



Gas Hydrate Treatments in Pipeline Using Locally Sourced Material as Green Inhibitor

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Abstract: Hydrates had been a lengthy-standing issue in the oil and gas sector, causing significant flow assurance problem. It may form obstructions due to the decline in pressure and low temperature in oil and gas pipelines. Its impact can be felt in drilling risers, chokes, killing lines, and preventing blowouts. Hydrate plugging of the pipeline would cost approximately more than \$1 million per day. In this work, the development of a local inhibitor for the treatment of hydrate formation in oil and gas pipeline under different conditions were studied using a mini hydrate flow loop. A biodegradable and water-soluble inhibitor (Caricaceae Plant Extract Kinetic Inhibitor, CPEKI) was developed from plant extract of caricaceae plant family that was sourced locally. This was done in order to reduce the cost of importing conventional inhibitors like that of Mono Ethylene Glycol (MEG) and Methanol (MEOH). The experiments were carried out with an initial loop pressure of 150 psi and temperature of 29°C. Different weight concentration of CPEKI, MEG and MEOH were tested under varying conditions of temperature and pressure. The induction time for hydrate formation and inhibition at different conditions were also recorded. From the results analysis, it was observed that the CPEKI shows a very good inhibitory performance throughout the processes with an optimum concentration of 0.05wt% against MEG and MEOH inhibitors. Similarly, the relationship between pressure and temperature as a function of time also indicates that CPEKI performed very well compared to MEG and MEOH. Consequently, it is confirmed that CPEKI is eco-friendly and cheap and therefore suggested for field trials.

Keywords: Hydrate, Inhibitor, MEG, Flow, Gas, Material

1. Introduction

Gas Hydrates are crystalline solids in which guest molecules (usually gas) like those of methane, ethane, propane, butane, nitrogen, carbon dioxide and hydrogen sulfide of appropriate size are tapped into cages formed by hydrogen bonding between water molecules (host).

Hydrates had been a long-standing problem in the oil and gas sector, causing significant flow control issues. Appropriate conditions for the formation of gas hydrate commonly occur during hydrocarbon production operations, especially in coastal activities (subsea developments). Well-cooled streams may cause disturbed hydrates and other cubics such as waxes and asphalt to precipitate. Hydrates will result in significant capital (CAPEX) and operating costs (OPEX) if allowed to take place. Approximately 70 percent of flow control capital spending is used on hydrates annually.

The deposition blocks oil and natural gas pipelines and interferes with hydrocarbon movement along with its intrinsic concerns about safety [14, 18]. When production remains shut down, plugging oil and gas hydrate will cost more than \$1 million every day [4]. Two major forms of hydrate formation are thermodynamic hydrate formation and kinetics of hydrate formation. Great progress had been made in thermodynamic hydrate formation since 1934, but there are many difficulties in researching hydrate forming kinetics, such as understanding the hydrate formation process or inhibition kinetics. Therefore, the research of hydrate composition kinetics is important for many requirements including petroleum storage and distribution, refrigerant hydrate formers such as phase change materials, water desalination and gas separation. From the other end, chemical treatment is however needed to avoid hydrate due to some significant safety and operational problems associated with

the formation of hydrate in hydrocarbon transport pipelines. Besides the growth of hydrate in pipelines, issues associated with the formation of hydrate are indeed important in fracking operations. The industry is now more concerned with safe fracking operations for deep ocean than ever before. For example, traditional mono ethylene glycol and methanol are known on using thermodynamic inhibitors in the conventional approach of gas hydrate prevention.

