case, vapor phase is required to form hydrates. Typically, a thin film of hydrate forms at the interface. Since that water can transform entirely to ice, the ice phase fraction should be more than of the hydrate when formed from a gas phase guest. The intergrated area of the hydrate exotherm is expected to be smaller compared to the ice exotherm, because of the identical latent heats of formation.

This hypothesis is further proved upon heating, which is also known as endothermic reaction. From Figure 3, the formation of both ice and hydrates occurs below 0ºC, thus the nucleation temperature cannot be used directly to differentiate between ice and hydrate. However, the endotherms start at a given temperature, based on phase equilibria. The exotherm and endotherm for both ice and hydrate phases are almost equal in area, as shown in Figure 3.This verifies the hypothesis has been made earlier.

From the experiment, the induction time of blank sample were also investigated to be compared with samples that had been added with natural polymer. For blank sample that consisted of distilled water, the induction time is 92.2 minutes.

B. Effect of natural polymer on induction time

Based from part A, the hydrate formation is determined by the second peak of exothermic. From this, the induction time can be determined by finding out the second peak value of each samples.

- ***Chitosan***

The chitosan with different concentration (wt %) were tested and Table 2 list the results obtained from the experiment using micro-DSC. For 0.1 wt%, the induction time is 98.4 min, whereas for 1.0 wt% chitosan, the induction time is 98.5 min.

From this result, as the concentration of chitosan increase, the induction time also increases.

Table 5 : Induction time of chitosan and distilled water

Sample	Induction time (min)
Distilled water	92.2
0.1 wt% Chitosan	98.4
1.0 wt% Chitosan	98.5

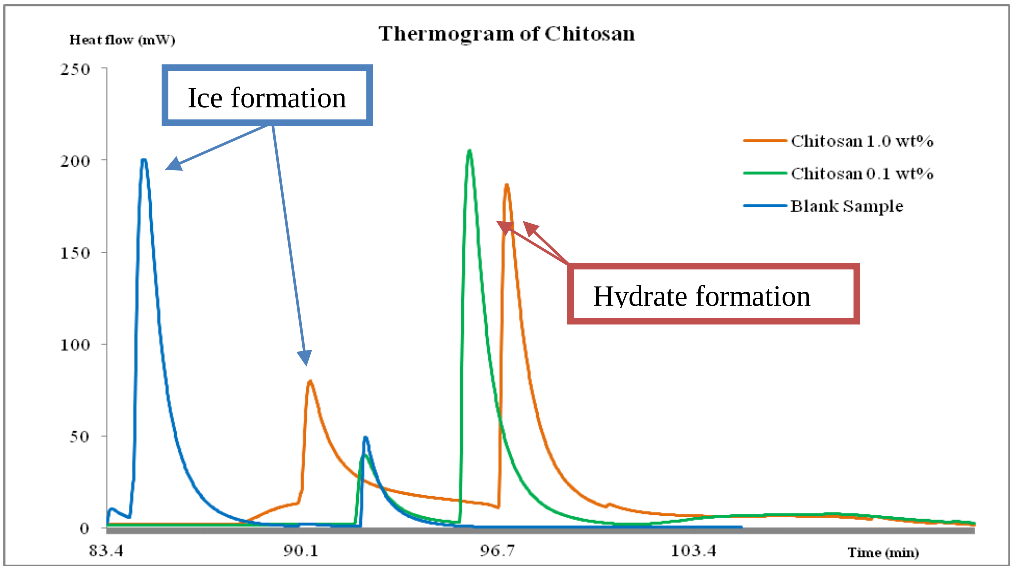


FIGURE 13 : Different concentrations of chitosan solutions (heat flow vs time)

- ***Starch***

The effectiveness of tapioca starch as kinetic inhibitor were tested by determining the induction time using different concentration (wt%) of tapioca starch solution. The results obtained from the experiment can be obtained from Table 3. The induction time for 0.1 wt% of starch is 91.5 min, followed by 1.0 wt% starch (96.7 min).

