Mitigation of Hydrate Formation Using a Water-Soluble Plant Polymer

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Abstract

This study investigated the effectiveness of two KHI samples, hereafter referred to as samples A and B, made from water-soluble plant polymers to mitigate hydrate formation. The effectiveness of samples A and B in preventing hydrate formation when combined with a Thermodynamic Hydrate Inhibitors (THI) called Monoethylene Glycol (MEG) was also evaluated. The inhibitor efficiency was studied in hydrate formation experiments conducted in a 12-meter laboratory hydrate closed loop. Sample A efficiently prevented hydrate formation at a concentration of 0.05wt%, while the optimum dosage of sample B was 0.06wt%. The performance of samples A and B significantly improved when blended with MEG. The hybrid of 0.04wt% Sample A and 0.4 wt% MEG reduced hydrate growth in the loop. The final pressure was 88 psi indicating less gas was used in forming hydrates than in the uninhibited system with a pressure of 54 psi. The hybrid of 0.4wt% sample B and 0.07wt% MEG also significantly reduced hydrate growth in the loop giving a final pressure of 102 psi at the end of the experiment. The plant polymers samples effectively prevented hydrate formation in the 12-meter hydrate flow loop when applied in low dosages. Subject to validation from a field test, the plant polymer inhibitors can provide cost-saving benefits if used to replace or augment the traditional THIs.

Keywords: *Hydrate inhibition, Flow assurance, Plant polymer, Flow loop, Offshore flowlines*

1. Introduction

Emerging technologies and societal developments have contributed significantly to the increase in world energy demand. The search for more hydrocarbons that will help bridge this increasing demand and yield the requisite revenue and profit for industry players in the upstream oil and gas business has led to severe development of the deep and ultra-deep offshore environment. However, offshore oil and gas production is not without challenges; ranging from harsh marine environment (low temperature and high pressure), unpredictable environmental loads (waves, wind and current), and deep water depths, amongst others. These issues must be accounted for to ensure that flow assurance problems such as wax production, asphaltenes, hydrate formation, corrosion, scale formation, slugging etc., are eliminated or reduced to the minimum. Natural gas hydrates are cage-like structures, also known as a clathrate, formed when gas (often methane) and water occur in the right conditions of low temperature and high pressure. It consists of 85 mole % of water (host molecules) and 15 mole % of gas (guest molecules) and, as a result, shares the characteristic physical properties comparable to that of ice, especially in appearance and mechanical properties.

Recent research suggests harnessing the potential of gas hydrates as an essential energy source and a medium for storing and transporting natural gas because the volume of gas created upon its dissociation is 150 times greater than the hydrate solid. However, it is still a dreaded operational problem, especially in subsea oil and gas production, as plug acceleration due to pressure gradient can cause damage to the production facility, and its remediation presents high safety and technical difficulties with significant cost implications. This understanding has sparked great interest in preventing hydrate formation in gas production systems.

Four conditions must be satisfied for hydrates to form in a subsea production facility, namely: Presence of (i) water, (ii) light hydrocarbon gas (guest molecules), (iii) high pressure and (iv) low

temperature (Bai *et al.,* 2010). Other factors that affect but are not necessary for hydrate formation include turbulence, nucleation sites, surface for crystal formation, agglomeration, and the salinity of the system (Sloan and Koh, 2007). Hydrates are classified into three structures based on the arrangement of the water molecules in the crystal structures: structure I (sI), structure II (sII) and structure H hydrates. The nature of the guest molecules (size and composition) influences the hydrate structure. The two most abundant hydrate structures in the petroleum industry are the sI and sII. Hydrate formation occurs in four stepwise stages: (i) Diffusion of gas into water, (ii) Nucleation, (iii) Crystal Growth and (iv) Agglomeration. Nucleation cannot occur without the diffusion of gas into the interstitial cavities of the water molecule, and nucleation births crystal growth in the continued presence of water and formation conditions, leading to agglomeration, which may block and impede flow through the pipeline. (Ripmeester, 1987).

