Use of Locally Formulated Inhibitor from Agro Waste for Gas Hydrate Inhibition in a Mini Flow Loop

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Abstract - Gas hydrate formation can lead to financial losses due to production downtime and damage to equipment. As a result of this, the Oil and Gas Industry is doing all it can to avoid/reduce its occurrence. The modern day inhibitors are majorly synthetic, expensive and lead to environmental pollution, therefore, there is a need for less expensive and environmentally friendly inhibitors. This paper compares the inhibitory capacity of conventional kinetic hydrate inhibitors (KHIs), N-vinylcaprolactam (N-VCap) and 2-(Dimethylamino) ethylmethacrylate (2-DMEM) with Locally Formulated Kinetic Hydrate Inhibitor (LFKHI) produced from agro waste based starch. Experimental runs were carried out on a mini flow loop using different weight percentages of 0.01, 0.02 and 0.03 of the various inhibitors. The plots of pressure, temperature and time clearly showed that in all the weight percentages, the LFKHI performed better. The LFKHI is eco-friendly and biodegradable since it is produced from agro waste based starch, and is cheap and water-soluble. LFKHI is being recommended for field trial.

Keywords - *Gas Hydrate, Agro Waste, Locally Formulated Kinetic Hydrate Inhibitor*

I.   INTRODUCTION

Gas hydrates are glass-like, compounds that are made of gas and water molecules [1]. They are ice-like solids that form when free water and low molecular weight gases such as methane, ethane, propane and butane combine at high pressure and low temperature. Non-hydrocarbon gases such as carbon dioxide, Nitrogen, Hydrogen sulphide are also known to form hydrates under certain conditions. The lower-boiling point hydrocarbon molecules C_1-C_4 and their mixtures are more problematic because it is believed that their hydrate or clathrate crystals are easier to form. The formation of gas hydrate mainly occurs in offshore subsea pipelines at high pressure and low temperature [2]. Gas hydrates have three well-known structures namely; structure I, structure II and structure H [3,4,5,6].

Gas hydrate is a flow assurance challenge for production, handling and transport of natural gas fluids. It is common for hydrate crystals to cause plugging and/or blockage of pipelines,

transfer lines, valves and/or safety devices and/or other equipment, resulting in shut down, production loss, the risk of explosion or unintended release of hydrocarbons into the on-shore or offshore environment. Paraffin wax deposition and hydrate formation are mainly the examples of such problems that cost the industry millions of dollars in lost production and cleaning operations [7]. Mitigating this problem by putting in place measures to prevent hydrate formation, costs industry over a billion US dollars annually [8].

Despite the fact that gas hydrate is a threat to flow assurance in the offshore environment, gas hydrates also offer many potential benefits and can be used for carbon capture and sequestration [9], natural gas storage [10], coal mine gas separation [11], desalination [12] and separating undesirable (toxic or incombustible) species from biogases [13].

Gas hydrate can be prevented by removing free water in the gas stream, insulation of pipeline, heating/depressurizing the system and injection of chemicals - thermodynamic inhibitors and Low Dosage Hydrate Inhibitors (LDHIs). Injection of chemicals with much emphasis on the use of LDHIs is a common practice in the remote and offshore environment. During well-testing, startup and gas lift activities, hydrates can even occur given high pressure drops and high initial temperature. One of the ways of preventing gas hydrate by removal of water is through adsorption of water onto for example, silica gel, alcohol/glycol or hygroscopic salts. The use of glycols is limited under severe cold conditions, especially below -40°C as they are rendered significantly ineffective. If removal of water is extremely required at less than -40°C, molecular sieves or solid desiccants are preferable, however, they are extremely costly.

There are two broad chemical methods used to overcome or control gas hydrate, namely: thermodynamic and kinetic hydrate inhibition. The thermodynamic approach functions by preventing hydrate formation through the addition of 'antifreeze' agents to the production fluids. These inhibitors are added at high concentrations (10-60 wt. %) and they alter the chemical potential of the aqueous or hydrate phase so that hydrate dissociation curve is displaced to lower temperatures or higher pressures. Examples of thermodynamic hydrate inhibitors include methanol, Mono Ethylene Glycol (MEG), Di

Ethylene Glycol (DEG), ethanol, etc. The kinetic approach generally attempts to:

(a) Prevent the smaller hydrocarbon hydrate crystal agglomeration into larger ones (this is achieved in the industry by anti-agglomeration using Anti Agglomerants, abbreviated as (AA) and/or

(b) Inhibit and/or retard crystal growth (achieved in the industry by kinetic hydrate inhibition using Kinetic hydrate inhibitors, abbreviated as KHI).