Table 6 : Induction time of starch and distilled water

Sample	Induction time (min)
Distilled water	92.2
0.1 wt% Starch	91.5
1.0 wt% Starch	96.7

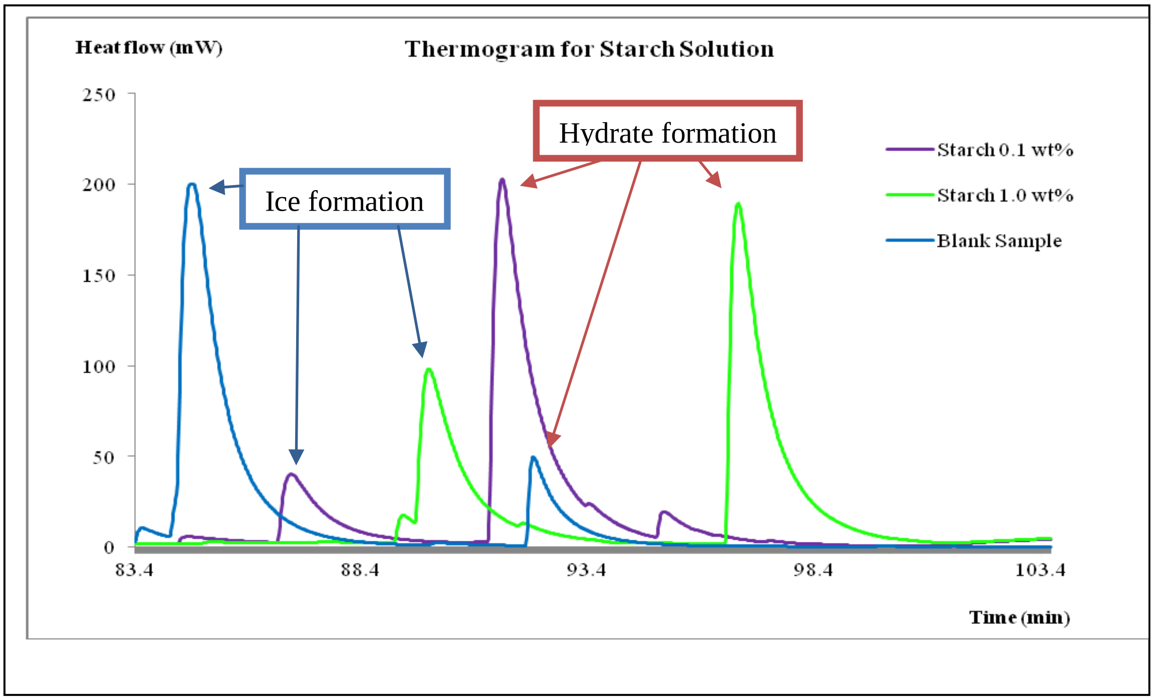


FIGURE 14 : Different concentrations of starch solutions (heat flow vs time)

- ***Comparison of chitosan and starch***

The comparisons between all of the samples can be visualized as in Figure 4.From the figure, it can be conclude that 1.0 wt% chitosan have the longest induction time as compared to other samples.1.0 wt% Chitosan had able to delay the induction time by 4.5 min.

The summary for induction time for each of the five sample were then presented in the following figure (Figure 10).

