EFFECT OF CHITOSAN AS GAS HYDRATE KINETIC INHIBITOR

By

HAZIQ BIN HASHIM

10668

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum Engineering)

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CERTIFICATION OF APPROVAL

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(PETROLEUM ENGINEERING)

Approved by,

_____

(MS. MAZUIN JASAMAI)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

APRIL 2012

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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(HAZIQ BIN HASHIM)

ABSTRACT

Gas hydrates are able to form in any location as long as there is the availability of free gas, water and the appropriate temperature and pressure. Hydrates may form and shut the gas flow rate partially or completely in the well bottom zone of layer, in a well bore, in well top pipes, in a system of field pipelines and installations and in underground system gas storage. *Deep Star*, a consortium focused on Gulf of Mexico deep water development technology issues, has concluded that replacement of hydrate-plugged lines in deep water environment cost one million dollars per mile on average. Thus prevent the hydrates formation is the best way to tackle the problems. Current practice nowadays is by using thermodynamic inhibition by injecting inhibitors such as methanol, glycol and others. Though it is still the widest method used, environmental concerns and operational complexity urge for new approach, which lead to the kinetic inhibitor. In this experiment, Chitosan is used to replace the common kinetic inhibitor, polivinylpyrrolidone (PVP) and tested the performance using equipment called micro-Pressure Differential Scanning Calorimetry. The result shows that sample with 0.4 wt% of chitosan is observed to be shifted the temperature of formation of ice/hydrate. The results of the present work can be used for the preliminary design for the continuous research of chitosan in petroleum industry, especially in gas hydrates problems. Also,this works provides the baseline for new kinetic inhibitor evaluations towards gas hydrates for better understanding.

ACKNOWLEDGEMENTS

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INTRODUCTION

1.1 Background Study

An inherent problem with natural gas, condensate and crude oil production or transportation is the formation of gas hydrates. The oil and gas industry is facing increasing costs in inhibiting gas hydrate formation due to the development of offshore gas reservoirs. Recent international estimates of the cost of the conventional inhibitor, methanol, alone are in excess of $150 million/year [1] .Gas hydrates are likely to form in subsea flow lines unless the water is removed down to the lowest dew point encountered, highly effective insulation is in place, or inhibitors are used. Since complete stripping of water from condensates and/or natural gas is prohibitively expensive, and effective insulation is beyond current economic limits, the most effective solution includes the use of hydrate inhibitors [2].The usual practice for avoiding the plugging of production facilities by hydrates is to add thermodynamic inhibitors such as methanol or glycol. Thermodynamic inhibitors have been in use for a long time, and continue to be the industry standard. This kind of inhibitor works as an antifreeze by involving the water in a thermodynamically favourable relationship, so that it is not available for reaction with the gas [10].

Recently, low-dosage inhibitors have been introduced in industry. Even though they are more expensive than conventional inhibitors (methanol and glycol) on a per unit basis, they have gained popularity because only small quantities are required to inhibit hydrate formation. In addition to the savings in operating costs, implementation of low-dosage inhibitors is expected to reduce environmental costs and capital expenditures. Methanol is toxic, and both methanol and glycol must be removed from hydrocarbon stream before going to the market (a regeneration system is required). Low-dosage inhibitors, on the other hand, do not need to be removed from the product stream; capital and operating costs associated with separation and recycling systems required when other families of chemical inhibitors are used, are thereby eliminated. Low-dosage inhibitors are usually non-toxic and/or biodegradable substances, which provide an environmental friendly technology. However, some of these chemicals have not been approved

in certain jurisdictions. Considerations of regional environmental regulations should be taken when selecting and deploying this new technology.

Therefore, a trend to develop green inhibitors exists. One class of green inhibitors is antifreeze proteins (AFP) or antifreeze glycoproteins (AFGP). These green inhibitors were added to a tetrahydrofuran hydrate forming system in separate experiments and the results showed that they were able to delay the nucleation of hydrates [3]. It was also reported that AFP could inhibit the formation of propane hydrates [4]. In a more recent study, it was reported that AFP was prepared from fish outperformed PVP in terms of delaying nucleation. There is also another type of green kinetic inhibitor such as using chitosan, a natural polymer composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N acetyl-D-glucosamine (acetylated unit) [5]. But still, nowadays, there a not a lot of research regarding the usefulness of chitosan as gas hydrates inhibitor, though chitosan has been widely use biomedical, biotechnology and others.

1.2 Problem Statement

Laboratory and field tests since 1991 have shown the feasibility of replacing the classical inhibitors (methanol and ethylene glycol) with kinetic inhibitors. Although the kinetic inhibitors may have limitation, they have been shown to be effective in preventing the formation hydrate plugs in field situation.

In petroleum exploration and production operations, gas hydrates can cause partial or total blockages in pipelines and processing facilities. Gas hydrates are likely to form in subsea flow lines unless the water is removed down to the lowest dew point encountered. Highly effective insulation is used or inhibitors are used. The first and two possibilities are generally prohibitively expensive or the technology for subsea application does not exist yet. In many cases, there is an economic advantage to using the kinetic inhibitors as it offer lower cost alternatives to classical inhibitors and are more environmentally friendly.

Yet, an analysis of the condition in the production facilities must be done to ascertain the applicability of a kinetic inhibitor especially for the new green kinetic inhibitor. Even though the green kinetic inhibitor claim to inhibit the hydrate formation by delaying the nucleation and crystal growth phases of hydrate formation, there are no much research and paper discussed about the fact plus there are no field testing yet with the new type of inhibitor. Thus it is desirable to study the formation of hydrates and also the mechanism and performance of the green kinetic inhibitor to prevent the gas hydrate formation.