Knowledge of the conditions that necessitate hydrate formation has provided a guide in proffering solutions to the dreaded menace. The following methods have been used to prevent hydrate formation: (i) Water removal, (ii) Insulation, (iii) Low-Pressure operation, (iv) Active Heating, (v) Flow rate regulation (Odutola, 2022[a]) and (vi) Chemical inhibition using thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs). Thermodynamic hydrate inhibitors (THI) prevent hydrate formation through the depression of the temperature at which hydrates form by altering the chemical potential of water, thereby shifting the equilibrium to a lower temperature and reducing the region where hydrates can exist. This is applicable to adding antifreeze to water to lower its freezing point. THIs include methanol, ethanol and glycols. These antifreeze compounds suppress the hydrate formation temperature with a drawback. Methanol and Mono Ethylene Glycol are the most used. Their injection rate remains a function of the water production and inhibition dosage. Inhibitor dosage is a function of design temperature, pressure, and composition of the produced fluid (Bai *et al.,* 2010).

Injection of Low Dosage Hydrate Inhibitors (LDHIs) in place of the thermodynamic hydrate inhibitors has been considered the most interesting option regarding new methods to prevent hydrate blockage, although they are not extensively used in the industry (Peytavy *et al.,* 2007). LDHIs are inhibitors used in much lower quantities compared to THIs. The required dosage concentration lies within 0.5-4wt % versus the water rate. LDHIs are further classified into Kinetic Hydrate Inhibitors (KHIs) and Anti-Agglomerates (AAs) Mitchell and Talley (1999) investigated the effect of a KHI, N-vinyl, N-methylacetamide-co-vinyl caprolactam (VIMA-VCap) on hydrate inhibition. The KHI successfully inhibited hydrate formation in a 4-inch, 2.8 mi long oil flow line operated by Imperial Oil Resources Limited (IORL). Swanson and Petrie (2005) discussed the use of Kinetic Hydrate Inhibitor with the addition of paraffin control additives for more than half a year in the Gulf of Mexico. The field application was conducted on a pipeline for a newly re-completed well which was predicted to have water cuts in the 20% range. Based on lab testing and computer modelling data, the kinetic hydrate inhibitor was chosen. The KHI provided lower operating costs and better environmental conditions than methanol, which had been used before the well was re-completed. It was seen that with KHI, there was no undesirable methanol in the crude and no oil/water quality issue.

Wu et al. (2007) performed a field test by adding a tertiary-polymer, VC-713 inhibitor, to a sea well mouth in Beihai. Under the field test condition of adding 0.5% VC-713 inhibitor, it was found from the experiments that VC-713 inhibitor did not reduce the effort of clearing away hydrate of methanol under the condition of hydrate formation. VC-713 was more economical than methanol, polymeric inhibitors exhibit a better efficiency, and a combination of THI/LDHI gave a better result. Lee et al. (2007) investigated the kinetic inhibiting effect of several cationic starches (Tapioca, Raifix, Raisamyl and Raisabond) in an experiment they performed with methane and methane/ethane mixtures. The starches exhibited a weak inhibitive effect for tapioca starch, increasing the induction time. When additives such as poly ethylene oxide (PEO) were added, the starch's performance was enhanced for all the starches used. It was thus concluded that the addition of starch and PEO influenced the induction time in the opposite direction of hydrate memory, thus giving a suppressed memory effect. Odutola et al. (2019) 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. 0.04wt% of modified starch was the optimal dosage of inhibitor in this study. The performance of modified corn starch was compared

with the performance of polyvinylpyrrolidone (PVP), N-vinyl caprolactam (PVCap), and 2-(dimethylamino)ethyl methacrylate (DMEM). The modified starch performed best. Talaghat (2014) investigated the performance of modified starch as a kinetic inhibitor in the presence of polyoxides. The result of the investigation showed that the induction time in the presence of Polypropylene oxide (PPO) and Poly ethylene Oxide (PEO) was prolonged compared to the inhibitor alone. The PPO's efficiency was more significant than the PEO as it had a longer induction time. The synergism between the inhibitor and PEO/PPO was evident, but a better result was achieved with the PPO.