Kinetic hydrate inhibitors and Anti-Agglomerants are added at low concentrations (<1 wt. %) and are commonly termed Low Dosage Hydrate Inhibitors (LDHIs). Both kinetic hydrate inhibitors and anti-agglomerants are usually have polymers with surfactant properties [14]. Thermodynamic and kinetic hydrate control methods may be used in conjunction with each other [15]. Examples of kinetic inhibitors are modified starch, poly (N-Vinylpyrrolidone) (PVP), polyethyleneoxide (PEO), poly (N-vinylcaprolactam) (PVCap), poly (N-Vinylacetamide) (VIMA), poly (N-Vinylvalerolactam) (PVVam) and poly (acryoylpyrrolidone) (PAPYD).

Another class of substances that can be used as inhibitors are starches although given their inherent characteristics is unsuitable for most applications. They need to undergo chemical and/or physical modification to enhance their positive attributes and/or to minimize their defects. Different starch products are used to control fluid loss in subterranean drilling, work over and completion fluids (for oil, gas or water) production [16].

Modifications can be either a physical or chemical process. Starch is chemically modified using the processes such as oxidation, cross-linking, stabilization and depolymerization. Physical modifications include pregelatinized and cold-water-swelling product. In this research, the physical modification of starch is adopted with emphasis on cold-water-swelling-product. Cold-water-swelling-starches are starch products that are gelatinized, i.e. starches that have lost their crystallinity, but which retain their granular form [17].

Deaton and Frost [18] conducted a research and from their experimental procedures, they determined the incipient hydrate formation requirements. In fact, they remain the earliest researchers to experience this breakthrough. They employed the technique called "the isothermal pressure-search method". By setting the hydrate prone set-up to a particular temperature, the pressure was increased incrementally until hydrates were observed. In a theoretical sense, as the pressure of hydrate forming system is increased gradually and left to settle for an infinite period of time (equilibration). The equilibrium pressure is the pressure at which there are observable hydrates formed at that particular temperature.

When a water-wet gas is rapidly made to transit an orifice, valve and other restrictions, that gas will expand thereby making it to produce hydrate. The hydrate occurs since the gas undergoes rapid cooling by Joule-Thomson (constant enthalpy) expansion. Rapid expansion in a wet gas line resulting in hydrate formation is a usual occurrence. Hydrate formation with rapid expansion occurs in lines carrying wet fuel gas.

Odutola et al [19,20] also supported the production of gas hydrate at the Joule Thomson valve due to cooling when gas is expanded, a research in which the mitigation performances of mono-ethylene glycol and methanol inhibition were compared. Lots of research has been made by various investigators on prevention of gas hydrates using various methods and approaches.

Investigation of binary mixtures's induction time was carried out by Talaghart [21] in the presence of kinetic inhibitors Poly Vinyl Pyrolidone (PVP) and L-Tyrosine. Gas hydrate formation pressure was also predicted using Peng-Robinson (PR) equation of state and different mixing rules by Karamoddin and Varaminian [22]. An integrated framework of flow assurance management strategy model on gas hydrate handling which determined operational limits of production systems so as to avoid gas hydrate plug formation in the case of unexpected shut-ins was presented. PVT Sim software was used to generate pressure - temperature operating envelope of the system and was operated using a state of the art modelling tool (OLGA). Their analyses were geared towards defining limits of operation in subsea production facilities to prevent hydrates formation.

Successful field testing of a high efficiency non-polymeric gas hydrate inhibitor in the offshore platform of Gulf of Paris near Trinidad that contained ten (10) gas lift injection wells was presented by Pakulsi et al [23]. This led to the entire field being converted from methanol protection and has been successfully treated using this method without complications since late 1996. Part of the pre-field testing done by Colarado School of Mines (CSM) research programme and the successful testing of a KHI (ISP, Graffix VC-713) in a 9.4km transmission line in the southern North Sea gas basin was reported by Bloys et al [24]. Elechi et al [25] also investigated the performance of Plant Extract, a locally sourced hydrate inhibitor on a mini flow loop. The result showed that the inhibitor was very effective

Recently, research direction in finding gas hydrate inhibitors has shifted towards dual function inhibitors. For the dual inhibitors, one can function as thermodynamic while the other acts as kinetic. Example of such dual function inhibitors is ionic liquids (ILs) [26]. Research shows that the effect of mixing synergents such as polyvinylpyrolidone (PVP), polyvinylcaprolactam (PVCap) and antifreezing polymers with hydrate inhibitors promote the inhibition performance of gas hydrate inhibitors [26,27,28,29]. Synergistic properties of PVCap with hexaalkylguanidinium and phosphonium bromide salts have been deeply studied [30,31,32].

Odutola et al. [20] clearly demonstrated that the combination of ethanol and methanol could reduce the water content of a sample gas stream thereby resulting in gas hydrate inhibition. Yang and Tohidi [33], reported that PVCap in combination with glycol ether significantly delays hydrate nucleation. Talaghat [34] also studied the synergistic performance of poly (ethylene oxide) (PEO) with modified starch.