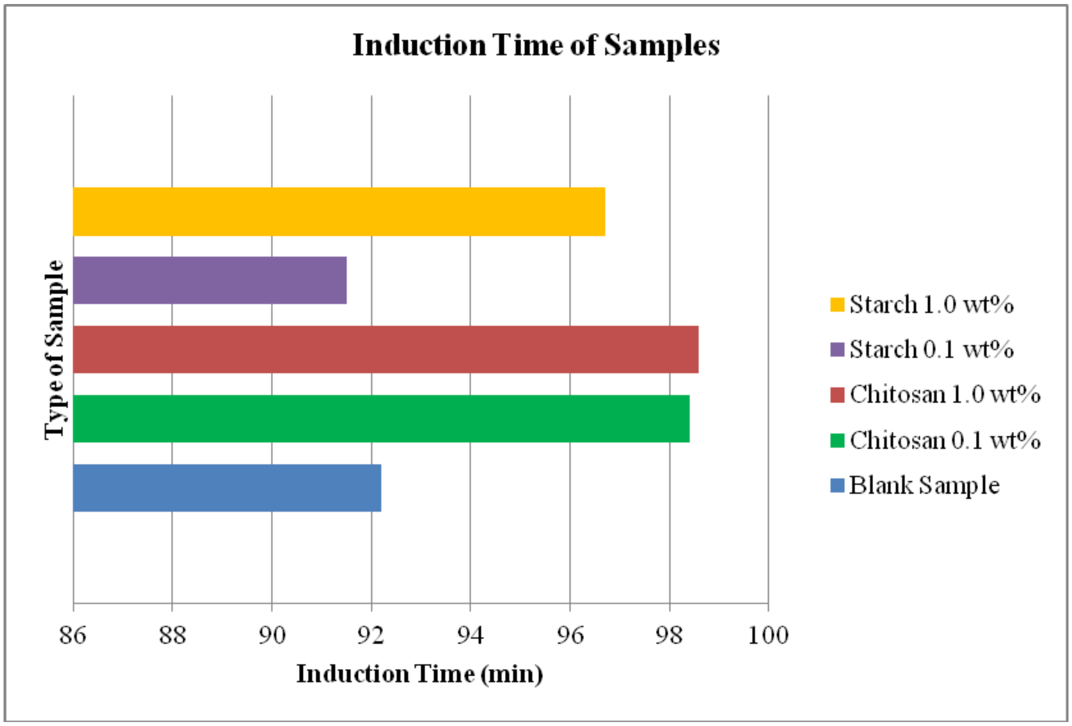


FIGURE 15:Induction time of samples

From Figure 15, the addition of natural polymer increases the induction time of hydrate formation.

1.0 wt% Chitosan solution recorded the highest induction time as compared to the other samples (98.6 min).The interaction of the inhibitor with impurities relates hydrate nucleation to heterogeneous nucleation.

Apart from that, based on the result, the higher the concentration of KI (in weight percent), has able to preserve more time taken for hydrates to form.

This proves that concentration of inhibitor effects the induction time of hydrate formation. The presence of the inhibitor will hinder that nucleation sites produced by the impurities, hence inhibits the process of hydrate nucleation and formation.

For starch, the optimum concentration is between 0.2 wt% and 1.0 wt%, because or 0.1 wt%, starch solution inhibitor efficiency is weak and does not inhibit hydrate formation.

However, as for chitosan, although a higher concentration yields a better result, the change in induction time is very little. This shows that the optimum concentration of chitosan to be used as KI would be around 0.1 wt% to 1.0 wt%.

CONCLUSION & RECOMMENDATION

Chitosan and starch were the two types of natural polymers used in the hydrate formation experiments to evaluate their performance as KI.

From the experiments carried out, it was found out that both chitosan and starch has the ability to delay the onset of nucleation. For chitosan, as the concentration of chitosan increase, the induction time also increase. Hence, the concentration of chitosan has an effect on the induction time.

However, for starch, the effective concentration is 1.0 wt%. Despite the positive result, the use of these natural polymers as a substitute for commercially use KI such as PVP is still undergoing. Apart from that, the presence of chitosan and start also reduces the rate of hydrate crystal growth .Finally, the optimum concentration of the chitosan practically is 1.0 wt% and for starch, 1.0 wt%.

Among the objectives of this project is to determine the optimum concentration of chitosan and starch to be used as KI. Unfortunately, due to the time constraint and maintenance of the machine, the author only managed to test for two concentrations of each of the natural polymers. It is recommended that experiments should be done with more variety of concentration so that the most optimum concentration of both natural polymers to be used as KI can be determined.

Besides that, the experiment also needs to be run at isothermal condition to further explore the effectiveness of the KI.

Apart from that, the experiments done were only once. Hence, there might be a few errors occurred during sample preparation or experiment run. To minimize these errors and increase the accuracy of the result, the experiment needs to be repeated several times.