Although THIs are relatively cheap per unit volume, large quantities are required to suppress the equilibrium temperature to below the lowest operation temperature expected in the system, and this will cause the infrastructure cost to add up to a significant amount (Brustad et al., 2005). Hence, it is necessary to search for a credible alternative in Low Dosage Hydrate Inhibitors (LDHIs) due to the economic and environmental issues of THIs. This

study evaluates the synergy between specific THI and KHI in preventing hydrate formation.

2. Materials and methods
2.1 Equipment

The equipment used in this study is a 12meter closed flow loop of 0.5inch diameter designed to mimic hydrate formation conditions in offshore horizontal flowlines and it was designed by Odutola et al (2017). The loop is fitted with a control panel, pumps (manual and electrical), a freezer, a flow meter, an inhibitor mixing vessel, a gas cylinder containing methane gas, electric sockets differential pressure meter, and pressure and temperature gauges. The flow loop is lagged with fibre wool and Arma-flex to prevent heat transfer from the environment into the loop. The hydrate flow loop is situated in a temperature-controlled room to avoid temperature gradients between the flowing media and the surrounding. The loop was designed to withstand a maximum pressure of 3500 psi. A diagram of the laboratory setup is shown in figure 1. A detailed description of the loop components and their functions is documented in Odutola et al. (2017).
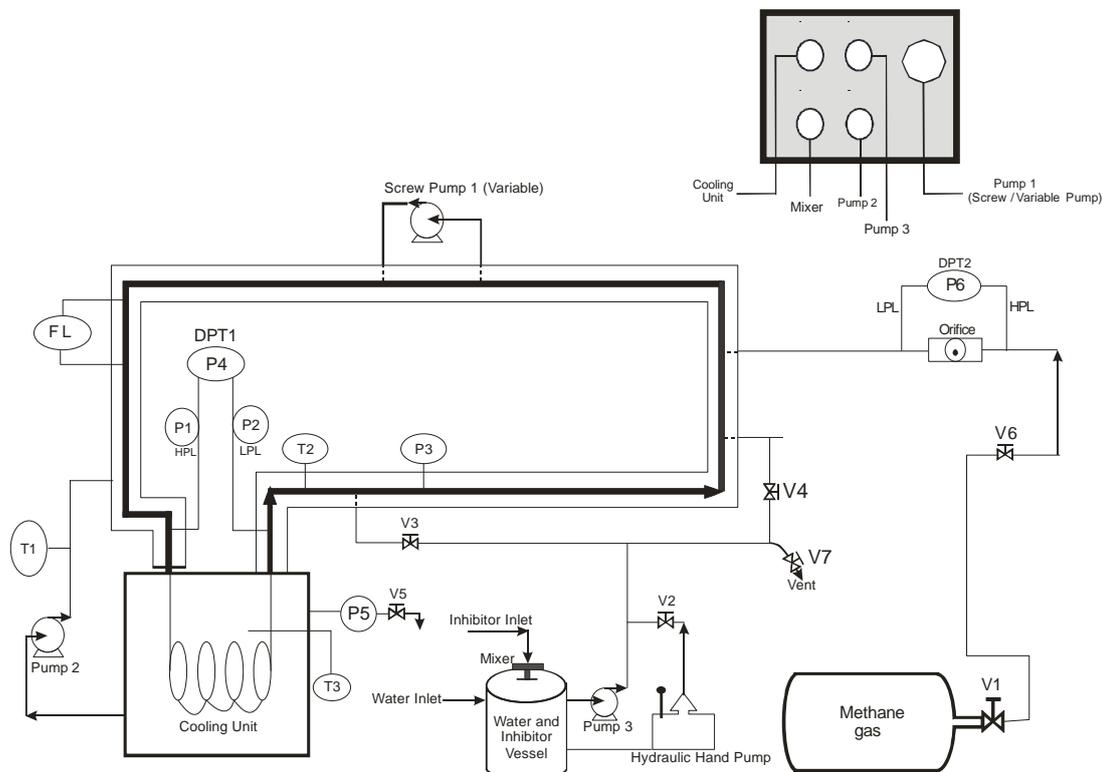
Fig 1: Flow diagram of the mini fluid flow loop (Odutola et al., 2017)