1.3 Objectives

In order to study and evaluate the hydrate nucleation prior to green kinetic inhibitors performance evaluation, these are the objectives that need to achieve:

1) To study and understand the mechanism of gas hydrate formation
2) To study the new type of green kinetic inhibitor, chitosan and evaluate the effect of the chitosan in terms of degree of deacetylation (DD) and molecular weight (MW) with induction time
3) To study the effect of concentration of the chitosan solution with the induction time of gas hydrates.

1.4 Significant of the Project

In order to evaluate the effectiveness of chitosan as green kinetic inhibitor, experiment will be done and data such as thermogram, heat flow, heat capacity, pressure-temperature graph, and enthalphy can be obtained. Thus, by using these data's, analysis on isothermal studies can be done which allow the detection of transitions like crystallizes, phase changes and curing of the gas hydrates either with existence of chitosan or not.

1.5 Scope of Study

The scope of study for this project is been divided into three stages. The first stage of study consists of researching and understanding the problems regarding the background gas hydrates, to the industry rule of thumb in handling the problem, especially in offshore pipeline during production and transportation system. This include the understanding the different properties and conditions that favor the formation of gas hydrates in the pipeline in different regions of the world.

In the second stage, with all the information needed for gas hydrates, research continue with the understanding the properties of the chosen kinetic inhibitor for this projects, called chitosan. In this stage, the scope of study will be including the study of chitosan's properties, chitosan's manufactured, chitosan's use and past experiments using chitosan for kinetic gas hydrates.

Lastly, in the third stage of this project, experiments will be carried out using the chitosan as kinetic hydrates inhibitor. Further evaluation has to be done by measuring the hydrate formation in the sample of water with Differential Scanning Calorimetry (DSC). Using chitosan, its effectiveness acting as kinetic hydrates inhibitor will be measured based on these parameters:

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

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

1.6 The Relevancy of the Project

Hydrates formation always become a major concern in transportation of the crude oil using offshore pipelines. Among all alternative, hydrate inhibitor is the most economical and also effective to handling the problems. In the market, thermodynamics inhibitor already dominates the industry for a long time, but not for kinetic inhibitor. And among all these alternative, environmental issue is the concern. Using chitosan as a green kinetic hydrates inhibitor is still new for the industry and less paper are published regards with these topics.

1.7 Feasibility of the Project

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

LITERATURE REVIEW

2.1 Gas Hydrate Introduction

A gas hydrate is a crystalline solid that forms under the specific conditions of temperature and pressure, which are thermodynamically appropriate to that gas. "Hydrate" refers to the fact that water molecules surrounding a central molecule of a different kind form them. In the case of gas hydrates, this central molecule is a low molecular weight gas, such as those, which commonly constitute natural gas such as methane, ethane, propane, and iso-butane, SO2, N2, H2S, CO2, and more than one hundred formers have been identified [2]

The water molecules form a repetitive geometric lattice, which is commonly referred to as a cage. Without the gas molecule at the center, the highly organized cage structure would be in dynamic equilibrium with free flowing water molecules, perpetually forming and collapsing. In the presence of the central gas molecule, given the right conditions of temperature and pressure, the water molecule-based cage forms a geometric. This structure is stabilized by the additional van der Waals forces acting between the gas molecule and the surrounding water molecules [9]. When nuclei come in contact with other nuclei and join together to form larger particles, the process is called agglomeration. Attraction between polar molecules inside the cages of water molecules causes the agglomeration.

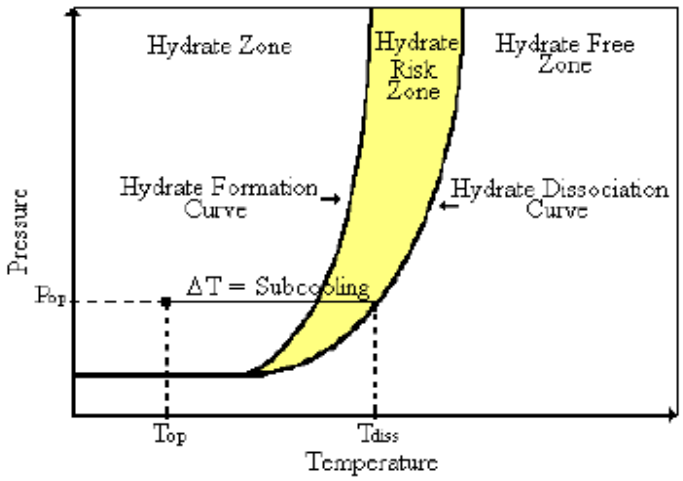

Figure 1. Schematic pressure vs. temperature diagram for a given gas composition [2]

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Hydrate crystal nucleation and growth is a kinetic process, meaning that hydrates do not appear instantaneously with the onset of thermodynamically favourable conditions. The lag between the time when system conditions favour hydrate formation and the appearance of hydrates is known as induction time [8]. Figure 1 is a generic pressure vs. temperature curve illustrating the range of system conditions including the hydrate zone (formation is favoured), hydrate-free zone (formation is not thermodynamically favourable), and hydrate risk zone. Dissociation and formation curves are illustrated and a graphic explanation of subcooling (Tdissociation - Toperating) is given. Operating temperature (Top) and dissociation temperature (Tdiss) for the operating pressure (Pop) are illustrated.

2.2 Type of Gas Hydrate

Hydrates are classified by the arrangement of the water molecules in the crystal, and hence the crystal structure. Two types of hydrates are commonly encountered in the petroleum business is Type I and Type II, sometimes referred to as Structure I and II. A third type of hydrate that also may be encountered is Type H (also known as Structure H), but it is much less common. The comparison of the hydrates can be seen through Table 1 as per following.