REFERENCE

[1] P.K Notz, S.B.Bymgardner, B.D. Schaneman, J.L Todd, "Application of Kinetic Inhibitors to Gas Hydrate Problem," *SPE Production and Facilities*, pp. 256-260, Nov. 1996.

[2] T.A Swatson, M.Petrie and T.R. Sifferman, "The Successful Use of Both Kinetic Hydrate and Paraffin Inhibitors Together in a Deepwater Pipeline with a High Water Cut in the Gulf of Mexico," Presented at SPE International Symposium on Oilfield Chemistry, 2005.

[3] Long. J. et al.: "Kinetic Inhibitors of Natural Gas Hydrates," paper presented at the 1993 73rd Annual GPA Convention, New Orleans, 7-9 March.

[4] L.M.Frostman et.al: "Anti-Agglomerant Hydrate Inhibitors for Prevention of Hydrate Plugs in Deepwater Systems," paper presented at the 2000 SPE Annual Technical Conference and Exhibition, Texas, 1-4 October.

[5] Lederhos J P, Long J P, Sum A, Christiansen R L,Sloan E D. *Chem Eng Sci*, 1996, 51(8): 1221

[6]Yongjun Xu, MinlinYang, Xiaoxi Yang, "Chitosan as Green Kinetic Inhibitors for Gas Hydrate Formation," *Natural Gas Chemistry*, vol.19, pp.432-435, (2010).

[7]Ju Dong Lee, Huijie Wu, Peter Englezos, "Cationic Starches as Gas Hydrate Kinetic Inhibitors," Natural Gas Chemistry, vol.62, (2007) pp. 6548-6555.

[8] Kelland M A, Svartaas T M, Ovsthus J, Tomita T, Mitzuta K. *Chem Eng Sci*, 2006, 61(13): 4290 .

[9] John J.Caroll, "*Natural Gas Hydrates: A Guide for Engineers,*" 2nd ed, Gulf Professional Publishing, 2009, pp. 131.

[10] Luca Del Villano, Roald Kommedal, Martin W. M. Fijten, Ulrich S. Schubert, Richard Hoogenboom, and Malcolm A. Kelland, "A Study of the Kinetic Hydrate Inhibitor Performance and Seawater Biodegradability of a Series of Poly(2-alkyl-2-oxazoline)s," *Energy & Fuels,* (2009), vol.23, pp. 3665–3673.

[11] Nicolas von Solms, Lars Jensen, (2011, Oct.). Green Gas Hydrate Inhibitor. *AiChe Journal*. [Online]. Available: https://aiche.confex.com/aiche/2011/webprogram/Paper240849.html

[12] Lars Jensen,Hans Ramlov,Kaj Thomsen and Nicolas von Solms. (2009,March).Inhibition of Gas Hydrate Formation by Low-Dosage, Environmentally Benign Inhibitors. *SPE News*. [Online] 36(7) pp.4.

[13] Lars Jensen. (2011,Jan.) Gas Hydrates – New Developments. SPE News. [Online] 43 (15) pp.5.

[14] Martin A.Abraham, *"Sustainable Science and Green Engineering"* , 1st ed. Elsevier B.V. 2009, pp.34.

[15] Tarek Ahmad,Paul D.McKinney, Advance Reservoir Engineering, Gulf Professional Publishing, Oxford, 2005.

[16] Phillips, N.J. "Development and Commercial Application of a Novel Kinetic Hydrate Inhibitor".1997, 8th International Oul Field Chemical Symposium, Geilo, Norway.

[17] Peter Michael Oduor-Odote, Marcin H. Struszczyk and Martin G. Peter, "Characterisation of Chitosan from Blowfly Larvae and Some Crustacean Species from Kenyan Marine Waters Prepared Under Different Conditions," *Western Indian Ocean J.* Mar. Sci. Vol. 4, No. 1, pp. 99–107, (2005).

[18] Majeti N.V.,Ravi Kumar, “A Review of Chitin and Chitosan Applications,” Reactive and Functional Polymers**,** Vol.46, No.1, pp. 1–27, (2000).

