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EXPERIMENTAL INVESTIGATION OF MODIFIED STARCH FROM WHITE CORN AS A KINETIC INHIBITOR OF GAS HYDRATE

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Abstract

Economic and environmental considerations have motivated the search for kinetic inhibitors from readily available and inexpensive materials to effectively control gas hydrate formation and provide flow assurance in oil and gas production systems. This work experimentally investigated the effect of modified starch in inhibiting gas hydrates. The starch from white corn was modified by oxidation and applied in low dosages (0.01wt%, - 0.05wt %) in a constant volume experiment conducted in a laboratory hydrate flow loop used to simulate subsea pipelines. The pressure time profile for experiments conducted was evaluated based on the gas dissolution time, nucleation time, and hydrate growth time. The effectiveness of the modified starch was indicated by how much gas was used up in forming hydrates during the experiments conducted. 0.04wt% of modified starch was the optimal dosage of inhibitor in this study as it showed less reduction in pressure implying less gas was used. When the performance of modified corn starch was compared with the performance of similar experiments done in the same equipment using polyvinylpyrrolidone (PVP), N-vinylcaprolactam (PVCap), and 2-(dimethylamino)ethylmethacrylate (DMEM) as hydrate inhibitors, Modified starch performed best. Modified corn starch is an efficient, inexpensive and environmentally friendly hydrate inhibitor.

***Keywords**: Modified starch; Kinetic hydrate inhibitor; Flow assurance; Offshore production; Hydrate inhibition.*

1. Introduction

Natural gas is typically composed of methane, which is often accompanied by higher molecular weight hydrocarbon gases and non-hydrocarbon gases. Hydrate formation is a big flow assurance challenge to surface production. It can block surface production facilities and flow lines, causing a reduction in production, increased back pressure, and, ultimately, a rupture or explosions. Subsequently, this can lead to environmental and equipment damage as well as the loss of life. Flow assurance is of dominant importance in systems where associated problem troubleshooting and subsequent intervention are time consuming [1]. Flow assurance deals with the continuous flow of hydrocarbon from the reservoir through surface production facilities and transport channels to the point of sale in harmony to production plans.

Gas hydrates are ice-like crystalline inclusion compounds that are formed at high pressure and low temperature conditions in the presence of water and gas hydrate formers such as methane, ethane, or propane [2]. Hydrate formation is greatly influenced by the nature of the reservoir fluid produced. Hydrates can be formed both in oil and gas systems when one or more hydrate guest molecules (Figure 1) is present in the reservoir fluid. The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules. These crystalline compounds are divided into three main types of crystallographic structures: structure sI, structure sII, and structure sH (Figure 1). The most abundant hydrates are of types of structure sI and sII. The third structure, sH, is rarely seen outside the laboratory [3].