	Type 1	**Type 2**	**Type H**
Water Molecules per Unit Cell	46	136	34
Cages per Unit Cell			
Small	6	16	3
Medium	-	-	2
Large	2	8	1
Theoretical Formula			
All cages filled	X . 5 3/H_2O	X . 5 2/3 H_2O	5X . Y . 34 H_2O
Mole fraction hydrate former	0.1481	0.1500	0.1500
Only large cages filled	X . 7 2/3 H_2O	X . 17 H_2O	-
Mole fraction hydrate former	0.1154	0.0556	-
Cavity Diameter(Å)			
Small	7.9	7.8	7.8
Medium	-	-	8.1
Large	8.6	9.5	11.2
Volume of Unit Cell (m^3)	1.728 * 10 ^-27	5.178 * 10 ^-27	
Typical Formers	CH_4, C_2H_6, H_2S, CO_2	N_2, C_3H_8, i-C_4H_{10},	

Table 1 Comparison of Type I, Type II and Type H hydrates [6]

As per said previously, the relevant ones to the oil and gas industry are structure I and structure II, which consist of a combination of three types of cavities. These cavities are a pentagonal dodecahedron (5^{12}, where 5 is the number of edges, 12 is the number of faces), a tetrakaidecahedron ($5^{12}6^2$, which has twelve pentagons and 2 hexagons), and a hexakaidecahedron ($5^{12}6^4$), as illustrated in Figure 2.

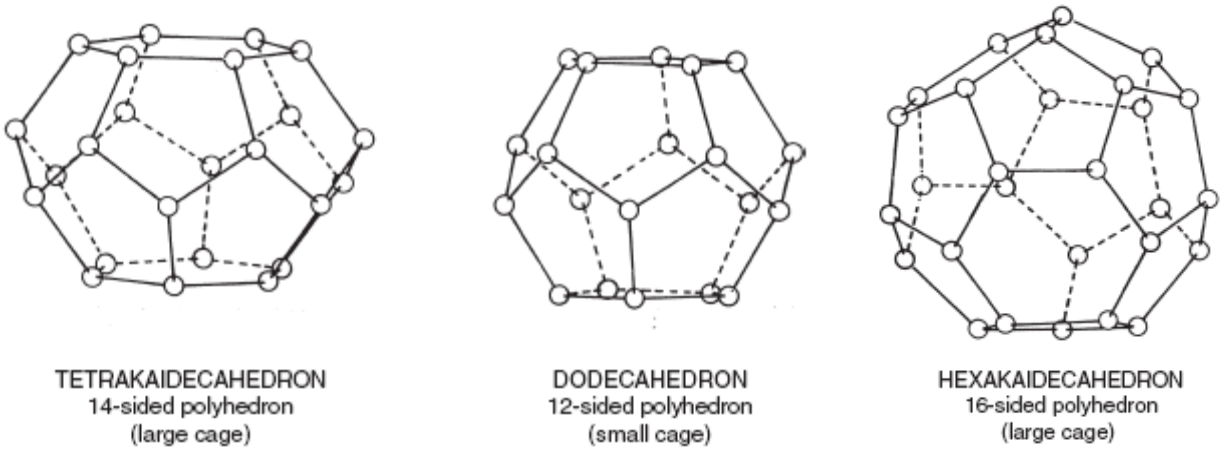


Figure 2 Three cavities in gas clathrate hydrates [6]

Some of the common Type I hydrate formers include methane, ethane, carbon dioxide, and hydrogen sulfide. In the hydrates of CH_4, CO_2, and H_2S, the guest molecules can occupy both the small and the large cages. But, the ethane molecule occupies only the large cages. On the other hand, among the common Type II former in natural gas are nitrogen, propane, and isobutane. It is interesting that nitrogen occupies both the large and small cages of the Type II hydrate while propane and isobutane only occupy the large cages.

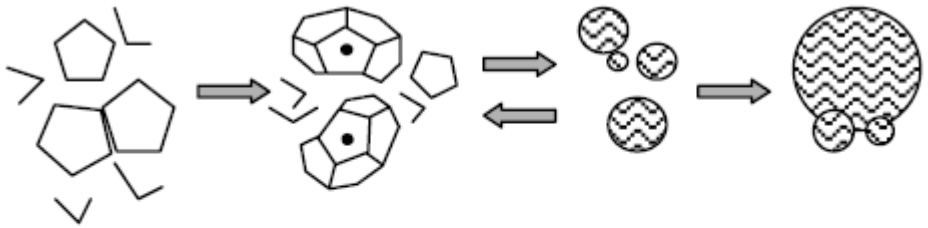
2.3 Gas Hydrate Formation

Given the time required to reach equilibrium, gas hydrates form predictably at specific thermodynamic conditions. The analogy of gas hydrates to ice is helpful for describing hydrate formation. The resulting regular geometric arrangement, or *crystal lattice*, which is formed, is the one that is most thermodynamically stable (has the lowest free energy). Bonds between

molecules are also strengthened when pressure is applied to the system, and individual molecules are forced closer together; under these conditions they also lose freedom of motion and form a solid with a specific crystal lattice. Given specific conditions of temperature and pressure, and a constant composition (e.g.: no impurities in the water), ice always forms from water in a predictable way. As expected, from an examination of the case of ice formation, these solids form at high pressures and low temperatures.