[19] E.Dendy Sloan, Carolyn Koh, Amadeu K.Sum, Natural Gas Hydrates in Flow Assurance, 2011, Gulf Professional Publishing, USA.

[20] Setaram."Micro DSC VII Commissioning Utilisations." France, Setaram Manual B/DSC7A. 2003.

Appendix (a)

Sample calculation of sample solutions

For the preparation of natural polymer solutions, the following formula is used to obtain required weight percentage of the solutions.

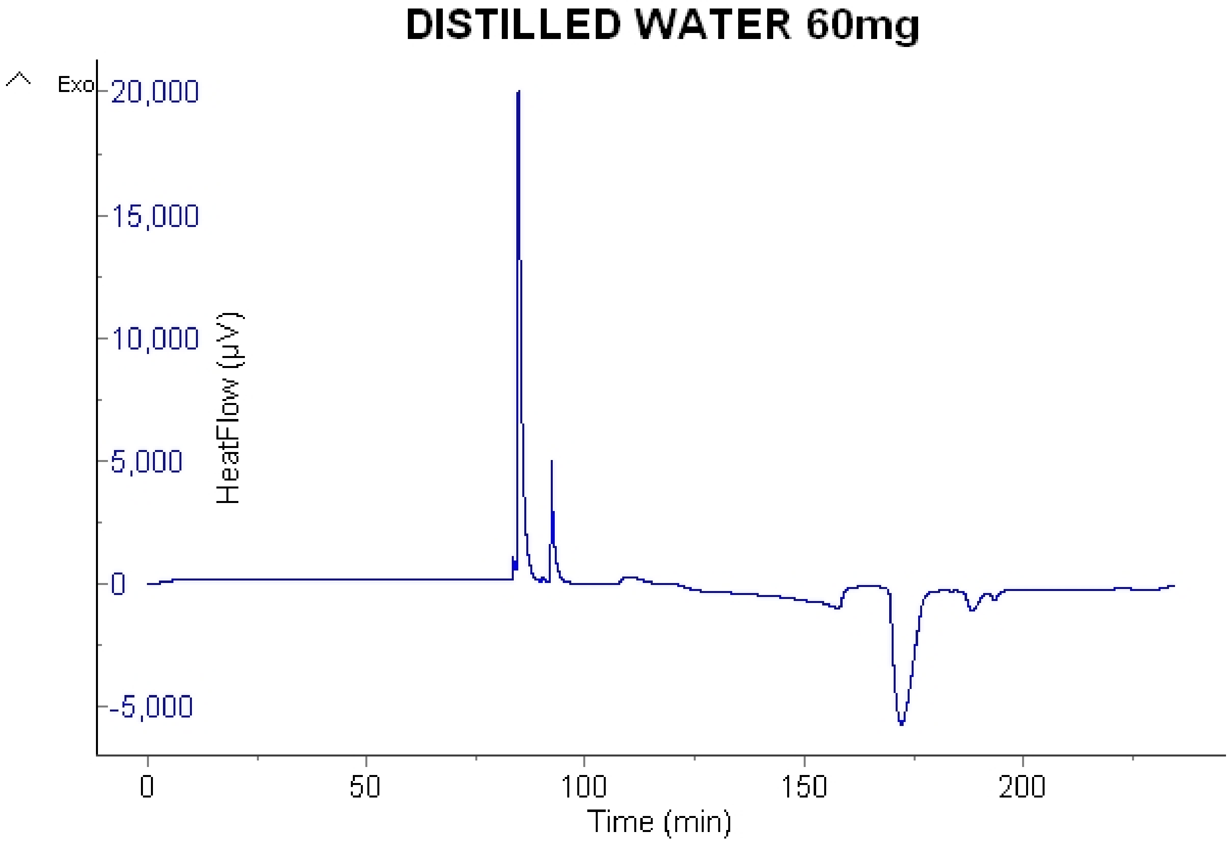
$$\boxed{\text{Weight percent} = (\text{Weight of solute} / \text{weight of solution}) \times 100}$$