Experimental investigations have shown that N-vinylcaprolactam (N-VCap) and 2-(Dimethylamino)

ethylmethacrylate (2-DMEM) among the patented conventional inhibitors are highly effective, hence the need to compare them with the inhibitor obtained from agro waste. Moreover, not much has been said about the use of agro wastes as gas hydrate inhibitors, given the clamour for pollution free environment. This study seeks to fill this gap and at the same time, reduce pollution to the environment caused by agro wastes.

II. MATERIALS AND METHOD

The materials used include Compressed Natural Gas (CNG) of specific gravity of 0.5. Water, ice blocks. The inhibitors used are water soluble and they include

- Locally Formulated Kinetic Hydrate Inhibitor (LFKHI) from agro waste starch
- 2-(Dimethyl amino) ethyl methacrylate (2-DMEM)
- N-Vinyl caprolactam (N-VCap)

Table 1, shows the constituent of the compressed natural Gas. The equipment used is a Mini Hydrate Flow Loop [35]

TABLE I.   COMPOSITION OF COMPRESSED NATURAL GAS (CNG) USED (TOTAL SUPPORT, PH)

Composition	Formula	Mole Percent
Methane	CH_4	98.44
Carbon Dioxide	CO_2	1.50
Total		99.94

Fig. 1 shows the Process Flow Diagram while the actual Mini Flow Loop is fig. 2. The loop is made of 316 stainless steel with 0.5 in internal diameter, encased in a polyvinylchloride (PVC) pipe that is 4-inch in diameter and is built on an external framework. The total length of the Mini Flow Loop is about 12m (39.4 inches) long. The process is regulated with three switches built into a control panel. The refrigerating unit and the 4-inch diameter PVC pipe mimic the offshore environment. The loop has three pumps, three temperature gauges and a manual pump. A mixing vessel for mixing the inhibitor and water in their different weight percentages, a CNG bottle and flow meter are all part of the loop [25].

The Locally Formulated Kinetic Hydrate Inhibitor (LFKHI) was produced from an agro waste. The agro waste is a source of bioactive compounds such as starch, dietary fibre, amino acids, minerals, vitamins and phenolic compounds. The phenols act against oxidative oxygens. Phenolic compounds are secondary metabolites produced in plants that have common structure based on aromatic ring with one or more hydroxyl substituents. They are divided according to their chemical structures into flavonoids (flavonols, flavanols and anthocyanins), phenolic acids, tannins and saponins [36]. These compounds prevent coagulation, acts as antioxidants and also form stable complexes in aqueous solutions which also help to act as anti-agglomerants. The presence of these compounds in the LFKHI makes it a very good hydrate inhibitor.

The agro waste was made into a paste and then modified using the physical modification process of Granular Cold Water Swell-able (GCWS) method. The solvent used for the modification is Alkaline-Alcohol mixture, with Sodium Hydroxide (NaOH) serving as alkaline while local ethanol (Kai-Kai) served as the alcohol. The agro waste paste and the alkaline-alcohol mixture were stirred vigorously for about thirty minutes to obtain the Locally Formulated Kinetic Hydrate Inhibitor (LFKHI).
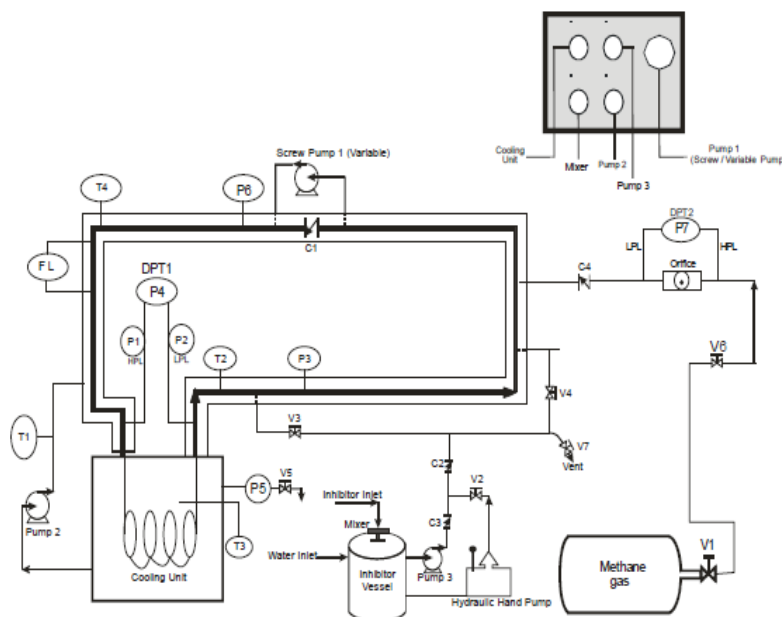

Figure 1.   Flow Diagram of Mini Fluid Flow Loop [35]

Figure 2.   Hydrate Mini Flow Loop [35]

III. EXPERIMENTAL PROCEDURES

Before the experiment commences fully, the mini loop is flushed with water to ensure that dirts/debris and rust is removed from the loop. This is done by switching on pump 3 on the control panel to draw water into the loop through valve 4 till a pressure of 25 psia is reached then valve 4 is closed. The trapped water is removed by opening valve 5, 6 or 7 as the case may be and the process is repeated many times depending on how rusty/dirty the loop is.

