

## Evaluation of Hybrid Hydrate Inhibitor (HHI) in Dissociating Hydrate Formation in Offshore Flowlines

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### **Abstract**

The presence of gas hydrate creates flow assurance challenges in the production of oil and gas. In the major offshore, swamp, and onshore production operations, hydrate plugs the production flowlines, hence downtime and intervention costs. Thus, because of these challenges, there is a growing necessity for superior chemical inhibitors to address the limitations of existing inhibitors needed to hinder the formation of hydrate. This research is intended to evaluate the performance of hybrid hydrate inhibitor (HHI) developed from monoethyleneglycol (MEG) and polyvinyl caprolactam (N-Vcap) as compared to the conventional kinetic hydrate inhibitors (KHI) as MEG or N-Vcap. Experiments were carried out using a mini flow loop with 1 to 7 weight percentages of MEG, N-VCap, and HHI. Analysis from pressure vs. time, temperature vs. time, and pressure-temperature versus time plots were also made. From the result obtained, the HHI at 5, 6, and 7 weight percent did perform better than of MEG at various weight percentages and having the capacity of delaying and dissociating hydrate formation; it is therefore suggested for field examination.

**Keywords:** *Gas hydrates; Mono ethylene glycol (MEG); Polyvinylcaprolactam (N-Vcap); Hybrid hydrate inhibitor (HHI); Mini flow loop apparatus.*

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## **1. Introduction**

The production and transportation of oil and gas in a deepwater environment cause hydrate formation when water and hydrate guest or hydrate former are present. Natural gas hydrate has been described to be crystalline compounds, formed when free water and low molecular weight gases such as methane, ethane, propane, and butane and even non-hydrocarbon gases such as nitrogen, carbon dioxide, and hydrogen sulfide come together at favorably high pressure (>200psig) and low temperature (0- 40°C) [1-2]. Hydrate structures are classified by the array of water and hydrate former molecules in the crystal. Hydrate structures are of three types, namely: sI, sII, and sH hydrates, and the structure of anyone to be formed is dependent on the volume and the kind of gas molecules that are confined by the water molecules. The SI molecules are produced by methane, ethane, and carbon dioxide gas molecules, while the sII structure is formed by bigger gas molecules such as propane and normal butane as well as nitrogen [3-4]. Whether structure I, II, or H, hydrate plug causes the same flow assurance challenge. Before 1934, it was established that in the presence of free water, solid ice plug and corrosion problems could occur in a gas transmission line, but during a gas transmission inspection by Hamerschmidt [5], he discovered that the formation of the solid plug in the transmission line was not ice but gas hydrate. This gave birth to a new discipline in Engineering known as Flow Assurance Engineering, as he demonstrated from his experiment that these blockages were hydrates of gas. The oil and gas industry is relentlessly taking severe measures in preventing gas from forming hydrate because of its tendency to block pipelines, which leads to downtime and extra cost. Hydrate prevention methods and techniques cost in the oil and gas industry could be estimated to be about one billion U.S. dollars yearly [6]. The benefit of the method is the avoidance of downtime as gas hydrates are not allowed to form. Gas hydrate triggers operating expenses (OPEX) if it is allowed to take place. Annual

approximation of an operating charge when hydrate is formed, or the prevention of hydrates is greater than \$500m. Natural gas hydrate plugging may cost more than \$1 million each day if production is shut down.

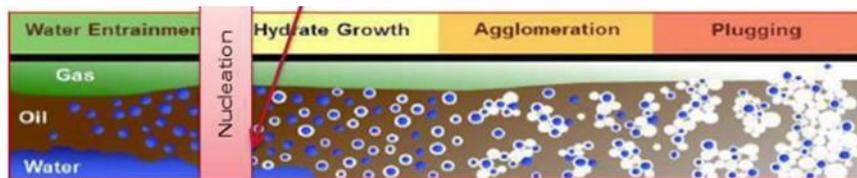


Figure 1. Conceptual model of hydrate formation in the multiphase system [39]