Example calculation of 1 wt% of Starch solution

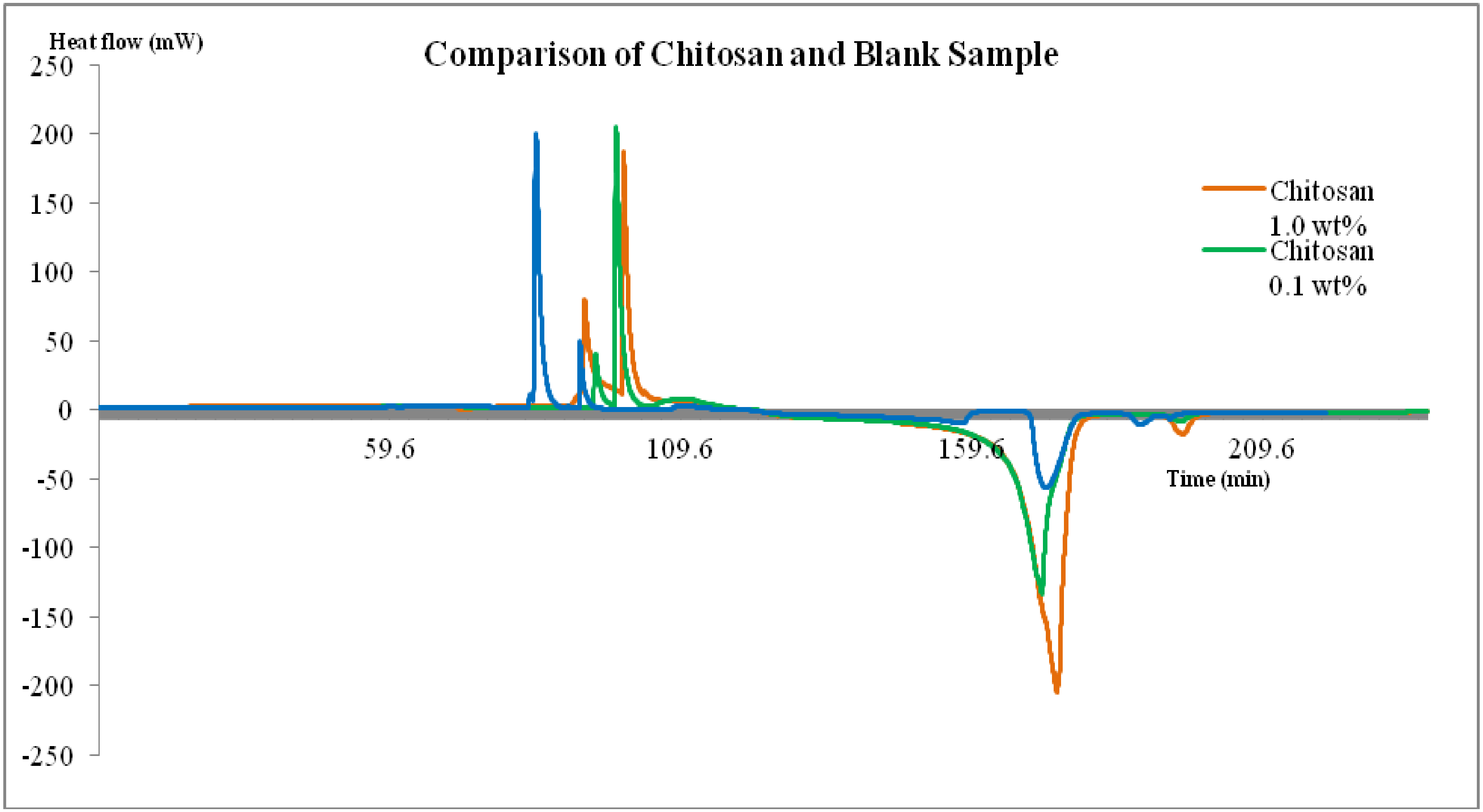
$$1\ \text{wt\%} = (x / 100) \times 100$$