For the hydrate formation experiment, about 2660 ml (2616.2g) of water is measured into the inhibitor vessel, water is drawn into the loop as in the process of flushing above. The pressure is built up to 150 psia by turning on the CNG cylinder using valve 1 and orifice and then closed after this pressure is attained. Water is drawn into the refrigerating unit and circulated around the PVC pipe by turning on pump 2 so as to reduce the temperature of the fluid in the 1/2 inch internal diameter (ID) pipe to that which allows for hydrate formation. The screw pump is set at 150V to cause agitation and mixing of the fluid. The cooling process is facilitated by adding ice blocks into the refrigerating unit. 0.7m of the 0.5 inch pipe spiral coil is immersed inside the cold water in the refrigerator with the aim of increasing the retention time of fluid under test in the area where hydrates is likely to form and this is will occur in the coldest part of the mini flow loop. The different readings for temperature, differential pressure, and pressures are noted down at an interval of two minutes through the duration of 120 minutes.

The same procedure is taken in order to inhibit hydrate formation using the various inhibitors mentioned earlier. Water and a specific volume of inhibitor for the mitigation are added into the inhibitor vessel. The inhibitor usage is based on the weight percent in water phase to be used for the experiment (0.01, 0.02 or 0.03 wt% of inhibitor and the rest percentage is water) and then the experiment is commenced as usual. For hydrate formation experiment, key pointers to hydrate formation are rise in the loop temperature, rapid decrease in the loop pressure, sudden rise in differential pressure, plugged ¼ inch pipe at the sample test point (Valve 5) and effluent colour from the sample test point or Valve 5 [35].

Different inhibitor weight percentages of 0.01, 0.02, and 0.03 were used for the conventional kinetic hydrate inhibitors N-VCap, 2-DMEM and the locally formulated inhibitor (LFKHI). The effectiveness of the LFKHI is assessed based on the performance of N-VCap and 2-DMEM, which are used as controls.