As shown in Figure 1, the process of hydrate formation at high pressure and low temperature occurs in the following stages: water entrainment, nucleation, hydrate growth, agglomeration, and plugging. The hydrate formation process begins with the gas (guest) molecule being trapped into the water (host) molecule under a favorable low temperature and high pressure condition. Gas hydrates growth studies presented by Englezos and others [7] were based on the theory of mass transfer. They outline the growth of hydrate into a three-step process. The first step was the transfer of the gas molecule into the liquid phase, the second step was the dispersion of the gas molecule through an immobile liquid diffusion stratum that surrounded the hydrated particles, and the last step was the amalgamation of the gas molecule into the prearranged water structure of the hydrated particle. The nucleation could be seen as a microscopic process involving clustering thousands of water and hydrate former molecules together and their further development into hydrate nuclei. In other words, nucleation is the building up and breaking down of hydrate clusters currently in the liquid medium. By the time these small nuclei attain a critical size, a continuous hydrate growth process starts. The hydrate continues its growth linearly until the liquid medium is entirely transformed into hydrates. An inclusive understanding of gas hydrate nucleation and growth is important and defines both the fundamental hydrate science and hydrate-based engineering [8].

Uchida and others [9] obtained a model on heat transfer that described the formation of hydrating films at the water-liquid carbon dioxide interface. They estimated that the linear rate of film growth along the interface was in a range of 102-104  $\mu\text{m/s}$ , and the film thickness was about 0.13  $\mu\text{m}$ . More significantly, the work by Freer and others [10] consent well with that of Uchida and others [9] in that the film growth rate was proportional to the degree of sub-cooling. Mochizuki and Mori [11] related a heat-transfer-controlled cross growth of a hydrating film at the boundary between liquid water and an immiscible hydrate-forming fluid. From their studies, it was observed that the propagation rate was temperature-dependent which indicates that diffusion is a restrictive factor. Hydrate crystal formation is not the main cause of flow obstruction; its deposition and agglomeration are the main causes of flow restriction and hydrate plug.

As reported by Amodu [12] and Freij-Ayoub and others [13], the prediction of gas hydrate formation to circumvent hydrate formation has attracted the interest of many researchers. There are various methods of use in the prediction of hydrate formation. Methods that are currently in use include Gas gravity method, K-factor method, Katz correction, the Peng–Robinson Equation of state (EOS), other thermodynamic software such as CSM Gem, Multi Flash, OLGA, PVTSIM, HYSYS, and the likes. However, Katz and his co-workers were the first to suggest the K-factor and the Gas gravity methods. These methods effectively predicted hydrate formation in sweet gases. Wilcox and others [14] built the first model to predict hydrate formation conditions using the K-value method. Their model utilizes the vapour–solid in the equilibrium constant in predicting hydrate forming conditions. Elgibaly and Elkamel [15] prepared an all-inclusive neural network model for forecasting hydrate formation conditions for a variety of pure gases. The model was designed using 2387 input-output patterns collected from diverse, consistent sources. The predictions made from their model gave similar results when it was compared to existing correlations and real experimental data. Another model called the Response Surface model was used by Averbuch and others [16] for the prediction of

hydrate formation temperature. The model was simple, deterministic, and probabilistic. They were able to describe the time of hydrate formation as a function of the wide range of input parameters. The artificial Neural Network (ANN) method was adopted by Heydari and others [17] to estimate gas hydrate formation temperature. The ANN model was made to function with 167 raw data, with temperature and pressure range of 32-74°F, 50-4200 psia, respectively. 149 samples were used to guide the network, while 18 samples were used as the test set. The result from the best ANN structure was compared with the result of the Sloan model. ANN showed better results in comparison. The merit of this ANN is that it saves computational time. However, the model was limited to the specific gravity of 0.554 to 1. Odutola *et al.* [18] carried out a study on hydrate prediction where they use ANN for predicting hydrate formation conditions. In their research, 459 hydrate formation experimental data points of temperature and pressure were gathered from Katz chart and Wilcox and others [14]. The result obtained from the study shows that the ANN accurately predicted the hydrate formation temperature with a regression coefficient of 0.98 for natural gas within the range of 49 psi to 4200psi and specific gravity of 0.55539 to 1.