Gas composition, water chemistry, and stream turbulence are variables that affect hydrate formation as well. Gas composition determines which of the hydrate structures will develop and at what temperature and pressure the solid will form. Each hydrate is formed under specific pressure and temperature conditions according to the hydrate former Water salinity is an example of a water chemistry effect: dissolved salts are known to give a hydrate inhibitor effect. Turbulence, causing efficient mixing of water and hydrocarbon phases, is a kinetic effect, producing faster hydrate formation.

Lederhos *et al,* 19966 proposed that gas hydrates form in an autocatalytic reaction mechanism, when water molecules cluster around natural gas molecules in structures similar to the ones shown in Figure 3. This attraction between neighboring guest molecules is termed "hydrophobic bonding", which can be described as an attraction between the apolar molecules inside the clusters [B]. Large and small clusters forming structures I and II are termed "labiles" because they are easy to break down, but relatively long-lived. Labiles can dissipate, or grow to become hydrate unit cells or agglomerations of unit cells forming what are known as "metastable nuclei" [C]. Then, growth can continue until crystals are stable, indicating the onset of secondary nucleation [D].



A. Initial condition pressure and temperature in hydrate forming region, but no gas molecules dissolved in water.

B. Labile Clusters Upon dissolution of gas in water, labile clusters form immediately.

C. Agglomeration Labile clusters agglomerate by sharing faces, thus increasing disorder.

D. Primary Nucleation and growth when the size of cluster agglomerates reaches a critical value, growth begins.

Figure 3. Autocatalytic reaction mechanism for hydrate formation (Lederhos et al, 1996) [2]

2.4 Gas Hydrate Prevention.

As stated earlier, gas hydrates are a significant problem in the natural gas industry. Gas hydrates are likely to form in subsea flowlines unless the water is removed down to the lowest dew point encountered, highly effective insulation is in place, or inhibitors are used. Since complete stripping of water from condensates and/or natural gas is prohibitively expensive, and effective insulation is beyond current economic limits, the most effective solution includes the use of hydrate inhibitors.

The earliest solution of using the hydrate inhibitors is thermodynamic inhibition. The tactic of this is to keep the system out of the hydrate formation condition. Thermodynamic inhibition can be achieved by heating the system beyond the hydrate formation temperature at a given pressure by injecting thermodynamic inhibitors such as methanol, glycol, or salt solutions. Thermodynamic inhibitors are chemical compounds added in high concentrations (10-60wt. %), to alter the hydrate formation conditions, allowing hydrates of the new mixtures form at lower temperatures or higher pressures. Using thermodynamic inhibitors implies regeneration units, which involves higher operating costs. Handling of methanol (the most effective thermodynamic inhibitor) is complicated because of its toxicity and flammability. Furthermore, methanol contamination of the hydrocarbon can compromise the value of the product and give downstream processing problems. Ethylene glycols such as mono-ethylene glycol (MEG) are less flammable,

and reduce losses, but are more expensive and less available than methanol. Salt solutions might be used in hydrate inhibition but they are corrosive, less effective than methanol or glycols, and could cause scale deposits in the process equipment.

Though thermodynamic inhibition is still the widest method used worldwide, but its associated costs, environmental concerns and operational complexity have made researchers look for a different approach to the problem.

2.5 Low-Dosage Inhibitors

Low dosage hydrate inhibitors (LDHI) are a recently developed hydrate control technology which can be more cost-effective than traditional practices such as the use of thermodynamic inhibitors e.g. methanol and glycols. The low-dosage inhibitors divided into two classes. The class referred to as *kinetic inhibitors* delays the nucleation and growth of hydrate crystals for substantial periods of time. The second class of inhibitor prevents agglomeration of hydrate crystals so that transportable slurry is maintained. This class is known as the anti-agglomerants.

2.5.1 Kinetic Inhibitors introduction.

Kinetic inhibition is a well-known technique in the oil industry for scale prevention but its use in hydrate inhibition is a relatively new technology. These chemicals can be effective at very low concentrations (< 1wt. %). They do not alter the thermodynamic conditions of hydrate formation. It delay hydrate nucleation and subsequent crystal growth [9]. Kinetic inhibitors are assumed to retard crystal growth by binding to the surface of hydrate particles in the early stages of nucleation and preventing the particle from reaching its critical size (the size at which particle growth becomes thermodynamically favourable). The duration of kinetic inhibition can be from several hours to days, which may exceed the residence time of fluids in process flowlines.

After testing more than 750 combinations of different chemical inhibitors, Long et al (1994) found high molecular weight polyvinylpyrrolidone (PVP) to be a good hydrate inhibitor [11]. In a similar study, involving the testing more than 1500 commercially available chemical combinations, three more chemical compounds with kinetic inhibition properties were found at

the Colorado School of Mines. These products were poly(N-vinylcaprolactam) or PVCap, a terpolymer, Nvinylpyrrolidone/ N-vinylcaprolactam/N, Ndimethylmethacrylate, with the commercial acronym of VC- 713 and a co-polymer of N-vinylpyrrolidone and Nvinylcaprolactam (VP/VC) made with different ratios of each constituent monomer.

2.5.2 Green Kinetic Inhibitors - Chitosan

One of the classes of green inhibitors is natural polymers, like starch. It was found that a little part of starch alone was able to delay the onset of nucleation in about 1.5 hr. Chitosan is a natural polymer with linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N acetyl-D-glucosamine (acetylated unit). Figure 4 illustrates the chemical structure of chitosan. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%) .As most of the present-day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives. However, these naturally abundant materials also exhibit a limitation in their reactivity and processability. Chitosan is recommended as suitable functional material, because this natural polymer has excellent properties such as biocompatibility, biodegradability, non-toxicity and adsorption properties. Recently, much attention has been given to chitosan as a potential polysaccharide source. Chitosan can be degraded by soil microorganisms and water microorganisms. This makes chitosan environmental friendly. It has been widely used in diverse fields ranging from waste management to food processing, medicine and biotechnology.