The major problems with the use of thermodynamic inhibitors are the high cost and ecological problems of thermodynamic inhibitors due to the increased concentration of thermodynamic inhibitors. The creation of eco-friendly low-dose hydrate inhibitors (LDHI) has therefore been an intriguing topic for academics and business sector. Low-dose hydrate inhibitors are grouped into inhibitors of kinetics and anti-agglomerates (AA) (KI). Although kinetic inhibitors deter or delay hydrate formation by prolonging the induction period for hydrate formation, non-agglomerants prevent jamming of the pipe line. The environmental consequences of marketing LDHIs has led to research on more environmentally friendly LDHIs [17, 21]. Typically, the volume of kinetic inhibitors used varies from 0.01 to 0.1% with chemical properties varying information from multiple thousand to millions [28]. First type of kinetic inhibitors used was polyvinyl pyrrolidone (PVP), a commercially available water-soluble material containing lactam chains. An efficient gas hydrate kinetic blocker containing lactam circles was formulated as a polymer. Three other economically available polymers of the lactam ring were tested and proved to be much more successful. These three polymers have been identified as kinetic inhibitors of the second generation. Such polymers' names and acronyms are polyvinylcaprolactam (PVCAP), terpolymer, N-vinylpyrrolidone/N-vinylcaprolactam / N-dimethylaminoethacrylate (VC-713) and N-vinylpyrrolidoneco-N-vinylcaprolactam (VP/VC) [15]. The scale of the lactam ring in kinetic inhibitors is identical to the five and sixmember hydrate structure. Because of the electro negativity of nitrogen and oxygen in the amide group of the lactam ring, it might solubilize on the hydrate particle and obstruct hydrate formation.

2. Hydrate Formation Problem

Hydrate incidence raises significant functional and health concerns along with huge losses in revenue. Hydrates may form obstructions due to the drop in pressure and low temperature in natural gas pipelines, particularly when temperature drops dramatically, like shutting down of a well or streaming via a choke. The greatest chance for hydrate accumulation is solid deposits of waxes and asphalt. Remediation of hydrate blockages can also pose significant technical issues with substantial cost consequences. Hydrates may have major safety consequences during fracking operations. Hydrates could develop when drilling risers, chokes, killing lines, and preventing blowouts [10]. In addition, the naturally found hydrates close to the surface could also pose a potential threat during drilling by injecting

gas onto the reservoir causing well-managed complications and potential for flameouts. As the offshore industry moves into the latest deep sea and ultra-deep water areas, the problems of hydrate formation are becoming more important. Deepwater reservoir fluids tend to still be at fairly low temperatures, and somehow this, combined with low room temperatures in deep waters and higher flow line pressures needed to move the fluids up to very long production risers, means that hydrates are far more likely to develop in such processes [11]. This leads to higher running costs and can frighten standard hydrate mitigation strategies.

2.1. Thermodynamics Concept of Hydrate Formation

Without understanding the concepts involved, the study of thermodynamics cannot be accomplished, particularly when it has to do with scientific research. Thermodynamic principles such as hydrate formation, stability, equilibrium, hydrate kinetics, mole fractions, driving forces, solubility and determination of correct operating conditions help to properly interpret the hydrate formation state. Else it's wrong to say. Many thermodynamic principles that will help to explain this research work will be discussed in subsequent discussions.

2.2. Minimum Condition for Hydrate Formation

In 1946, Deaton [9] conducted an investigation, from their experiment they determined the nascent hydrate formation requirements [9]. Throughout the inquiry they adopted a technique called "the isothermal pressure research method." Hydrate prone apparatus was set –up to a specific temperature, and there was enormous pressure until hydrate was observed. In theoretical perspective, it means that as the pressure of the forming system is gradually increased and allowed to settle for a limitless period of time (equilibrium state). In order to observe hydrate formation, there must be an existence of a driving force. The said driving force is capable of measuring system potential for formation of hydrate. For example, if the intrinsic conditions to form hydrate is predicted at 4°C and 4500kpa. Undoubtedly, by given these factors the system will never allow gas hydrate to form. The explanation here seems to be that with this condition at stability, hydrate will not form because the necessary force to form hydrate is zero (0).

2.3. Gas Hydrates Problems in Petroleum Industry

The development of methane hydrate is a serious challenge facing exploration and production drilling operations [16, 37]. During deep-water drilling, the development of methane hydrate may have adverse effects on well-control and safe operation [25]. Those kinds of hydrates are developed when, during deep water drilling, shallow sediments containing natural gas are found. Gas reaches the drilling fluid leading to low temperature and high pressure hydrate formation [12]. If the mud that was used in the drilling phase hasn't been inhibited, it may form hydrate leading to unexpected gas kicks that block the tube, annular clearance, or blowout

prevention (BOP) [34]. Also during deep water drilling, the hydrostatic pressure of the drilling fluid column and the fairly low temperature of the sea bed will boost the state of hydrate thermodynamics culminating in a gas kick [2, 5]. Gas hydrate even occurs during shut-in, start-up in our offshore production facilities in well heads jumper parts and risers [20].