$$\underline{x = 1\ \text{g of starch powder}}$$

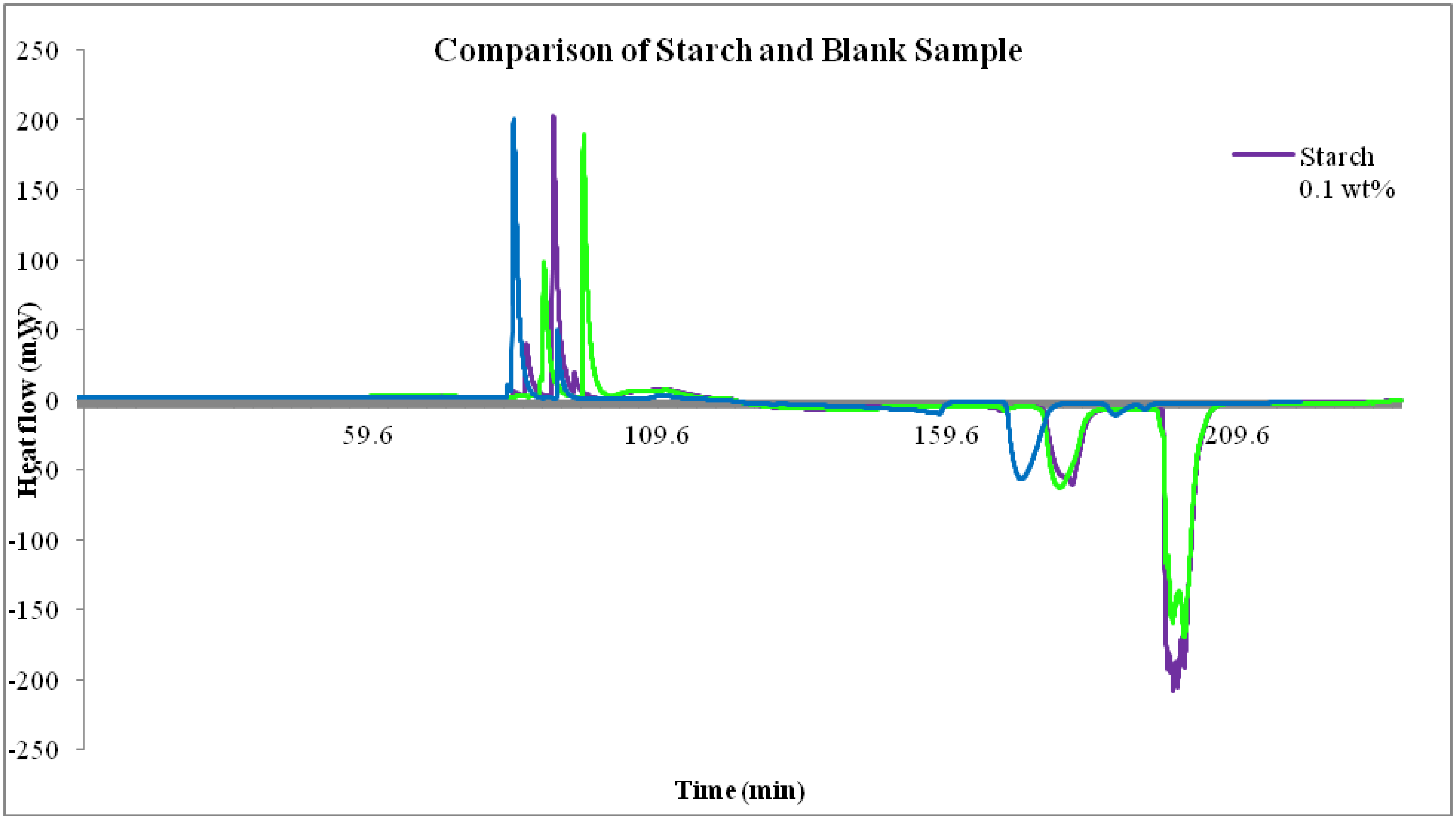
Appendices (b)