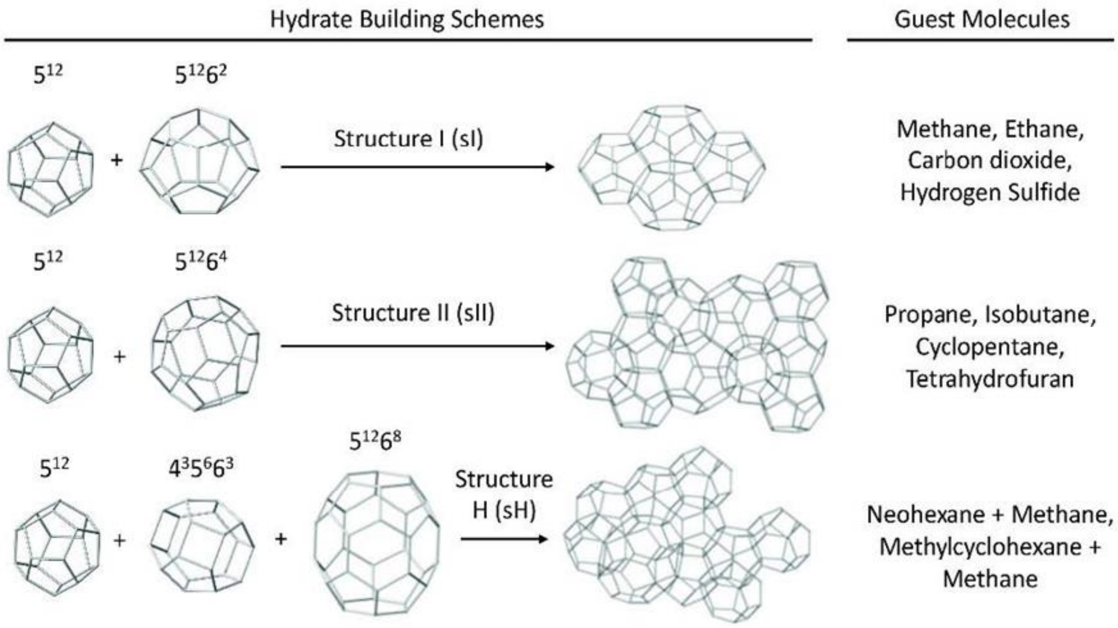

Figure 1. Structures of the gas hydrates sI, sII and sH [3]

In the petroleum industry, hydrates usually form at the liquid-gas interphase where free water and small hydrocarbon molecules are in contact. The mixing and turbulence of the flow further increase the contact between the two thus causing the formation of more hydrates. Hydrates then start to agglomerate until they eventually plug the pipe. [1].

Over the years, thermodynamic Inhibitors (THIs) such as methanol and glycols have been used to prevent the formation of gas hydrates and avoid plugging of transportation and processing facilities [4]. However, the use of THI in offshore developments is costly due to the high treatment volume (10–60 wt. %) required [5].

Cost considerations motivated the search for chemicals required at a low dosage to prevent hydrate plug formation. These groups of inhibitors are called Low Dosage Hydrate Inhibitors (LDHI) and are usually surfactants and polymers. LDHIs are usually dosed at a concentration of 0.1-1.0 wt % (active component) based on the water phase.

LDHI does not prevent hydrate formation but it interferes with hydrate nucleation, growth and agglomeration of hydrate particles [4]. LDHIs are subdivided into kinetic inhibitors (KI) and anti-agglomerates (AA). Kinetic Inhibitors (KIs) delay hydrate nucleation and/or crystal growth while anti-agglomerators (AAs) prevent the agglomeration of hydrates so that all the hydrate crystals are transportable and do not build up in the pipe [2]

Due to the negative environmental impact of some of the existing LDHI, research has shifted towards obtaining environmentally friendly LDHI, such as modified starch. When starch is modified, it becomes highly hydrophilic and has a high capacity to create hydrogen bonds with other entities in solution. Modified starch, which is polar/hydrophilic, attaches and pulls on the hydrogen bonds of the water molecules in the gas-hydrate system. Subsequently, this pulling force becomes greater than the unidirectional force pre-existing within the gas-hydrate system thus breaking the hydrate system and inhibits its formation. Erfani *et al.* [6] proposed a mechanism for the hydrate inhibition effect of starch (Figure 2). The anhydroglucose unit of starch fits within the hydrate structure in a manner similar to that for a hydrophilic pendant lactam group.