Gas hydrate formation could be mitigated by several methods like Insulation, thermal heating, dehydration or water removal, System depressurization or pressure reduction, and inhibitors injection-chemical methods [19-20]. Among all, chemical injection is considered more cost-effective, particularly in a deep offshore environment where the ease of accessibility is restricted. Production and transmission lines can be heated or "hot-oiled" to raise the system temperature or depressurized to lessen the system pressure, while insulators are used to decrease the amount of heat loss to the environment. However, there are several problems associated with these techniques. There have been cases of pipe damages due to overheating and high costs due to power requirements during heating with hot oil.

Chemicals for hydrate treatment are grouped into thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs) [21-22]. THI is a chemical used for hydrate inhibition that alters the hydrate formation pressure and temperature (thermodynamic). In doing this, it shifts the hydrate formation region to a more reducible temperature and higher pressure. THIs comprises glycols and alcohols. Thermodynamic hydrate inhibitors are added at relatively high concentrations of about 10-50 (weight % of water cut) in the aqueous phase [23]. THI restrains hydrate formation by minimizing the temperature to which hydrates form by altering the chemical strength of water. This effect is very similar to adding antifreeze to water to lower the freezing point. Thermodynamic hydrate inhibitors prevention methods control or eliminate items essential for hydrate development, including water, high pressures, and low temperatures. Removing any one of these items from the system negates hydrate formation [24]. However, removal of these items often is not viable or impossible, particularly in gas production wells where there is no control over produced fluid composition and bottom-hole pressure and temperature. These inhibitors change the temperature and pressure of the system to a value where hydrates are not formed [25]. LDHIs, on the other hand, are polymers or surfactants that delay hydrate nucleation, growth, and agglomeration. LDHIs, as the name implies, are required in low concentration (usually < 3 weight % of water) in the aqueous phase [26]. LDHIs are only used to solve the hydrate problem that is not critical, as they cannot eliminate hydrate once it has been formed [27]. LDHIs, unlike the THIs, put off the hydrate growth and prevent hydrate from agglomeration. LDHI is grouped into two categories: Kinetic hydrate inhibitors (KHIs) and Anti Agglomerate (AA). Kinetic hydrate inhibitors (KHIs) are low molecular weight water-soluble polymers or copolymers that avoid hydrate plug by gluing to the hydrate surface and delaying hydrate crystal nucleation and growth. According to Fu and others, [28] these inhibitors can lower hydrate formation by 11°C (20°F) at concentrations less than 3000 ppm. KHI performances under simulation condition of the North Sea and Gulf of Mexico operation was evaluated by Sloan [29]. With the shut-in period allowed, the performance of the KHI was obtained as the highest degree of sub-cooling time. The outcome indicated that a level of sub-cooling varies with the required shut-in time. This gave rise to the dawn of the first generation of KHI, which was able to handle sub-cooling for at least 24hours and up to 8°C. The second generation offered at least 48 hours and could handle sub-cooling

up 13°C. The higher the sub-cooling was, the more rigorous the condition; thus, its application carefully considered the degree of sub-cooling. Anti-agglomerates (AAs) are surfactants that prevent the agglomeration of hydrate crystals by suspending the free water as small droplets within the system. The hydrate crystals are allowed to form but are kept in small sizes and are well dispersed within the hydrocarbon liquid. AAs stabilize the hydrate crystal by sticking to their surface, enabling them to be dispersed in the continuous oil phase and hence making the hydrate stay in a slurry form and are being transported without forming a hydrate plug. This method is valuable in the highly sub-cooled system and during shut down with the cold restart process. AAs are surfactants like alkyl aromatic sulphonates (Dobanex series) and alkyl polyglycosides (Dobanol) as patented by the shell as AAIs [30]. Statoil and SINTEF also published work on some surfactants, including alkyl phenyl ethoxylates and berol [31]. AAIs can be used for deepwater applications and have completed successful field trials in the deepwater Gulf of Mexico production systems [32]. For deepwater gas applications, AAIs should be applied where there is satisfactory condensation, such that there is an in-situ water cut of less than 50% [33]. Hydrate prevention with methanol and glycol can be quite expensive because of the high treatment volumes required and additional expenses for waste-water treatment and on the other hand, LDHIs do not completely stop hydrate from forming because they do not cause a hydrate curve shift. Owing to these shortcomings on the side of THIs and LDHIs, a chemical combination that can overcome this shortcoming is pivotal. The used of kinetic hydrate inhibitor with the addition of paraffin-control chemical in the Gulf of Mexico was discussed by Swanson and others [34]. The study was applied on a pipeline for a new re-completed well which was predicted to have a water cut of about 20%. The injection of KHI was done after the production rate had stabilized. It was observed that inhibitor provided lesser operating cost with a better environmental condition than the methanol, which had been used previously before it was completed.