IV. RESULT AND DISCUSSIONS

Various plots were used in the analysis of this work. The different plots were done for both the uninhibited (hydrate formation experiments in Fig. 3) and inhibited (hydrate mitigation as seen in Figs. 4, 5, 6, 7, 8 and 9). The plots are pressure versus time, temperature versus time, pressure and temperature versus time.
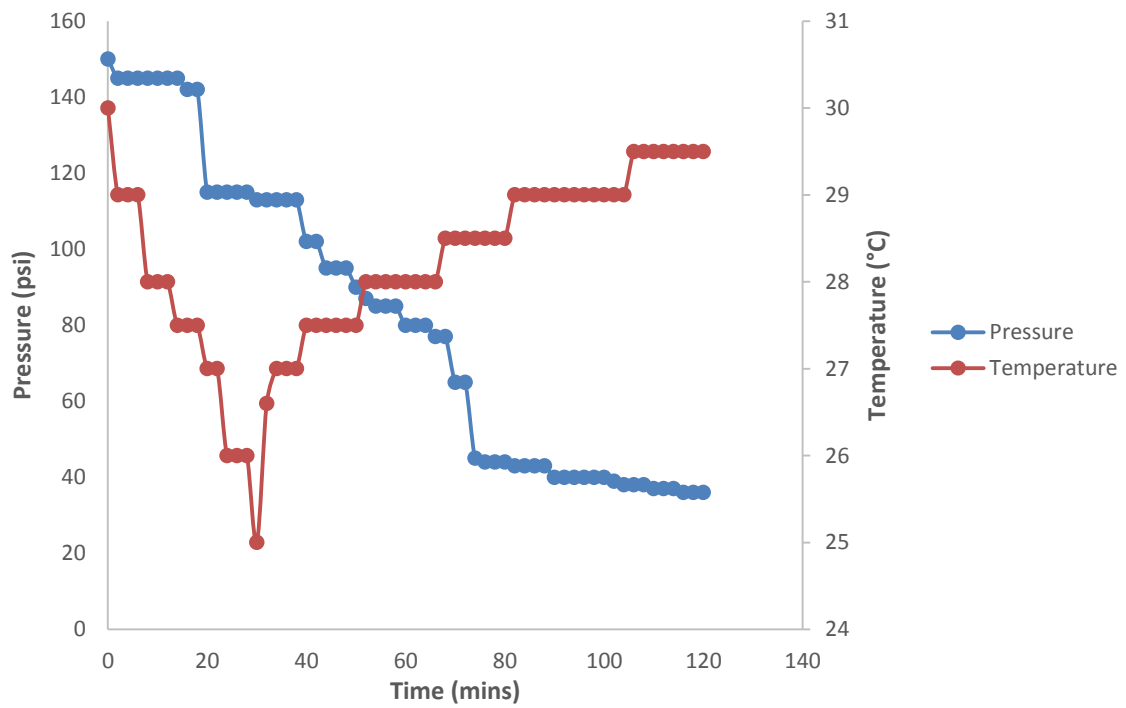
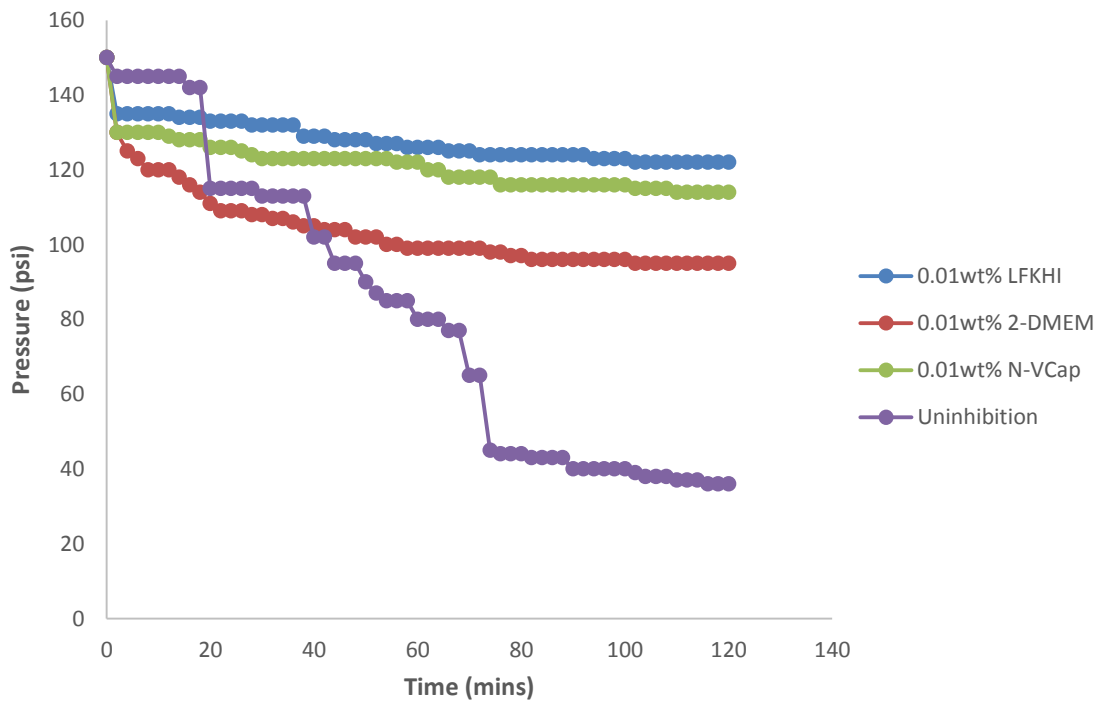Figure 3.   Pressure and Temperature versus Time for Uninhibited System