2.3.1. Flow Assurance Issues

The oil and gas produced from the well head is transported to the processing plant through the pipeline. If the pipeline temperature and pressure falls within the hydrate region [25], gas hydrate may occur. When this temperature and pressure falls into the hydrate zone, condensation (water) is felt, slowly forming solid crystals that build up and result to blockages (or plugs) of onshore and offshore pipelines [13]. The pipe plug splits the tubing onto two pressure sections in both the root of the well or the source of high pressure gas as well as the plug and a secondary section under reduced pressure between both the plug and the gas recovery system. A pipe blast in the highly pressurized region can occur as a result of the increased pressure. Once the change in pressure rises here between input and output parts, the pipe will be affected by the plug. Both issues can damage manufacturing equipment and endanger personnel safety [25]. Hydrate deposition is always unwanted, however, as crystals cause flow lines, chokes, valves and instrumentation to be blocked, line capacities to be curtailed [10]. Another issue for stream guarantee is muddy hydrates, the hydrates being formed would be less thick and incremental. The deposition of hydrate can occur as strongly as feasible at any position and state where these sands maintain a small deposit in the natural gas pipeline [24]. Nasheed [23] used a pressure temperature diagram to predict that some flow assurance problems may occur.

2.3.2. Gas Hydrates Formation Interfaces

Gas hydrate is shown here as a multi-phase flow problem involving oil, fluid natural gas, water, and solid hydrates. Reijnhout [27] study outlined 5 various domains at which gas hydrate can form and accumulate in natural gas production as follows: gas / liquid, liquid / liquid, gas / solid, liquid / solid and solid / solid. The gas is called hydrocarbon fuel, while the liquid is petrol air, or condensate. Solid is the gas hydrate surface or the pipe wall. The three driving forces in the cycle have been highlighted as the cooling and stress elevation of the fluid induction, according to Odutola and Sloan [24, 28]. The formation of hydrate starts the moment the pressure and temperature within the hydrate region reaches the point of equilibrium. This happens at the interface of water / petroleum fluid (oil or gas) forming a casing structure surrounding water / oil droplets (thickened in oil / water). The tube walls [26] are another location for hydrates to develop in the shape of contaminants. After its first stage, hydrate continue to grow. As hydrate deposition is such an exothermic cycle, heat needs to be extracted [24]. Hydrate compost in the system influences the rheological behavior of the moving fluid at a time when ample hydrate is formed [6].

When hydrated grains mix and polymerize into larger components, the atoms will continue to grow and form larger hydrate concentrations and accumulation, resulting in an increase in slurry viscosity which will, in turn, restrict flow and eventually lead to pipe line plugging [30, 32].

2.4. Hydrate Inhibition

For the oil and gas sector, gas hydrate avoidance is a desirable option to prevent working with the hydrate development zone [10, 30]. Hydrate induces accidental shutdown, or in most situations, by shooting up the temperature /decreasing the device pressure, results in irregular operating state. Talaghat [31] suggested that gas hydrate can be mitigated by applying the thermodynamic inhibition and low Dosage hydrate inhibition methods.

2.4.1. Thermodynamic Inhibition

Thermodynamic inhibition is the common tradition method employed in recent time. The possible ways of applying thermodynamic inhibition are by removing water particles in the gas pipeline, heating/depressurizing the gas pipeline, insulation of pipeline, injection of salt solution and injecting of a thermodynamic inhibitor.

2.4.2. Active Heating/Depressurizing the System

The heating of the flow line is a method of preventing the formation of hydrate. This solution is done by increasing the temperature of the unit above the hydrate formation temperature. Regardless, it is better to apply the heat to precisely locate the specific area of the hydrate plug. Adequate energy is needed to dissociate the rapidly formed solid hydrate to prevent the flow line from ramping up compression and possible breakup. The cost of flow line ventilation, including chemical treatment, is quite expensive. On the platform for the pipeline, approximately 5 to 10 megawatts of heating power is generated. The heating process could not handle any distance lengths, less than 20 miles, but the heating method to prevent pipeline plug could not have been accomplished for a pipeline length of about 50 miles or more.

When depressurizing a hydrate plug tube, depressurizing through either edge is absolutely dangerous. Dyke [10] proposed that the simplest method would be to lower pressure beneath hydrate deposition pressure at a room temperature sufficient to reverse the equilibrium reaction. Sudden decompression must be stopped, according to Bai [3]. This can negatively impact the pipeline and worsen the hydrate and form ice problem. These implies that depression should really be enforced from both edges of the pipeline in the plug region. In the submarine environment, the two sides of the solid hydrate cannot be accessed. In such cases, operated submarine vehicle (ROV) would be required to stabilize the pressure, or alternatively coiled tubing.