Pakulsi *et al.* [35] carried out a hydrate inhibitors combination study on a subsea well in the Gulf of Mexico with a 4 inflow line. The result from their study showed that performance in terms of hydrate dissolution was increased, and secondary costs such as pump cost, corrosion transportation, and crane costs were reduced. The operators realized good performance at a reduced cost. The essence of this paper is to evaluate the performance of hybrid hydrate inhibitor (HHI), being the mixture of monoethylene glycol (MEG) and polyvinyl caprolactam (PVCap), and compare it with the performance of these individual inhibitors.

## 2. Materials and method

The materials used include compressed natural gas (CNG) of specific gravity of 0.5 (methane content 98.44 % mol. and CO<sub>2</sub> 1.5 % mol.), ice blocks, and water. The equipment used is the hydrate flow loop apparatus [36]. Whereas the inhibitors used, include N-Vinyl. The hydrate flow loop process diagram is displayed in Figure 2.

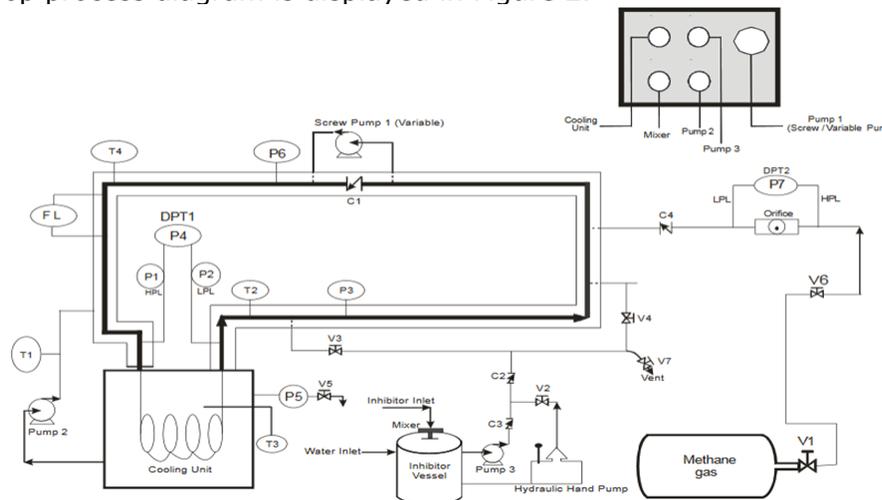


Figure 2. Process flow diagram for the hydrate studies [37]

The loop replicates a typical offshore gas pipeline exposed to the region of hydrate formation owing to its low temperature. The loop is made of stainless-steel tubing with a measured length of 12 m (39.4 inches) and 0.5-inch internal diameter. This steel tubing lies concentrically in a 4-inch polyvinylchloride (PVC) pipe where water is constantly being circulated to cool the stainless-steel pipe. This PVC pipe is insulated to prevent absorption of heat from the surrounding into the system [37]. The loop was designed to withstand the pressure of 3500psi and temperature of 50°C. The key component of the loop includes a control panel (shelter the three switches that regulate the whole process with a refrigerating unit), three electrical pumps and a manual pump, five pressure gauges and two differential pressure gauges, three temperature gauges, an inhibitor vessel, CNG bottle and flow meter [36].