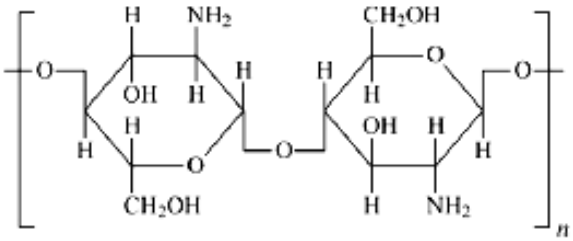


Figure 4 The construction of chitosan [5]

2.5.2.1 Production of Chitosan

Chitosan is commercially produced by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.). Extraction of chitin and chitosan was mainly employed by stepwise chemical methods [7]. Briefly, shells were ground to smaller sizes and minerals, mainly calcium carbonate, were removed by extraction with dilute hydrochloric acid followed by stirring at ambient temperature. The protein was extracted from the residual material by treatment with dilute aqueous sodium hydroxide and thereby prevents contamination of chitin products from proteins. The resulting chitin was deacetylated in 40 - 45% sodium hydroxide at 120ºC for 1- 3 hours with exclusion of oxygen, and followed by purification procedures to form chitosan with a cationic nature. The alkali removed the protein and the deacetylated chitin simultaneously. Depending on the alkali concentration, some soluble glycans would be removed. In the deacetylation process, some of the acetyl groups were removed from the molecular chain of chitin. This shortened the chain lengths of the chitin molecule, eventually leaving behind a polymer with a complete amino group called chitosan. This treatment produces 70% of deacetylated chitosan [7].

2.5.2.2 Properties of Chitosan

The physical, chemical and biological properties of chitin and chitosan depend mainly on two parameters: degree of deacetylation (DD) and molecular weight distribution, both of which are affected by the source of chitin and the method of preparation. The DD also plays a significant role in affecting the molecular weight of chitosan. A lower DD leads to a higher molecular weight

Chitosans are known for reducing the rate of hydrate crystal growth. Adsorption of the inhibitor on the hydrate crystal structure is considered as a key process in kinetic inhibition because it is believed that the adsorption of inhibitor alters the growth pattern. The hydrophilic pendant lactam ring of the known kinetic inhibitor is believed to play a key role. The action of kinetic inhibitor has also been attributed to the disruption of hydrate formation whereby the inhibitor prevents the contact between water and the hydrate forming substance, e.g. by blocking

transport of gas to the hydrate surface. Moreover, hydrogen bonding between inhibitors and hydrate surface is significant and the strength of the attractive interaction was correlated by the inhibiting strength. Chitosan are known to be highly hydrophilic and have high capacity to create hydrogen bonds with other entities in solution. It is possible that the anhydroglucose unit of chitosan fits within the hydrate structure in a manner similar to that for the hydrophilic pendant lactam group. Therefore, chitosans should have good inhibition effects for gas hydrate formation.

2.5.3 Kinetic Inhibitors Performances Evaluation

These compounds are designed to delay nucleation and/or prevent crystal growth. The performance level of kinetic inhibitors can be investigated by different methods such as hydrate formation rate, subcooling, total volume of hydrates formed, plugging of a flow loop or stirred cell but the main technique remains the determination of the induction time [12]. The efficiency of a kinetic inhibitor on gas hydrates is essentially based on the induction time (ti). The ti value is the period between the moment the system enters the hydrate region and the moment the gas hydrates formation takes place [13].

Traditionally, rocking-cell, autoclave and flow-loop testing are used for evaluating the kinetic inhibitor performance. These testing methods commonly required large quantities of chemical, can be time consuming and also require a large number of replicate runs to statistically evaluate kinetic inhibitor performance. Thus, to overcome those, a differential scanning calorimeter (DSC) can be utilized to study the nucleation of hydrates in a stable water-in-oil test matrix. DSC is a rapid and versatile technique that can be efficiently used for analytical, thermodynamic, and kinetic studies. Specific gastight pressure-controlled cells, which can accept any type of sample such as dense and viscous fluids that contain solids, are commercially available. The present work has shown that DSC could be a very useful tool for hydrate formation studies.

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

when the specimen undergoes thermal transition. The following experimental studies can be done using DSC for different emulsion and kinetic inhibitor:

1. Determination of dissociation points of hydrates as a function of pressure (measurements under thermodynamic equilibrium).
2. Kinetic measurements.
    - During cooling at constant scanning rate: determination of the maximum degree of supercooling and, eventually, kinetics of hydrate formation after nucleation.
    - Isothermal studies: hydrate formation at a fixed temperature; determination of the induction time and plotting of the TTT curves.
    - During heating at constant scanning rate: evolution of the amount of hydrates formed after different thermal treatments (isotherms, temperature gradients, quenching, etc.).