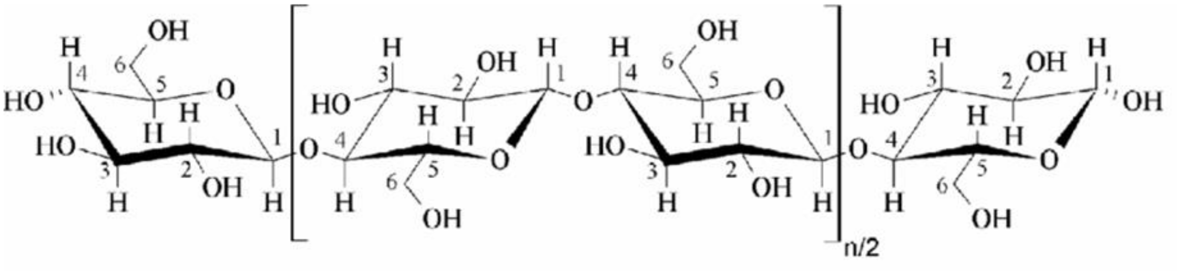

Figure 2. Anhydroglucose unit AGU(n)

Xu *et al.* [7] observed that pectic, which is cheap and naturally occurring, could tremendously improve the induction time of methane hydrate nucleation and retard hydrate crystal growth. During his investigation, the induction time extended 10 times than the commercial hydrate inhibitor. Lee *et al.* [4]) studied the performance of a number of cationic starches derived from natural starch as kinetic hydrate inhibitors. It was found that tapioca starch alone was able to delay the onset of nucleation by about an hour and a half.

Talaghat *et al.* [2] caried out an investigation on modified starch and polyvinylpyrrolidone (PVP) as a kinetic inhibitor. He showed that the rate of gas hydrate formation is directly proportional to the gas consumption. It was also observed that the gas consumed during the gas hydrate formation is reduced when PVP or modified starch is present in the liquid phase.

This work discusses the use of modified corn starch as a kinetic hydrate inhibitor. The gases used in the experiment are structure I hydrate formers.

2. Methodology

The study was carried out in two phases: the first phase was the experimental modification of starch, while the second phase was the use of the modified starch as a gas hydrate inhibitor in the experimental hydrate flow loop.

2.1. Modification of starch

Materials used in starch modification include 25g of soluble corn starch, 50mL of distilled water, pH paper, 2M sodium hydroxide (NaOH), 15% sodium hypochlorite (NaOCl) solution and 1M sulfuric acid. The equipment used for starch modification include analytical weighing balance (Model Radwag AS220/C/2), round bottom flasks, and glass beakers. To modify the starch, the following procedure was adopted:

25g of corn starch was first dissolved in 50mL of distilled water. Thereafter, the pH of the solution was adjusted to 10.0 using 2M sodium hydroxide (NaOH) solution. The adjusted pH solution was constantly stirred while 10mL of 15% sodium hypochlorite (NaOCl) was gradually added drop wise. After the addition of the sodium hypochlorite, the reaction was allowed to proceed for another 10mins. At the end of the reaction time, the solution pH was re-adjusted to 7.0 by gradually and carefully adding 1M sulphuric acid (H_2SO_4) solution with continuous stirring. The reaction mixture was allowed to stir for a few more minutes, after which the modified starch was left to settle out of the solution. The modified starch sediments were filtered and washed 3 times with distilled water; then, it was allowed to air dry under ambient conditions.

2.2. Hydrate inhibition

To check the effectiveness of the modified starch in inhibiting hydrates, experiments were conducted using modified starch as an inhibitor in a laboratory hydrate flow loop. Materials used in this experiment include compressed natural gas (CNG), modified starch as hydrate inhibitor (0.01wt% -0.05wt %), water, and ice-blocks. The equipment used in this study is a multi-component closed loop of 12m fabricated using 316 stainless steel pipe of 0.5 inch internal diameter, enclosed in an insulated 4inch polyvinylchloride (PVC) pipe (Figure 3). The loop was fitted with pumps, temperature gauges, pressure gauges, differential pressure transmitters, a gas mixing vessel, an inhibitor mixing vessel, and a natural gas cylinder.