2.2 Materials

The following materials were used in the laboratory experiment: water, methane gas, and hydrate inhibitor (MEG and plant polymer). Water

was used as the host molecule to form hydrates. The hydrate inhibitors were prepared to the required concentration by mixing the inhibitors with water. Also, water was used as the coolant

circulating in the loop. The refrigerator reduced the cooling water temperature to hydrate formation temperature at the prevailing loop pressure. Methane gas was used as the hydrate former (guest molecule). The low dosage hydrate inhibitors used in this experiment are two samples of Kinetic Hydrate Inhibitors (KHIs) extracted from a Niger Delta plant. The first sample (A) is a water-soluble poly-hydroxyl compound, while the second sample (B) is the same sample made alkaline in a sodium hydroxide solution. Mono Ethylene Glycol (MEG) is a common THI usually required in large volumes to prevent hydrate formation. Odutola (2022b) recorded the optimum MEG dosage for preventing hydrate formation in the laboratory loop as 3wt%. This study evaluates the synergy between MEG and the KHIs samples A and B.

2.3 Experimental procedure

Detailed procedures for conducting hydrate inhibition experiments in this loop are documented in Odutola et al. (2016). Methane gas was passed into the loop to mix with water during the 2-hour constant volume batch experiment conducted in the flow loop. The loop temperature and pressure from several gauges around the loop (Fig. 1) were recorded at 10 minutes intervals. The first experiment was to determine the hydrate formation conditions. Subsequent experiments were conducted to study the effectiveness of the KHI and the hybrid of KHI and MEG. The inhibitors studied are 0.05wt% sample A, 0.05wt% Sample B, 0.04wt% Sample A + 0.4wt% MEG, 0.04wt% Sample B + 0.4wt% MEG and 0.05wt% Sample B + 0.7wt% MEG. An efficient hydrate inhibitor will prevent or reduce hydrate formation; hence, there will be no increase in loop temperature due to the absence of the hydrate formation exothermic reaction. The loop pressure decline at the end of the experiment will also be minimal.

3. Results and discussion

Hydrate formation is an exothermic reaction; hence a significant rise in loop temperature indicates hydrate formation. Fig. 2 is the plot of loop temperature against time for the uninhibited system and the system containing Sample A, Sample B and their hybrids. Note that the loop temperature rapidly cooled down within the first 20 minutes of the experiment. After that, a temperature increase was observed in the experiment conducted without an inhibitor. This implies that the hydrate formation occurred and heat was given off, resulting in the increased loop temperature. For experiments conducted with Sample A, there was a steady decline in temperature, after which the loop temperature remained constant at 15ºC. This implies that sample A was efficient at preventing hydrate formation in the flow loop. However, Sample B was not efficient at preventing hydrate formation in the loop. This is obvious from the temperature/time plot for an experiment conducted with 0.05wt% of Sample B. There was an initial temperature decline and a rise in temperature after 60 minutes in the experiments conducted for Sample B. This implies that 0.05wt% was ineffective at preventing hydrate formation in the loop. The hybrid of 0.04wt% Sample B + 0.4wt% MEG was also not efficient at preventing hydrate formation in the loop, as evident from the increase in temperature observed (Fig. 2). The results show that the inhibitors 0.05wt% Sample A, the hybrid of 0.04wt Sample A + 0.4wt MEG and the hybrid of 0.05wt% Sample B + 0.7wt% MEG were efficient at preventing hydrate formation in the loop as no increase in temperature was noticed in these experiments.