METHODOLOGY

3.1 Research Methodology

The following chart is the step-by-step procedure for this project

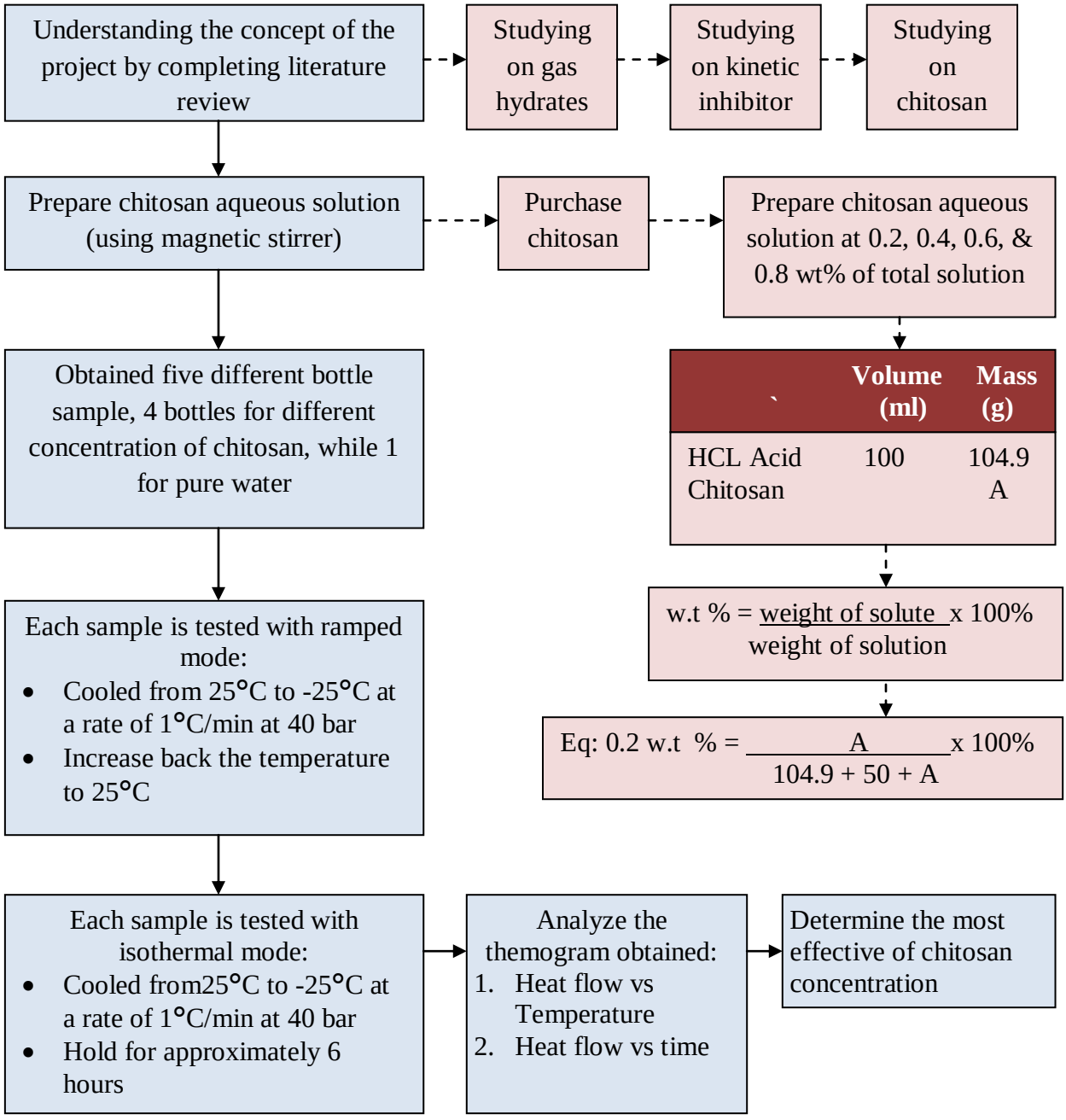


Figure 5 Flowchart of proposed experiment

3.2 Project Activities

- **Literature review**

  The first half of this project will be focus on research and collecting information regarding the Chitosan as Gas Hydrates Kinetic Inhibitor. The summar of the activities are as following:

  a) Gathering the information from journals, papers, article, books and published thesis
  b) Study the characterization of the gas hydrates
  c) Understanding the way to inhibit the gas hydrates using both thermodynamic and kinetic inhibitor.
  d) Study on the characterization of chitosan
  e) Prepare the literature review

- **Experiment**

  Below are the planned activities for the experiment:

  a) Survey on the availability of the machine, equipment needed.
  b) Purchase the chitosan and prepare the solution
  c) Study on the correct methodology of the experiment.
  d) Start the experiment using the Differential Scanning Calorimetry (DSC)
  e) Evaluate and discussing the result of the experiment
  f) Prepare the final report of the project.

3.3 Gantt Chart

No	Task Name	Week 1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of FYP topic							MIDSEM BREAK							
2	Preliminary research work														
3	Submission of Preliminary Report														
4	Literature review														
5	Experimental preparation														
6	Start the experiment														
7	Evaluate the experiment result														
8	Preparation of report and presentation														
9	Final presentation														
9	Interim Draft Submission														
10	Interim Final Report Submission														

Figure 6 Gantt Chart

3.5 Tools (eg. Equipment, hardware, etc.) Required

- Micro Differential Scanning Calorimetry (Micro-DSC)

Micro - DSC is designed for the study of samples (denaturation, transition, gelifi cation, reaction, etc.) in isothermal and scanning mode (no external cooling system is needed) over a wide temperature range (–45 to 120°C). The equipment available in the laboratory is product of *Micro- DSC Evo 7* by *Setaram Instrument.*

The equipment technical specifications are as following:

- Temperature range: -45 °C to 120 °C ; Cooling under 0 °C requires the use of an auxiliary thermostat
- Programmable temperature scanning rate (heating and cooling): 0.001 to 2 °C.min-1
- RMS Noise: 0.4 microW
- Resolution: 0.02 micro W / 0.002 microW
- Cells: 1 ml, made of Hastelloy C – Removable Batch, mixing batch, ampoule and high pressure
- Pressure (measured & controlled): 400 bar / 5800 psi or 1000 bar / 14 600 psi requires the use of high pressure cells and gas panel
- Weight: 37.4 kg (82.5 lbs)
- Dimensions: 40 / 53 / 58 cm (15.7 / 20.9 / 22.8 in)
- Power requirements: 230 V / 50/60 Hz