2.4.3. Insulation of Pipeline

Insulation is a sure way of maintaining the temperature of the gas stream and keeping it out of hydrate region. The three forms of insulation that are conventionally in the industry

includes the pipes coating, pipe-in-pipe (PIP) or bunding and vacuum-insulated pipes. Among all the insulation type, the most expensive is the vacuum-insulated pipe insulation.

2.4.4. Injection of Salt Solution

Through injecting CaCl_2 salt solution, the formation of hydrate can be reduced. This lowers the chemical activity of the water, thus increasing the volume of watersoluble gas [29]. But the biggest challenge is to use salt to induce corrosion from the carbon pipeline.

2.4.5. Injection of Thermodynamic Inhibitors

Thermodynamic injection is a mechanism used to remove hydrogen-bonded water molecules [1]. This process changes the hydrate phase's chemical ability to shift the equilibrium or dissociation curve to lower temperature or higher pressure. To be active with these thermodynamic inhibitors, higher concentrations of approximately 10–60 wt percent will be added. Conventionally used thermodynamic inhibitors are mono-ethylene glycol (MEG) and methanol (MeOH). Mono-Ethylene glycol (MEG) and methanol (MeOH) purchase costs are quite expressive But MEG is more expensive than methanol. Methanol is cheap per galling, with water flow rates higher than 2000 barrels per day (bpd), it is impractical to get adequate MeOH subsea in conjunction with the substance made. According to the [3] study, methanol could be injected down the pipes to the desired impaction position using braided piping up to 14,800 ft. This is mostly useful when tubing line displacement and bull heading are shut down in development. Mono-Ethylene Glycol (MEG) is favored instead of Diethylene Glycol since it could be subdivided and reused on the manufacturing platform from a processed liquid. Nevertheless, owing to its chemical toxicity, through the use of these inhibitors faced severe hazard. Health, safety and environment, corrosion, logistics concerns, high CAPEX and OPEX are the problems associated with these inhibitors [7, 32]. Hydrocarbon fractions are tainted by the inhibitors, the price of retrieving the missing inhibitor is quite expensive for the rejected liquid. Large tanks and injection facilities are needed for the implementation of these inhibitors.

2.5. Dehydration

Dehydration is a method used for removing water from Natural gas and Natural Liquids (NGL). It is usually done by injecting a liquid desiccant into a drying system. Glycol is the common liquid desiccant that is used. In onshore facilities, dehydration plant is mostly used. Dehydration may not be applied in the subsea due to dehydration plant space restriction [32].

2.6. Low Dosage Hydrate Inhibition

The alternative approach that also meets the industry standard remains low dosage hydrate inhibitors (LDHIS) [13, 15, 23]. Low-dose hydrate inhibitor application required a small inhibitor concentration for injection (< 1% of the water weight) [35]. They stabilize the pumping and storage

capacities very effectively. Low-dose hydrate inhibitors (LDHIS) have been developed to delay the aggregation of hydrate due to health, safety and environmental concerns of thermodynamic inhibitors [2]. Because of the decrease in storage size, injection rate, pumping requirements and piping facilities, using LDHIS reduces operating costs economically.

2.7. Kinetic Inhibitors

Kinetic inhibition of hydrate (KHIS) delay hydrate cloud formation and crystal growth during the slow growth phase, hydrate particles might or might not be stopped from building up. If allowed, the prevention cycle will break down and catalytic hydrate will be increasingly formed. If hydrate is shaped to plug the pipe line this could have a harmful effect. KHIS's two categories are: Water-soluble KHIs and material KHIs. Water-soluble KHIs are polymers with a propensity to form hydrogen bonding with water, thus avoiding the deposition of hydrate [15]. These KHI polymers are based on copolymers or cyclic amide homopolymers (Lactam). Types of polymers are poly (N-vinylpyrrolidone) (PVP), poly (N-vinylcaprolactam) (PVCap), poly (N-vinylacetamide) (VIMA), poly (N-vinylvalerolactam) (PVVam) and poly (acryoylpyrrolidone) (PAPYD) or other amides such as N-methyl-N-vinylacetamide and ploy ethyloxazoline [13]. KHI is nonpolymer, tetrapenty lammonium bromide and butoxy ethanol are the category of inhibitors. Because they are unable to communicate with hydrated surfaces, these KHIs perform poorly, but they are good as synergists [15].