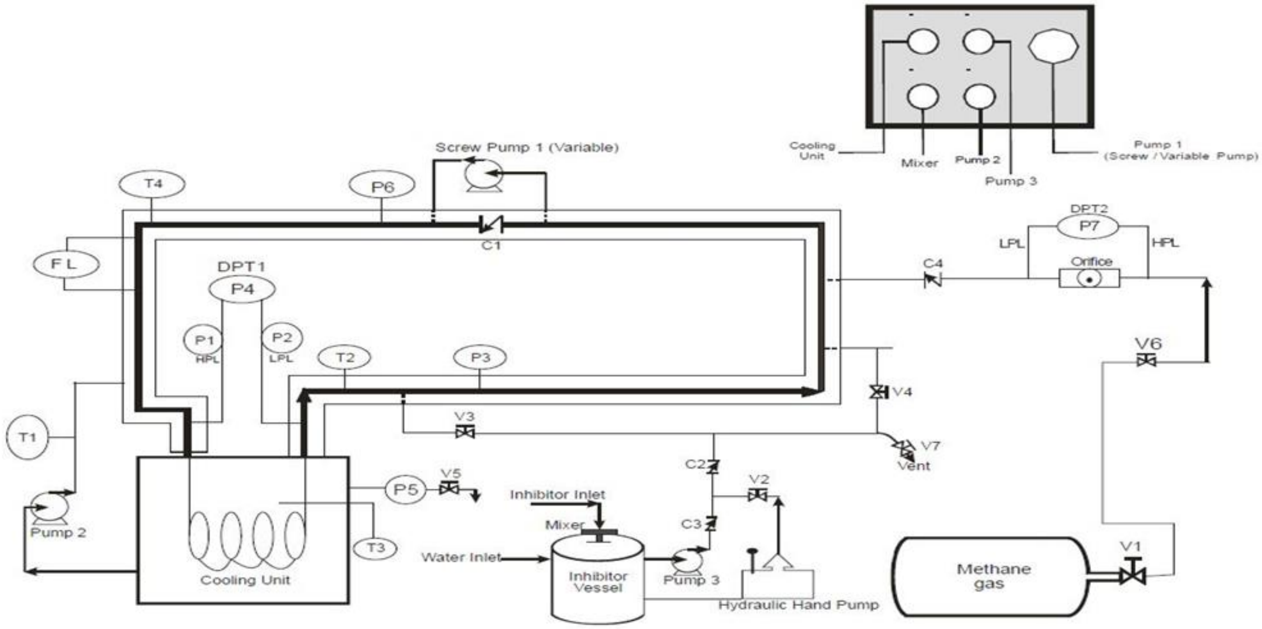

Figure 3. Process flow diagram of the flow loop [8]

The procedure for the control experiment (without inhibitor) is as follows:

a) Tap water was poured into the inhibitor vessel.
b) Valve 5 and pump 3 (Figure 3) were turned on to pump the content of the inhibiro vessel into the loop. Valve 5 is closed and pump 3 turned off when loop pressure attains 25psi
c) CNG was injected into the system by turning on valve 1, valve 6, valve c4, and the orifice. The valves were turned off after attaining a loop pressure of 150psi.
d) Ice was added to the refrigerating unit to facilitate the rapid cooling of the loop such that the loop can quickly attain hydrate formation temperatures.
e) The screw pump (pump 1) was turned on to cause agitation in the loop while the cooling water pump (pump 2) was also turned on to continuously circulate cooling water around the 0.5" pipe through out the 2 hours experiment.
f) The inlet and outlet pressures and temperatures, as well as refrigeration unit temperature and sample point pressure, were recorded every minute during the two-hour experiment
g) At the termination of the experiment, valve 5 was opened to observe hydrate formation in the ¼" pipe.

To investigate the effectiveness of modified starch in inhibiting hydrates, experiments were conducted with 0.01wt%, 0.02wt%, 0.03wt%, 0.04wt%, and 0.05wt% respectively of modified starch in 5 different experimental runs. The procedure is as follows:

a) 2660ml of water containing measured dispersed modified starch was poured into the inhibitor vessel.
b) Repeat step b to step g in the control experiment.