Figure 7 – *Micro DSC Evo 7*

DSC functionality is as following:

a) Measures amount of heat flow into samples (endothermic) and away from the sample (exothermic) when the specimen thermal transition.
b) Generate the thermogram that is including the result of heat flow convention whether endothermic or exothermic vs time or temperature

RESULTS AND DISCUSSION

4.1 Report on Samples Preparation

Chitosan is a semi-crystalline polymer, a weak base, which is insoluble in water, alkali or aqueous solution above pH 7 and common organic solvents due to its stable and rigid crystalline structure. The technical specs of chitosan are as following:

R&M® Chemicals

Chitosan, "Biochem":

CAS Number:		9012-76-4	
Catalogue Number:		4052-00	
Packing Size:		100 g	
Specification:			
Viscosity(1%, 20oC)		10-1500mPa.s	
Moisture contect	<10	%	
Degree of Deacetylation		70-97	%
Amino content		<6.5-8.5	%
Ash content		<1	%
Arsenic(As)		<0.0002	%
Heavy metals(as Pb)		<0.001	%

Appearance:
transparent to translucent white/yellow shapeless solid.

Figure 8 Chitosan Technical Specs

From the technical specs, it shows that chitosan has a transparent to translucent white/yellow shapeless solid. Example figure of the chitosan can be seen as Figure 10 below. Because of the water non-soluble characteristics, the chitosan need to dilute with others liquid, for example acids. Thus, hydrochloric acid (HCL) choose to be the medium for the dilution process due to the cost saving, availability and its characteristics of pH, which is less than pH 6.

Figure 9 Example Chitosan Sample

Initial plan was to using a 50 ml of HCL for all 4 samples, but, due to constraint, 10 ml of HCL will be used for the each sample. The concentration of HCL is 0.1M. Convert the 10ml of HCL equal to 12.01g. Following are the calculation of the weight of chitosan that need to use for each sample with concentration of 0.2 w.t % , 0.4 w.t % , 0.6 w.t % and 0.8 w.t % :

1. **Sample 0.2 w.t %**

$$0.2 = \frac{A}{12.01 + A} \times 100\%$$

$0.998A = 0.02402$

A = 0.0241g

2. **Sample 0.4 w.t %**

$$0.4 = \frac{B}{12.01 + B} \times 100\%$$

$0.996B = 0.04804$

B = 0.0482g

3. **Sample 0.6 w.t %**

$$0.6 = \frac{C}{12.01 + C} \times 100\%$$

$0.994C = 0.07206$

C = 0.0725g

4. **Sample 0.8 w.t %**

$$0.8 = \frac{D}{12.01 + D} \times 100\%$$

$0.992D = 0.09608$

D = 0.0969g

So, the using the Precisa Weighing equipments with weighing range of 220g with readability of 0.1 mg, chitosan was segregated into 4 different plate with different weight as per calculation before. After that, 10ml of HCL acid pour into 4 different 100ml beaker. The beakers then mix with the respected chitosan per grams per sample . The mixture then being heated for 20˚C for 30minutes using a magnetic stirrer. After 30 minutes, the chitosan dilute with acid and ready for the next step of the experiments.

Figure 10 Lab apparatus use for sample preparation, (From left) Magnetic Stirer, Precisa Weighing, HCL Acid and beaker

4.2 Report on Ramped Mode Experiment

Initially, the ramped mode test was used in the micro-DSC by following to the procedure in the methodology. This cooling-heating cycle was to observe the effects of chitosan to the ice / hydrate formation. Four different samples were prepared which are:

i. Distilled water
ii. 0.4wt% chitosan
iii. 0.6wt% chitosan
iv. 0.8wt% chitosan

Firstly, the sample was being prepared. For each cell, the required amount of chitosan / distilled water is 0.15ml since the cell total volume is 0.33ml and in order to prevent the chitosan from spilled out from the cell, the amount of liquid of samples are restricted to the amount. But before putting the sample inside the cell using the shrink, the weight of the blank cell is required. And after the sample already inside the cell, the cell is again weight to find the mass of the sample.

The cell then being put inside the micro-DSC and all the preparation for the experiment is being done by the lab technician as the equipments is highly valuable. After put the cell to the respected location, the setting for the experiments was being set at the computer. Information such as furnace temperature, experiment mode, pressures, mass of sample, rate of cooling/heating, and others were being set to the desired value, as the methodology prepared. For each samples, the experiment will take around 2 hours to finish.

Heat flow vs. temperature data were gathered and plot in the graph. From this graph, phase transitions can be determined by looking at the dips and peaks of the graph which represent the total heat flow in (endothermic) or out (exothermic) of the samples. Figure 12 shows a thermogram (heat flow vs. temperature) of all four samples.