Use of extract from the Palmae plant family as a corrosion inhibitor was examined by Lederhos [19]. The Chromatography-Mass Spectrometer (GCMS) revealed in their research the primary ingredient being oleic acid, palmitic acid and cetyl alcohol with carbonxyl class and dual bond which enabled the extract to be a better corrosion inhibitor due to double bond hydrogenation. Fourier Transform Infrared Red (FTIR) has shown that the appearance of tannins, alkaloids, flavonoids, and saponins, makes it a strong corrosion inhibitor.

Odutola [21] used the Colorado School of Mines (CSM) Gem technology to compare the impact of methanol and mono ethylene glycol on gas hydrate inhibition throughout gas extension. Methanol has been observed to be more effective than Mono Ethylene Glycol. In all these research, synthetic-based gas hydrate inhibitors were utilized. Nonetheless, in reducing gas hydrate, these inhibitors are shown to be active, posing environmental problems to biological, ecological and marine life. In our community, local materials that are easily discovered and accessible have to be applied and pose less danger to the health of the citizens. The need for natural materials as enhancing petroleum regeneration has been explored by several researchers. Elechi [12] conducted research utilizing plant extract as a gas hydrate inhibitor in a mini-flow loop using quantities of 1, 2 and 3wt%. A correlation has just been made with the modern gas hydrate blocker Mono Ethylene Glycol (MEG). It has been reported that the plant extract comprises of tannin, alkaloid, flavonoid and saponin bioactive components [22]. They observed that an active hydrate inhibitor

relative to MEG was the presence of these phytochemicals in the plant extract. The local inhibitor is an extract from liquid-soluble plants that includes alkaloids, saponins, flavonoids and tannins [22]. Flavonoids are anti-inflammatory and anti-coagulant agents that stop clotting. These are PolyPhenolic substances and are discovered in vegetables, fruit. They function as strong oxidants that safeguard against proactive oxygen. Tannins are a heterogeneous group of elevated molecular weight of Poly Phenolic compounds capable of forming crystals that are fixable and permanent. They are discovered in fruits, legumes and grasses. Poly Phenolics is a grade of chemicals consisting of hydroxyl group immediately linked with an aromatic hydrocarbon group.

2.8. Anti-Agglomerates

Anti-agglomerates (AAS) are polymers and surfactants that only perform very well with the composition of both hydrocarbon and water phases to avoid agglomeration or accumulation of hydrates in the pipe line. Anti-agglomerates (AA) deter hydrate crystal agglomeration and form a plug by modifying interfacial properties [8]. The inhibitor can be applied at low concentration (< 1 wt. %) to reduce the agglomeration and growth of hydrate particles such that a transportable hydrate slurry is formed.

Lee study the synergetic performance of the mixture of hydrate inhibition in the presence of mineral oil phase [36]. Shell has licensed other groups of surfactants as AAs [21, 27]. Alkyl aromatic sulphonates (Dobanax series) and alkyl polyglycosides (Dobanol) are included, but this particular series doesn't really seem to be available commercially. Recent Statoil, SINTEF and NTH published research on surfactants. Berol and alkylphenylethoxylates [33] are included.

3. Materials and Procedure

The material used for this work is a long mini-hydrate flow loop (approximately 39.4-inch (12m), formed with 316 stainless steel and 0.5 inner diameter wrapped in a Poly Vinyl Chloride (PVC) tube of four (4) inches.

At the beginning of every test, the loop is washed to get clear of the debris or contaminants that might be in the loop. This process begins by pumping water from the mixture vessel into the internal line by opening valve 4 until it achieves a pressure of 25psi. The water is removed with valves 5, 6 or 7 and the cycle can be reiterated as frequently as possible to assure the dust is washed completely. This same procedure is applied for the hydrate formation test, but again, upon reaching the pressure buildup of 25psia, the CNG bottle is turn on and then valve 1 and orifice are enabled to build pressure to 150psia after closing down the valves and orifice. Varying quantities of inhibitors are pumped into the mixing vessel in correct proportion to water in the scenario of hydrate mitigation and the same method is operated with pressure and temperature measurements taken over a time frame of 120 minutes at a time window of two minutes.