Figure 4.   Pressure versus time for 0.01wt% LFKHI, 2-DMEM, N-VCap and Uninhibition
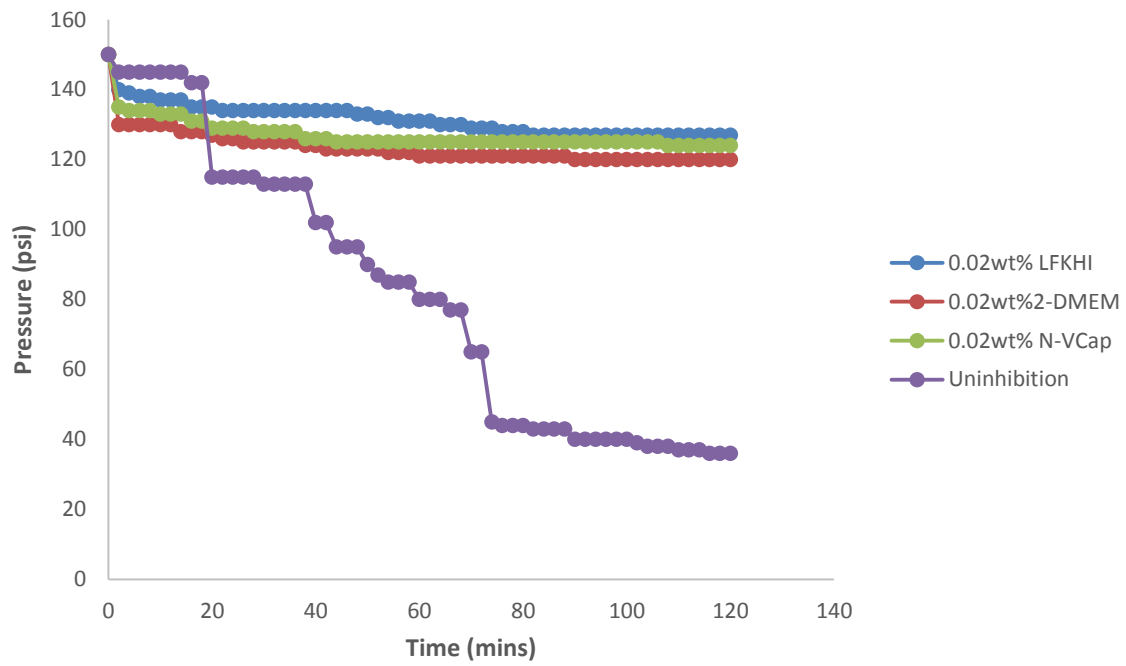
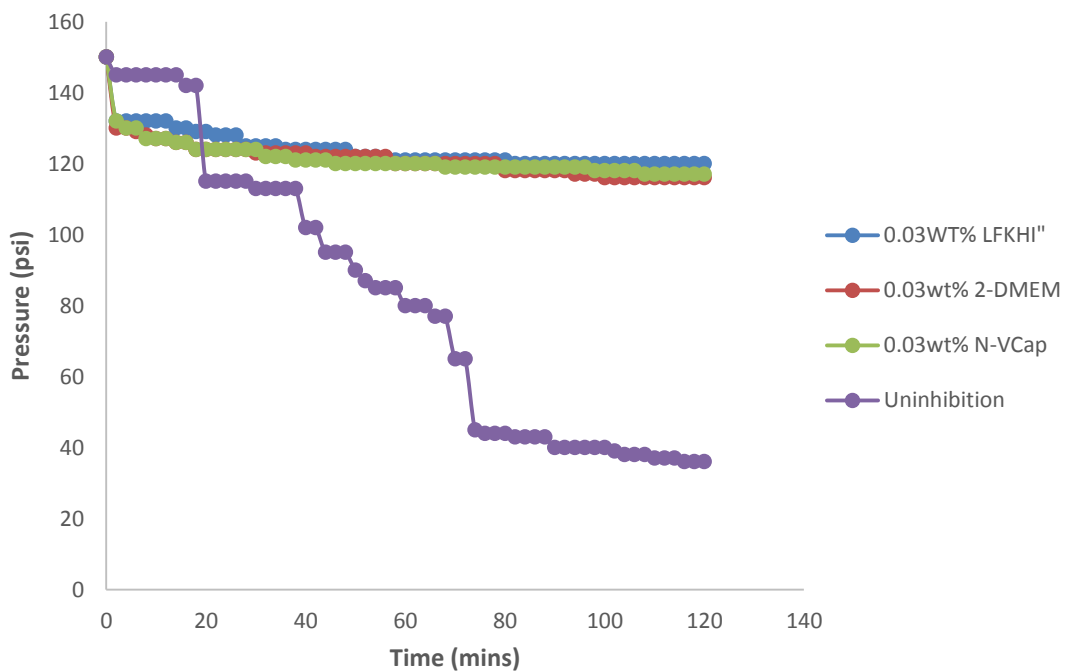Figure 5. Pressure versus time for 0.02wt% LFKHI, 2-DMEM, N-VCap and Uninhibition