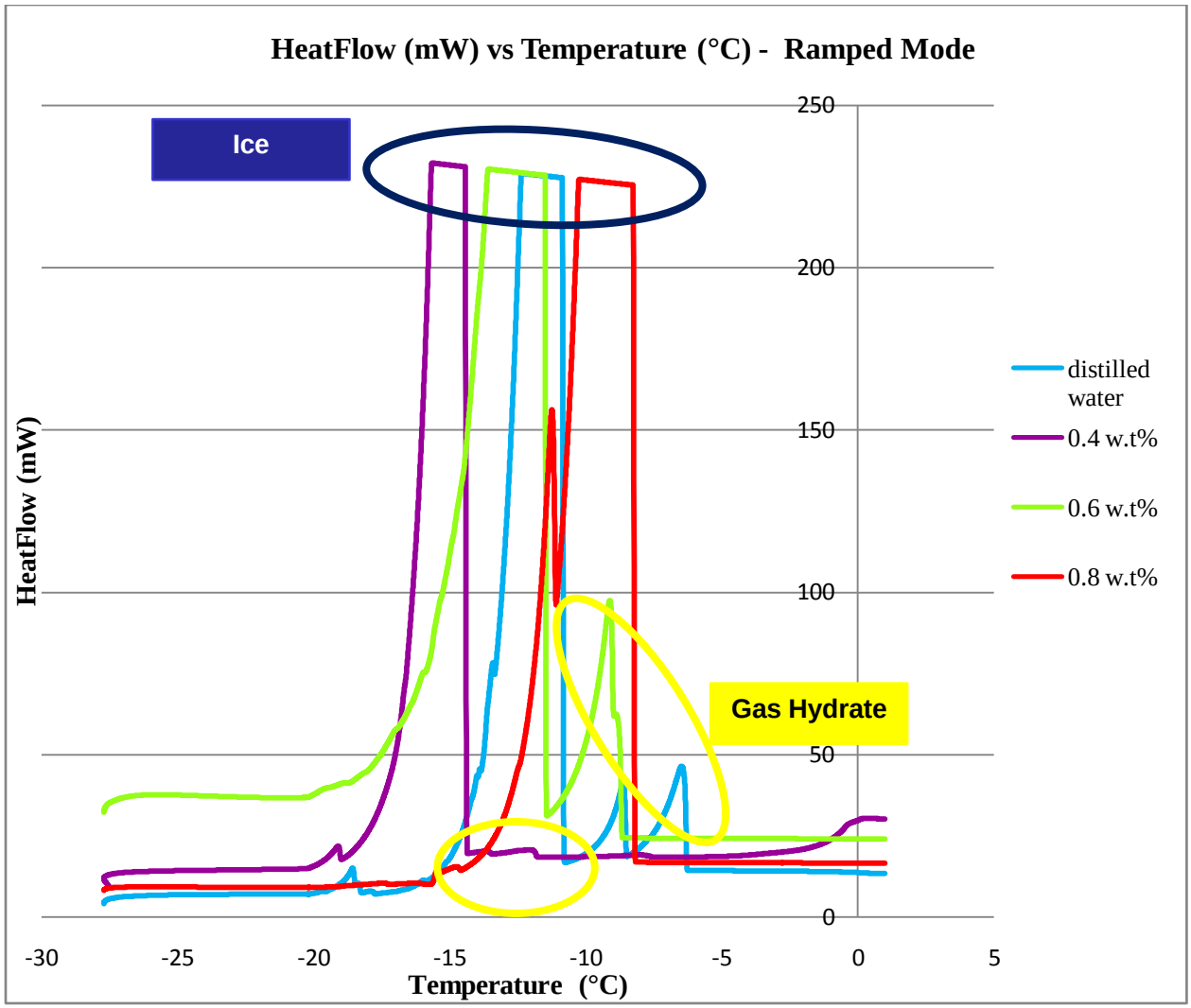


Figure 11 HeatFlow (mW) vs Temperature (°C) - Ramped Mode

Upon cooling, two exothermic responses were measured indicating nucleation and growth of both hydrates and ice phases and both exotherms occurred at temperatures below 0°C. Therefore, further analysis was needed to determine which exotherm corresponded to hydrate and ice nucleation.

Differentiating hydrate exotherms from ice exotherms is relatively straightforward. Hydrate formation from an immiscible guest requires contact between the water and the guest phase, in this case the vapor phase. A thin hydrate film typically forms at the interface. However, water can convert entirely to ice. Hence the ice phase fraction should be much greater than that of the hydrate when formed from a gas phase guest.

According to Figure 12 it is clearly seen that there are two peaks of exotherms and already being shows the hydrates and ice formation differently. Also, this experiment shows the effect of chitosan to the ice/hydrates formation. Based on Figure 12, as the chitosan concentrations is getting lower, the formation of ice/hydrates is shifted into lower temperature, which mean the concept of low-dosage- hydrates inhibitor is apply here.

Also, in the literature review part, chitosan are claim to be an anti-freeze protein, as which the kinetic inhibitor is inspired by the anti-freeze protein for enable them to survived in climate condition. Based on the Figure 12, its shown the effect of chitosan to shifted the ice formation to lower temperature, compared to distilled water.

CONCLUSION & RECOMMENDATIONS

Based on research, studies and experiments carried out throughout this period, it is still unclear whether chitosan can be a great substitute for common kinetic inhibitor such as PVP as for unforeseen reason, some experiments cannot be done. But, the experiments conducted proven that chitosan shifted the temperature drastically in the ice/hydrates formation. Also, from the results, the concept of kinetic inhibitor as low-dosage inhibitor was proven because the less concentration of chitosan prove to be the farthest temperature shifted during exotherms region. Also the claim that chitosan is a good anti-freeze protein are proven as the ice formation for chitosan sample required lower temperature to perform.

For recommendations of future research of this project, the lists are as following:

1. Continue the research with the Isotherms experiments in order to really prove the effectiveness of chitosan.
2. The ramped mode experiments can be test with 2-3 runs to find the optimum results
3. With the availability of Micro-DSC, we can find the effect of subcooling for differents pressure.
4. Researching more about chitosan and its understanding the characteristics. In order for that, there can be another experiments to find the addition information to helping the research about gas hydrates.

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