The experiments conducted in the loop were constant-volume batch experiments. Therefore, a significant reduction in the loop pressure at the end indicated that gas was used up in forming hydrates, and the inhibitor was inefficient at preventing hydrate formation. Figure 3 is a plot of loop pressure against time for the various experiments conducted in this study. A rapid pressure decline was observed in the experiment conducted without an inhibitor as the loop pressure reduced from 170 psi to 55 psi, implying that gas was used up in forming hydrates. The experiment conducted with 0.05wt% Sample B and the hybrid of 0.04wt% Sample B + 0.4wt% MEG recorded a rapid loop pressure decline from 170 psi to 55 psi. This implies that these two inhibitors were ineffective at preventing hydrate formation in the loop. The inhibitor made with 0.05wt% Sample A performed better than sample B. The pressure decline was from 170 psi to 65 psi at the end of the experiments, although hydrates still formed in this experiment due to the gas used up and pressure decline recorded. The hybrid inhibitor made with 0.05wt% Sample B and 0.7wt% MEG was the best inhibitor blend in this study. The pressure decline at the end of the experiment was from 170 psi to 102 psi, implying that less gas was used up and less hydrate was formed. The hybrid of. 0.04wt% Sample A and 0.4wt% MEG also gave a good result of pressure decline from 170psi to 98 psi, implying less hydrate formation in the loop.