3. Results and discussion

Constant volume batch process hydrate formation and inhibition experiment were conducted in the laboratory loop. Hydrate formation was indicated by a reduction of loop pressure because the extent of loop pressure reduction is an indication of how much gas was used up in forming hydrates in the loop. Hydrate formation was also indicated by a partially plugged ¼ inch sample point (valve 5).

The pressure – time plot for all experiments conducted in this study is presented in Figure 5, and it showed a similar trend of reduction in pressure with time. This trend has been divided into three stages namely as shown in Figure 4:

1. The first rapid pressure drop stage, corresponding to the dissolving of gas in the liquid phase.
2. The stable pressure stage, representing the induction of nucleation.
3. The second pressure drop stage, denoting the growth of hydrate crystals.

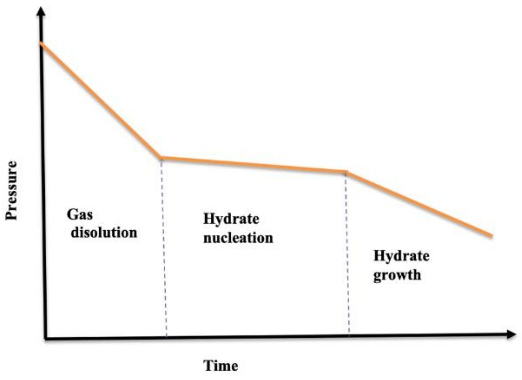

Figure 4. Three stages of pressure drop in the flow loop experiment

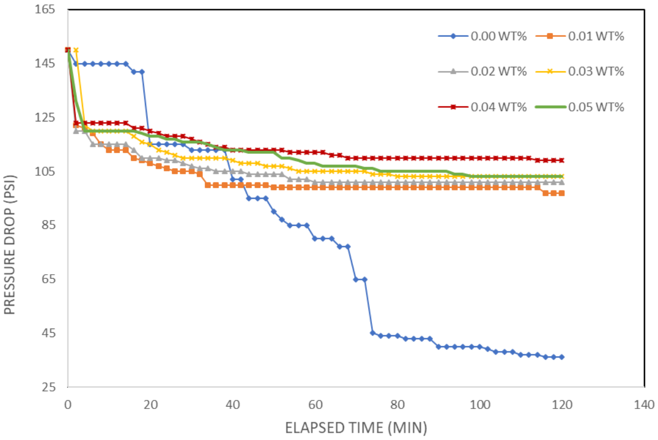

Figure 7. Comparative analysis of pressure drop versus elapsed time for 0.00wt % - 0.05wt% of modified starch

In the experiment conducted without inhibitor (0.00 wt% modified starch), the pressure of the loop decreased as the gas was used up in forming hydrates. The first stage of rapid pressure-drop lasted for 20minutes, and this was closely followed by the stage where pressure was stable for about 18 minutes and subsequently, the second rapid pressure-drop stage lasted for about 40minutes. At the end of the experiment, about 900mL of very cloudy effluent containing hydrates crystals was obtained from the loop. Notice the rapid reduction in the third stage indicating the rapid growth of hydrate in the experiment without inhibitors.

The experiment conducted with varying concentrations of modified starch showed a similar trend. There was a stage of rapid pressure drop followed by a stage where the pressure stabilized and, subsequently, a stage with a second significant pressure drop (Figure 5). The time of occurrence of these three stages in the experiments conducted with varying concentrations of modified starch is summarized in Table 1. It was observed that increasing the concentration of modified starch used in the system increased the gas dissolution time and hydrate nucleation. However, there was no definite pattern for the effect of increased modified starch concentration on hydrate growth.