### 3. Experimental procedures

Before starting the experiment, the loop was checked to ascertain whether it was functioning properly or not. Pumps, valves, power buttons were also checked. With these confirmed, the power source and power button on the control panel were put on to run the hydrate formation experiment. Water was turned into the inhibitor vessel and then used to flush the loop from dust and debris. After this, 2660mL of water was measured and turned into the inhibitor vessel. With the aid of valve 4 and pump 3, the water was pumped into the loop until the pressure of 25psi was attained. Pump 3 and valve 4 were put off after the system has attained that pressure. Valve 1 near the CNG cylinder was opened, and the CNG was introduced into the loop. The orifice on the CNG was regulated to 150psi and then turned off. Pump 2 was then put on to feed the loop with the cooled water from the refrigerating unit. Pump 1 and 2 kept were running throughout the practical session, which lasted for 120minutes.

The gas hydrate inhibition experiment procedure was slightly different from that of the gas hydrate formation. For the inhibition experiment, different weight concentrations of inhibitors with their corresponding weight percentages of water that made up to 2660mL were used. Their respective mixtures were properly stirred together and turned into the inhibitor vessel. And like the gas hydrate formation experiment, Pump 1 and 2 kept were running throughout the practical session, which lasted for 120minutes.

### 4. Results and discussions

The data from the experiment were used for various plots of pressure against time, temperature against time as well as pressure and temperature against time. These plots were used to analyze the results presented in this paper. Different plots were prepared for the water-gas system (Figure 3) and hydrate mitigation systems (Figures 4-10).

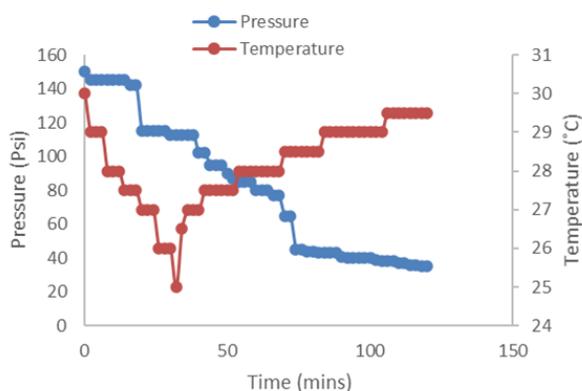


Figure 3. Temperature and pressure against time for gas-water (Un-inhibition) system

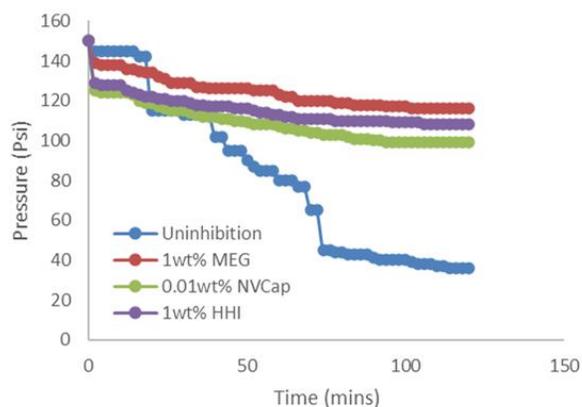


Figure 4. Pressure against time for un-inhibition, 1wt% of MEG, 0.01wt% of N-Vcap, and 1wt% of HHI

For the gas hydrate formation plot (Figure 3), the starting temperature and pressure were 30°C and 150psi, respectively. However, from 2 to 14minutes witnessed constant pressure of

145psi. The pressure dropped from 145psi to 142psi in 2minutes with temperature reduced to 27°C. The pressure drop indicates that the gas molecules were being encapsulated by the water molecules, and this establishes gas hydrate formation.

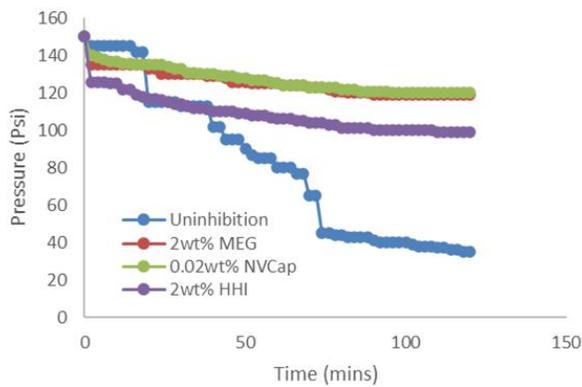


Figure 5 Pressure against time for un-inhibition, 2wt % of MEG, 0.02wt % of N-Vcap, and 2wt% of HHI