Figure 6. Pressure versus time for 0.03wt% LFKHI, 2-DMEM, N-VCap and Uninhibition
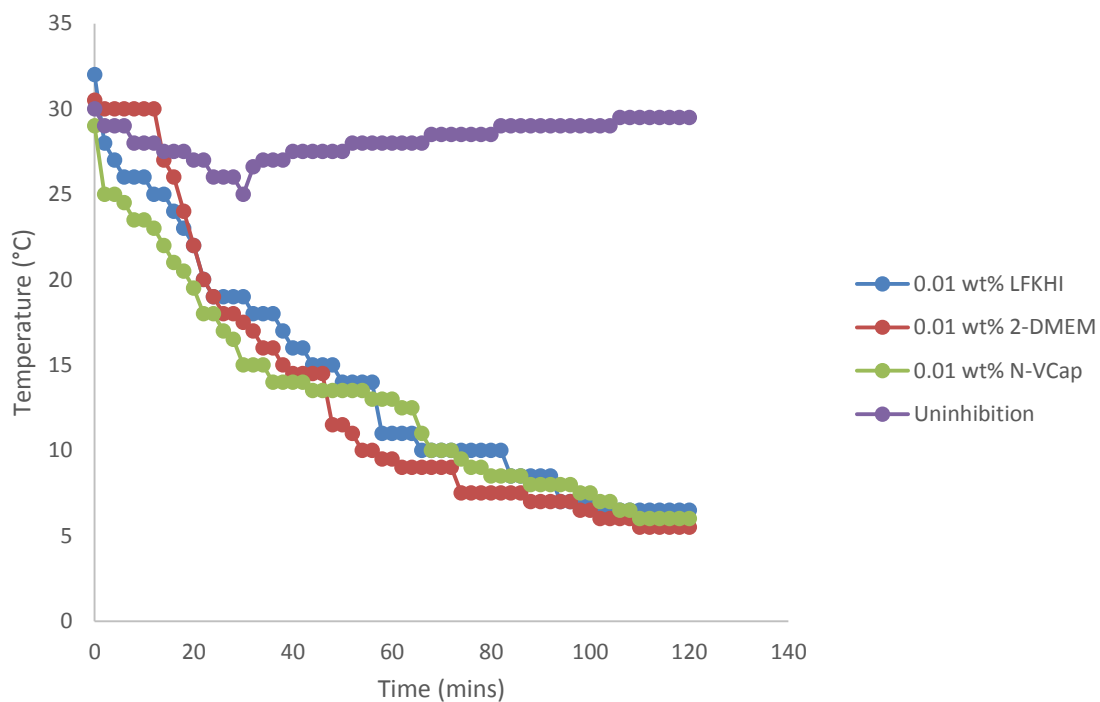
Figure 7.   Temperature versus time for 0.01wt% LFKHI, 2-DMEM, N-VCap and Uninhibition
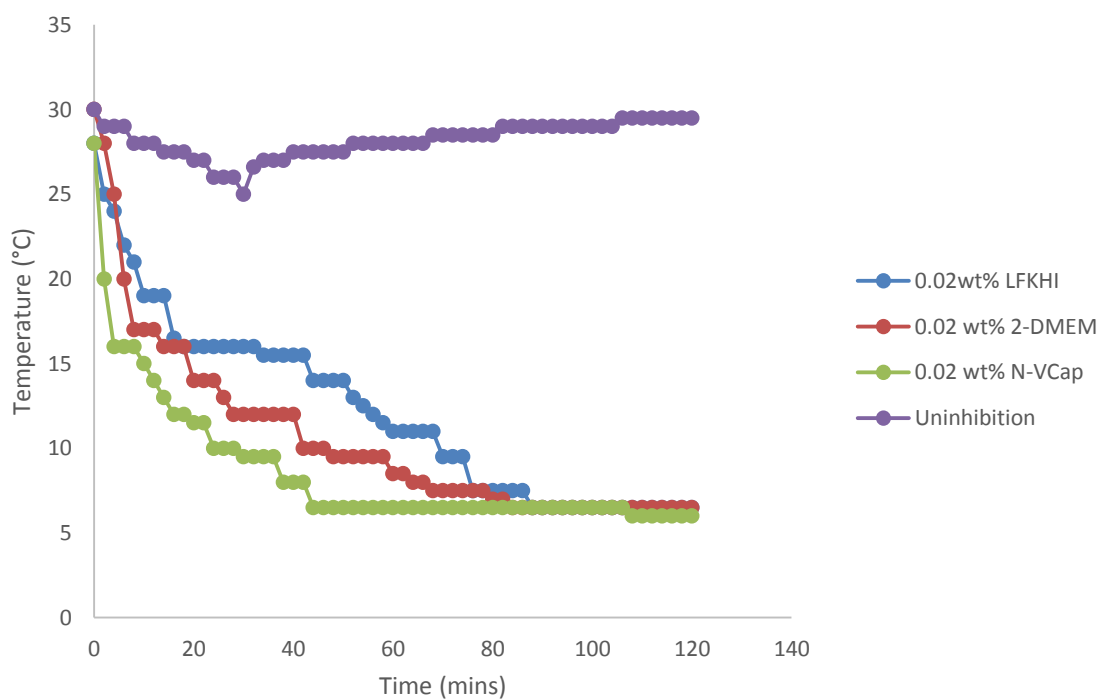

Figure 8.   Temperature versus time for 0.02wt% of LFKHI, 2-DMEM, N-VCap and Uninhibition
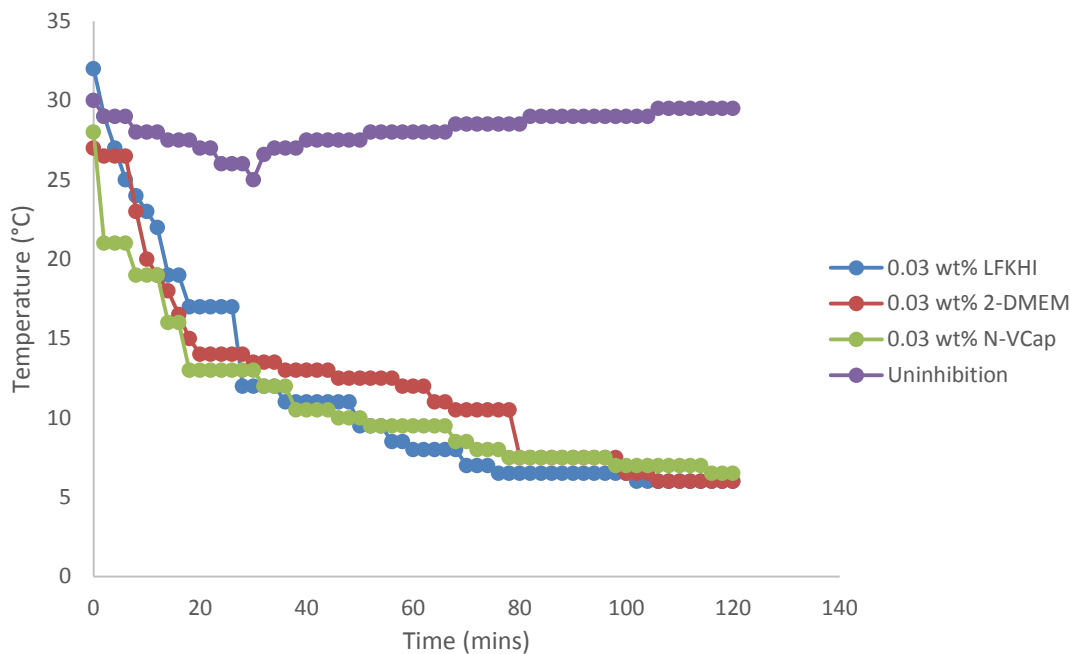
Figure 9.   Temperature versus time for 0.03wt% LFKHI, 2-DMEM, N-VCap and Uninhibition