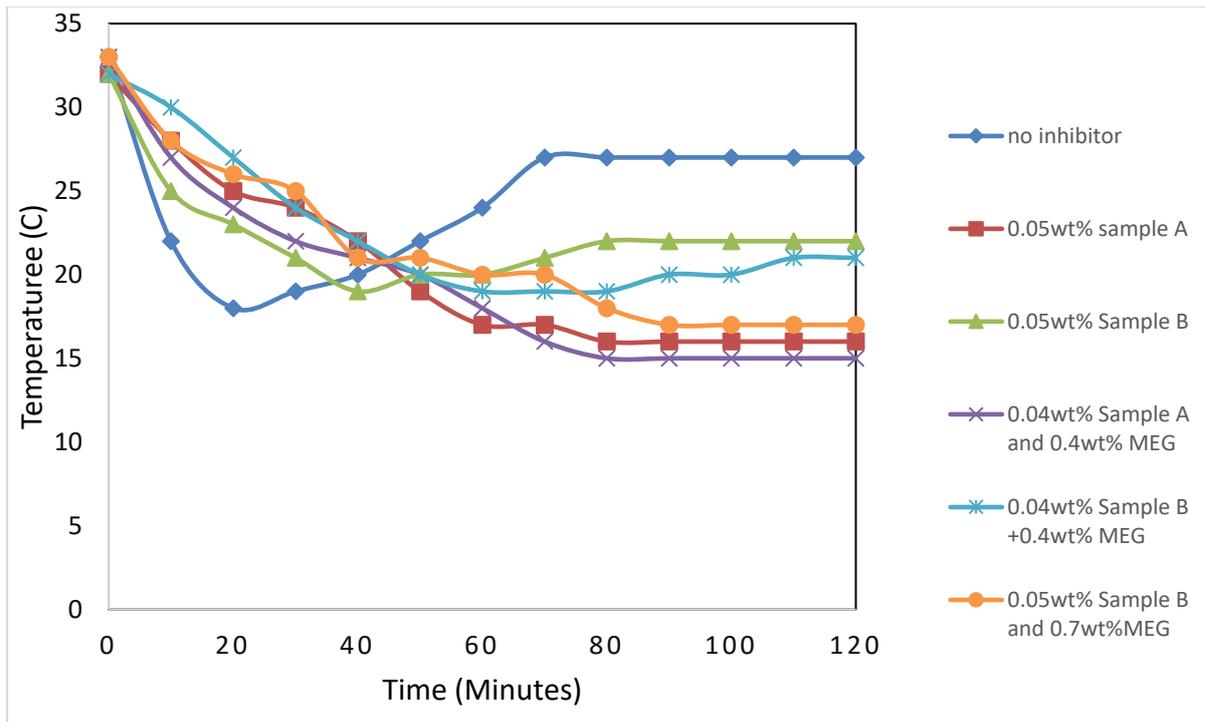
Fig. 2: Plot of loop temperature against time for all experiments conducted in the study
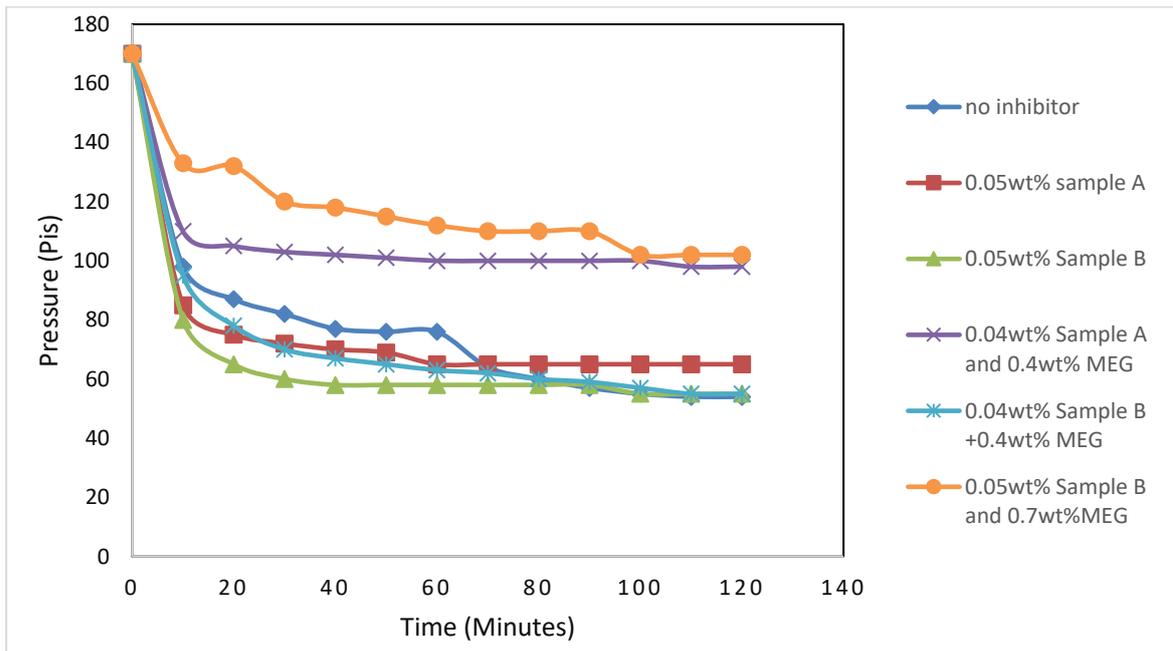
Fig. 3: Plot of loop pressure against time for all experiments conducted in the study

4. Conclusion

The Kinetic Hydrate Inhibitors proved to be good inhibitors requiring minimal volume in dosage and weight per cent in water. Increasing the dosage of the KHI will lead to an increase in the hold time and delay hydrate nucleation and agglomeration in the pipeline The sample-A of the KHI used is more effective than the second sample (B) because a lower quantity of the sample-A inhibitor is required to prevent hydrate formation compared to sample B. The presence of NaOH in the second sample B negatively affected the performance of the plant polymer. This is evident in the higher volume required to attain optimum dosage and higher volume of thermodynamic inhibitor required to effect a possible synergy. The use of the KHI presents an economic advantage in

the reduction of the operating expenditures (OPEX), and a similar reduction in capital expenditures (CAPEX) through the reduction in the size of the storage, pumping and piping facilities. In the event of facility maintenance shut-down, the hybrid is recommended as the synergistic effect of the KHI with thermodynamic inhibitors will further increase the hold time and enable it also to bear a higher degree of sub-cooling.

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