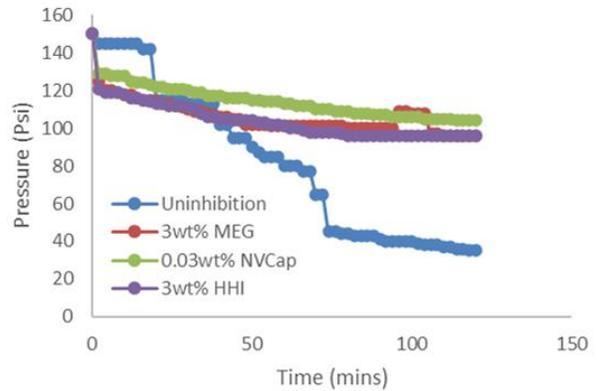


Figure 6. Pressure against time for un-inhibition, 3wt% of MEG, 0.03wt% of N-Vcap, and 3wt% of HHI

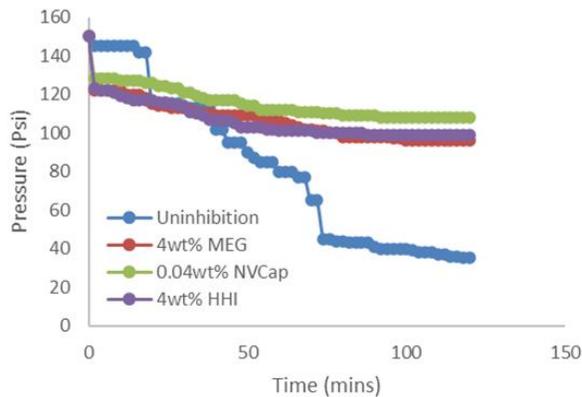


Figure 7. Pressure against time for un-inhibition, 4wt% of MEG, 0.04wt% of N-Vcap, and hybrid of 4wt% of HHI

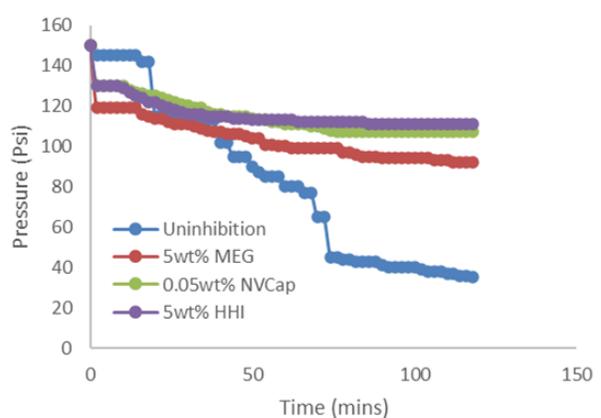


Figure 8. Pressure against time for un-inhibition, 5wt% of MEG, 0.05wt% of N-Vcap, and hybrid of 5wt% of HHI

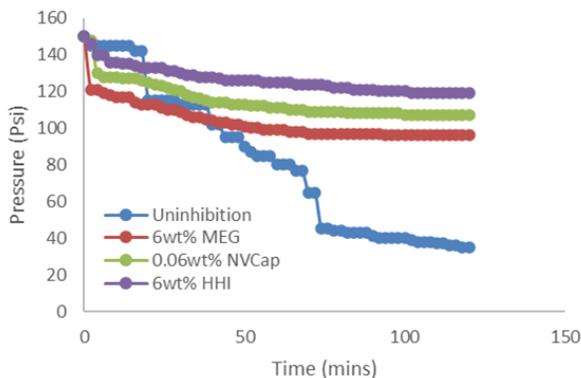


Figure 9. Pressure against time for un-inhibition, 6wt% of MEG, 0.06wt% of N-Vcap, and 6wt% of HHI