For the uninhibited experiment, the initial temperature was 30˚C at the pressure of 150 psi. For the first 20 minutes and 3˚C difference in temperature (30 ˚C to 27˚C), a sharp drop in pressure from 150 psi to 115 psi was observed. This was maintained for about 8 minutes before it declined to 113psi and then to 80 psi in another 34 minutes and then decreased to 36 psi at the end of the experiment as shown in Fig. 3. The steady pressure drops observed during the experiment indicates that gas was being encapsulated by water molecules in the 0.5-inch 316 stainless steel tubing which gives rise to hydrate formation. The temperature reading reduced from 30˚C to 25˚C in the first 30 minutes of the experiment. It began to rise from 26.6˚C at 32 minutes until it finally reached 29.5˚C, as seen in Fig. 3. The increase in temperature signifies that heat is been given off which is an indication of gas hydrate formation because the process of hydrate formation is exothermic in nature.

Fig. 4 shows the experiment conducted using 0.01wt% of the 3 inhibitors, the first 20 minutes recorded a pressure declined from 150 to 133 psi for LFKHI, 108psi and 123 psi for 2-DMEM and N-VCap respectively. After 60 minutes, the pressure further decreased to 126psi, 99psi and 120psi respectively. At the end of 120 minutes, the pressure declined to 122psi, 95psi and 114psi for each of the inhibitors. The pressure drop is lower for LFKHI compared to that observed for 2-DMEM and N-Vcap. This clearly shows that at 0.01wt% concentration, LFKHI has the highest inhibitory capacity while the N-VCap performed better than 2-DMEM.

From Fig. 5, using 0.02wt% of these inhibitors, it is observed that from 0 to 20 minutes, the pressure declined from 150 psi to 135 psi for LFKHI, 150 psi to 127 psi for 2-DMEM and 150psi to 129psi for N-VCap. After the next 90

minutes, the pressure drop for LFKHI is 127 psi, 120 psi for 2-DMEM and 125psi for N-VCap and finally to 127psi, 120psi and 124psi at the end of 120 minutes. LFKHI did best, followed by N-VCap which did moderately better than 2-DMEM.

The same scenario was observed from Fig. 6 using 0.03wt% of the inhibitors. Pressure declined from 150psi to 120psi for LFKHI, 150psi to 116psi for 2-DMEM and 150psi to 117psi for N-VCap at the end of 120 minutes. There was a general reduction in pressure compared to when applying 0.01wt% and 0.02wt% of these inhibitors. LFKHI remains the best inhibitor even at 0.03wt% concentration. 2-DMEM showed least capacity to inhibit hydrates.

Temperature reduced from about 32°C to about 6.5^{o}C for 0.01wt%, 28°C to 6.5^{o}C and 32°C to 6°C for 0.02wt% and 0.03wt% respectively of LFKHI as seen in Fig. 7. From Fig. 8, using 2-DMEM, temperature reduced from 30.5^{o}C to 5.5^{o}C for 0.01wt%, 30°C to 6.5^{o}C for 0.02wt% and 27°C to 6°C for 0.03wt%. N-VCap gave temperature decline from 29°C to 6°C, 28°C to 6°C and 28°C to 6.5^{o}C for 0.01wt%, 0.02wt% and 0.03wt% respectively as seen in Fig. 9. In all the weight percentages of the various inhibitors used there was no increase in temperature which means hydrate formation was inhibited.

V.   CONCLUSION

The LFKHI from the agro waste exhibited the highest inhibition effect compared to the conventional kinetic hydrate inhibitors in use when screened on the hydrate mini flow loop. The LFKHI can be improved upon and recommended

for field application. Agro wastes which constitutes nuisance in our immediate environment has been put to effective use by producing a LFKHI from it. This will help to reduce environmental pollution caused by local food vendors.

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