Table 1. Time for different stages in the experiment with modified starch

Inhibitor volume (wt. %)	Gas dissolution time (minutes)	Nucleation time (minutes)	Hydrate growth time (minutes)
0.00	20	18	82
0.01	30	70	32-18
0.02	48	65	7
0.03	70	48	6
0.04	70	48	4
0.05	76	44	7

Table 2 shows the pressures at the start of the experiment and pressures at the end of the experiment for each concentration of modified starch used in this study. The difference in pressure between the initial system pressure and the final system pressure is an indication of how much gas was used up in the constant volume experiment. A high volume of gas used is an indication of a poorly inhibited system as a lot of hydrates was formed with the gas used up. The difference in pressure for the uninhibited experiment was 114psi implying that most of the gas in the system was used up in forming hydrates. Note that 0.04wt% is the optimum inhibitor dosage in this study as it has the lowest pressure difference implying that less gas was consumed in forming hydrates when 0.04wt% of modified starch was used as an inhibitor in the 2 hours experiment conducted in the laboratory hydrate loop.

Table 2. Pressure variation of different stages in the experiment

Inhibitor volume (wt. %)	Initial system pressure (psi)	Final system pressure (psi)	Difference between initial and final pressure (psi)
0.00	150	36	114
0.01	150	97	53
0.02	150	101	49
0.03	150	103	47
0.04	150	109	41
0.05	150	103	47

3.1. Comparing the performance of modified starch with the performance polyvinylpyrrolidone (PVP), N-vinylcaprolactam (PVCap) and 2-(dimethylamino)ethylmethacrylate (DMEM)

Hydrate inhibition experiments were conducted by Odutola *et al.* [8] using the same equipment and conditions as described in this work. The inhibitors used in Odutola *et al.* [9] are poly vinylcaprolactam, poly vinyl pyrrolidone and and 2-(dimethylamino)ethylmethacrylate. Table 3 shows the time taken for the three pressure drop stages in the experiment conducted with 0.05wt% NVCap, 0.05wt% PVP, and 0.05wt% DMEM. Note that the concentration 0.05wt% of NVCap and PVP was the optimum concentration in a series of experiments conducted in the flow loop using these polymers [10].

Table 3. Time for different stages in the experiment with NVCap

Inhibitor volume (wt. %)	Gas dissolution time (minutes)	Nucleation (minutes)	Hydrate growth time (minutes)
0.05 NVCap	38	52	30
0.05 PVP	26	52	42
0.05 DEMA	14	36	70

Table 4 shows the initial pressure and final pressure of the experimental loop when 0.05wt% PVP, 0.05wt% NVCap, and 0.05wt% DMEM respectively were used as inhibitors in the experimental flowloop. Notice that the PVP and NVCap performed better than the DEMA. However, when these polymers are compared with the performance of modified starch, modified starch performed best. This is because, with 0.04wt% modified starch as an inhibitor, the lowest pressure difference of 41psi (Table 2) was recorded.

Table 4. Pressure variation of different stages in the experiment

Inhibitor volume (wt. %)	Initial system pressure (psi)	Final system pressure (psi)	Difference between initial and final pressure (psi)
0.05 NVCap	150	105	45
0.05 PVP	150	105	45

4. Conclusion

Corn starch can be successfully modified for use as a kinetic hydrate inhibitor. The modified starch can inhibit hydrate formation by increasing the gas dissolution time and the nucleation time. The effect of modified starch on hydrate growth time was not effectively captured by this study due to the 2 hour duration of the experiment conducted. 0.04wt% modified starch proved to be the optimum dosage of modified starch for preventing natural gas hydrate formation in the laboratory hydrate loop. Polyvinylpyrrolidone (PVP), N-vinylcaprolactam (PVCap), and 2-(dimethylamino)ethylmethacrylate (DMEM), modified starch performed best as its optimum dosage was 0.04wt% which is lower than 0.05wt% optimum dosage requirement of PVP and PVCap. Modified starch is an environmentally friendly alternative for hydrate inhibition.

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