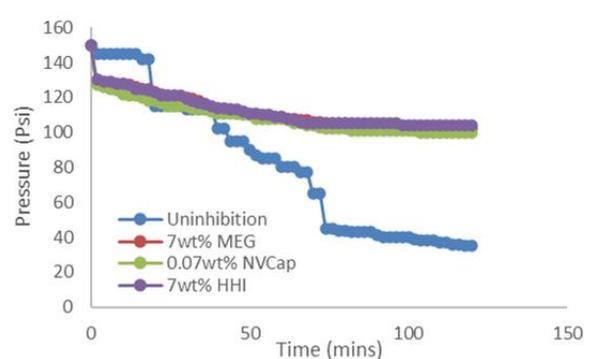


Figure 10 Pressure against time for un-inhibition, 7wt% of MEG, 0.07wt% of N-Vcap, and 7wt% of HHI

On the temperature end, as witnessed in the earliest 32minutes of the practical, the temperature reading reduced from 30°C to 25°C. 2 minutes later there was a temperature increase from 25°C to 26.5°C and then from 26.5°C to 29.5°C within another 2 minutes. This rise in temperature showed that heat was being given off. This further confirmed gas hydrate formation is owing

to the fact that gas hydrate formation is an exothermic process that evolves heat in the form of temperature rise within the system.

Figures 4-10 show pressure inclination for un-inhibition (gas and water) and various weight percentages for MEG, N-Vcap, and HHI systems. At the end of 120minutes, it was seen that the pressure drop for 1 wt % of MEG was 150psi to 116 psi, 150psi to 108psi for 1 wt of HHI, and 150psi to 99psi for 0.01wt% N-Vcap. On the other end, the final pressure for 0.02wt% of N-Vcap was 120psi, and MEG was 119 psi for MEG and just 99 psi for 2wt % of HHI. The final pressure recorded for 0.03wt% of N-Vcap was 104psi, while the 3wt of HHI and MEG were both 96psi.

From Figures 7 and 8, it was seen that, at the end of the 120minutes, the final pressure for 4wt% of MEG was 96 psi, 108 psi for 0.04wt N-Vcap, and 99psi for 4wt% of HHI. There was a drop in the performance of 4wt % of MEG and N-Vcap but a slight improvement in the performance of HHI against their previous one. The HHI at 5wt % gave a better performance than MEG and N-Vcap as the final pressure recorded these, 0.05wt % of N-Vcap was 107 psi, 92 psi for 5wt % of MEG, and 111 psi for the HHI. Also, the HHI at 6wt % gave a final high pressure of 111psi and that of 6wt% of MEG and 0.06 wt% of N-Vcap with final pressures of 96psi and 107psi, respectively. The final pressure for 7wt% of MEG was 102 psi, 110 psi for 0.07wt% of N-Vcap, and 7wt% of HHI was 104psi, as seen in Figure 10. The final pressure of the hybrid shows superior performance, followed by MEG and then N-Vcap.

There was gas hydrate mitigation using all the weight percentages of MEG, N-Vcap, and their hybrid, as their final pressure readings were far above that of the water-gas system. However, the HHI shows superior performance over MEG from 5wt%.

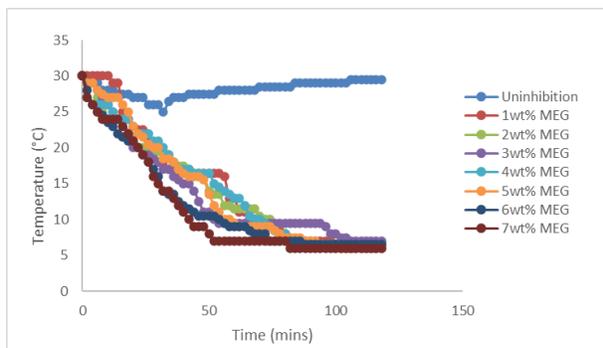


Figure 9. Temperatures against time for un-inhibition, 1wt% of MEG to 7wt% of MEG