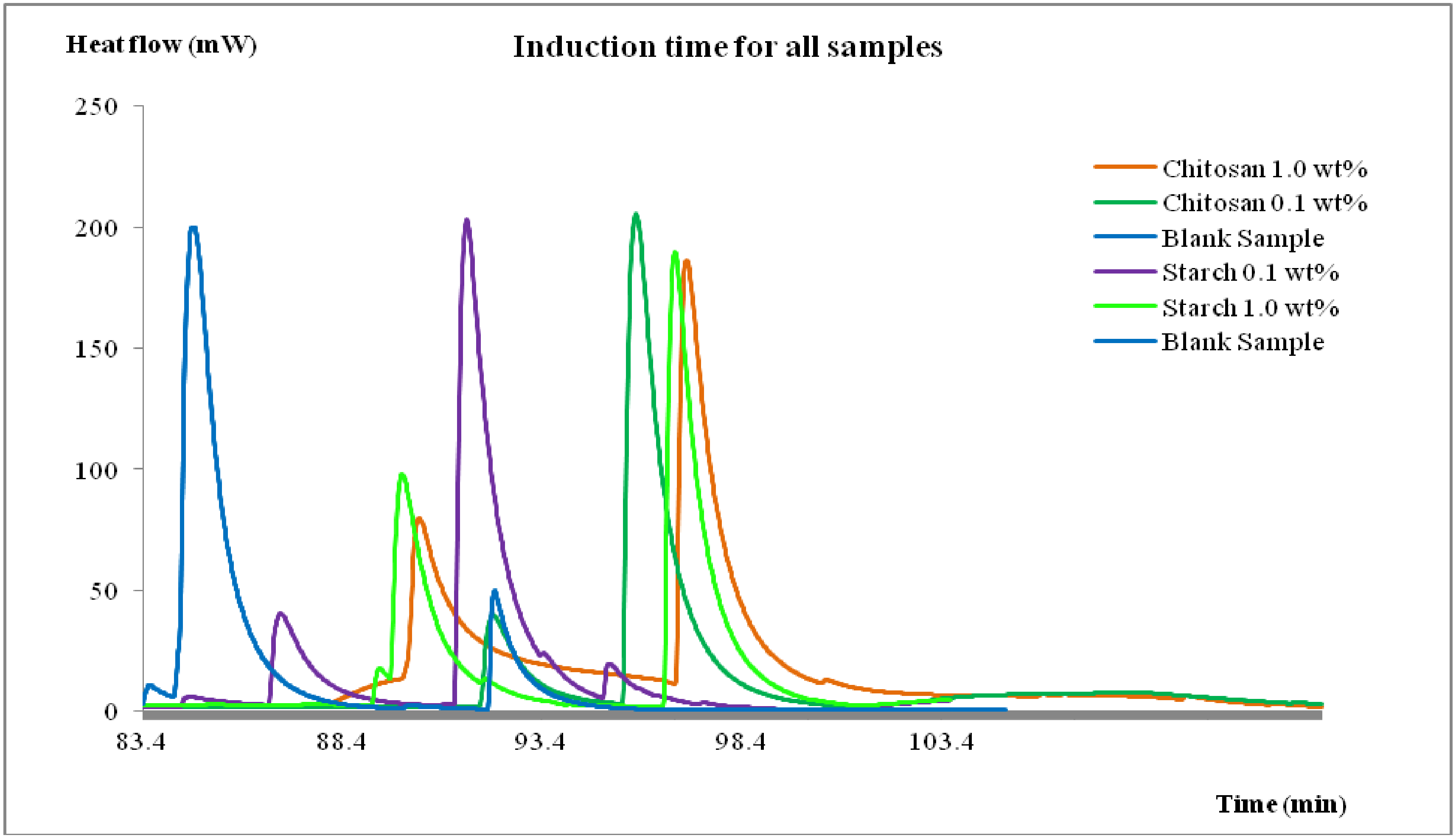
Blank sample thermogram



Comparison of blank sample and chitosan solutions at 0.1 wt% and 1.0 wt% concentration



Comparison of blank sample and starch solutions at 0.1 wt% and 1.0 wt%



Induction time for all samples