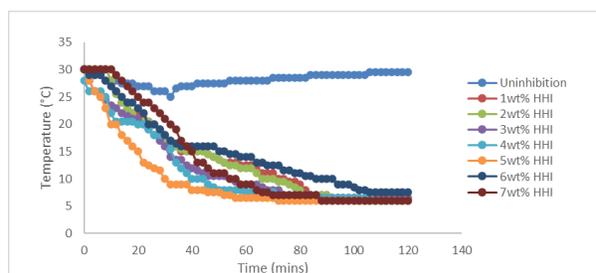


Figure 12. Temperatures against time for un-inhibition, 0.01wt% of N-Vcap to 7wt% of N-Vcap

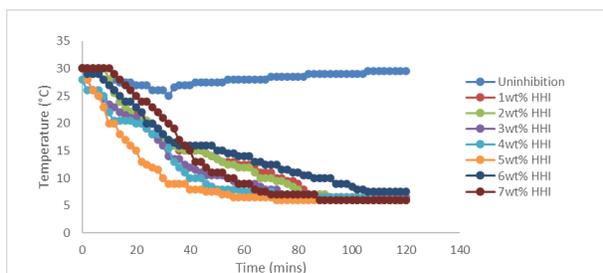


Figure 13. Temperatures against time for un-inhibition, 2wt% to 7wt % of HHI

From Figures 11, 12, and 13, it was noticed that at the end of the 120minutes, there was no temperature rise for all the concentrations of the inhibitors used (MEG, N-Vcap, and HHI) as against that of the uninhibited system (gas -water). There was a temperature drop in all the various concentrations of MEG, N-Vcap as well as hybrid. This further showed that all the various concentrations of MEG, N-Vcap, and the hybrid used mitigated gas hydrate formation.

The temperature drop at the end of 120 minutes was from 30°C to 6°C for 2wt%, 4wt%, 5wt%, and 6wt%. From 30°C to 6.5°C for 1wt%, and from 30°C to 7°C respectively for MEG. For N-Vcap, the temperature drop were 30°C to 6.5°C for 0.01wt%, from 30°C to 5.5°C for 0.02wt% and 0.03wt%. For 0.04wt %, 0.005wt % 0.06wt % and 0.07wt % the temperature was from 30°C to 6°C.

Finally, for the HHI, temperature decreases from 30°C to 6°C at 1wt %, 3wt%, 4wt %, 5wt %, and 7wt %. For the HHI at 2wt %, the temperature drop was 6.5°C, and that of 6wt

% was from 30°C to 7°C. There were no increases in temperature in all the weight percentages of the various inhibitors used, indicating that hydrate formation was inhibited.

The Chi-square method was used to determine the validity of the result obtained from the experiment in order to state whether or not there exists a relationship among the performance of THI, LDHI, and HHI. See Table 2.

$$\text{Chi square value } (x^2) = \sum \left( \frac{(o-\epsilon)^2}{\epsilon} \right)$$

Where: o is the observed value and final average pressure of each inhibitor;  $\epsilon$  is the expected value

Table 2. Statistical summary table

Inhibitor	(O) psi	( $\epsilon$ ) psi	(o- $\epsilon$ ) psi	(o- $\epsilon$ ) <sup>2</sup>	$\frac{(o-\epsilon)^2}{\epsilon}$
THI (MEG)	102.43	104.8	-2.38	5.66	0.054
LDHI (N-VCap)	106.43	104.8	1.62	2.62	0.025
HHI	105.57	104.8	0.76	0.58	0.0073

Chi-square value ( $x^2$ ) = 0.863; Degree of freedom (df) = 2; Significance level ( $\alpha$ ) = 0.05; Critical value (z) = 5.991

The analysis of the chi-square value and the critical value has shown that there was a significant relationship among the performance of MEG, N-Vcap, and the HHI.

## 5. Conclusion

Monoethylene glycol (MEG) and N-Vinylcaprolactam (N-Vcap) are valuable thermodynamic and kinetic hydrate inhibitors that show superior inhibitory efficiency at concentrations of 2wt% and 0.02wt%, respectively. However, the HHI at 5wt% to 7wt% recorded the lowest pressure drop in contrast with MEG. The low-pressure drop recorded by the hybrid shows its high inhibitory efficiency, and at these concentrations, thus the hybrid is preferable to the conventional inhibitors (MEG and N-Vcap) having the capacity over their respective shortcomings.

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