4. Results Analysis

4.1. Analysis of Gas Hydrate Inhibition and Uninhibited Plots

Experimental data have been reviewed and plots were made for the various experiments conducted for both inhibited and uninhibited.

Figure 1 shows a plot of pressure and temperature as a function of time for uninhibited (water and gas) experiment. The induction time is the point at which there was a rapid drop in loop pressure and corresponding temperature reduction. In Figure 1, it is observed that the pressure declined from 150psi to 121psi in the first 2 minutes of the experiment and remained steady till after 12 minutes when it drops to 116 psi. Also, there was a corresponding deviation in temperature drop from 30°C to 22°C. At the end of 120 minutes, the pressure declined to pressure of 96 psi and temperature to 6.5°C indicating formation of gas hydrate in the system. The steady decrease in pressure observed during the tests shows that gas was embedded in 0.5 inch 316 stainless steel tubing.

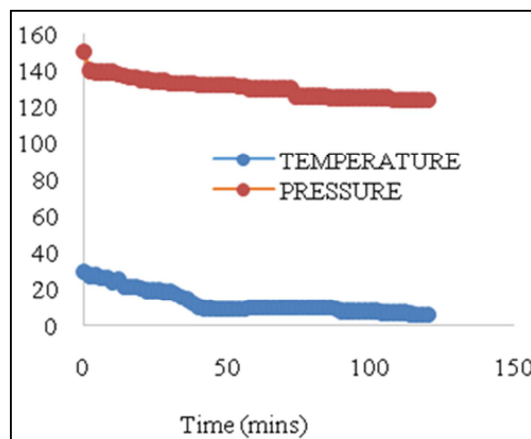


Figure 1. Plot of pressure and temperature as a function of time for uninhibited fluid.

In order to determine the inhibitory effect of Caricaceae Plant Extract Kinetic Inhibitor (CPEKI), a comparison has been made with conventional inhibitors (MEOH, MEG) for various weight percentage concentrations for each of the inhibitors used and uninhibited experiment against time as can be seen in Figure 2 – Figure 6.

Figure 2 shows the relationship between pressure of 1st concentration for MEOH, MEG, CPEKI and uninhibited against time. 0.01w% of CPEKI was used while that of MEOH and MEG were 1wt. % each respectively. From the plot (Figure 2), it can be seen that MEG performed better in inhibiting the system at pressure decline from 150psi to 125psi in 94 minutes. Similarly, In Figure 2, CPEKI maintained rapid decrease in loop pressure from 150psi to 110psi in 60 minutes of the experiment and suddenly experiences a spike in the system loop pressure within 6 minutes. This result in an increased pressure from 110psi to 118psi based on agitation in flow that could have form hydrate, was a mitigation [31] MEOH had a decrease in

pressure of 105psi.

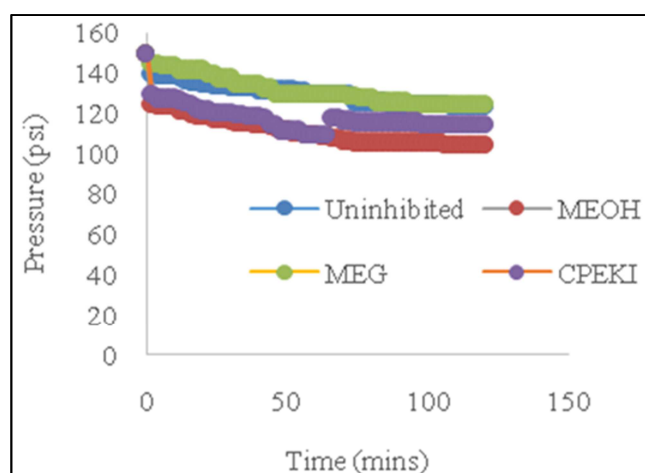


Figure 2. Pressure as a function of time for 0.01 concentrations of CPEKI, MEG and MEOH and uninhibited.

Again, Figure 3 present results of pressure for 2nd concentration of MEOH, MEG, CPEKI and uninhibited as a function of time. From the plot (Figure 3), It is observed that CPEKI with 0.02wt. % concentration had a good inhibition performance at declined pressure of 128psi in 106minutes as against MEOH and MEG with concentration of 2wt. % each. MEOH and MEG have the same pressure decline of 122 psi respectively.

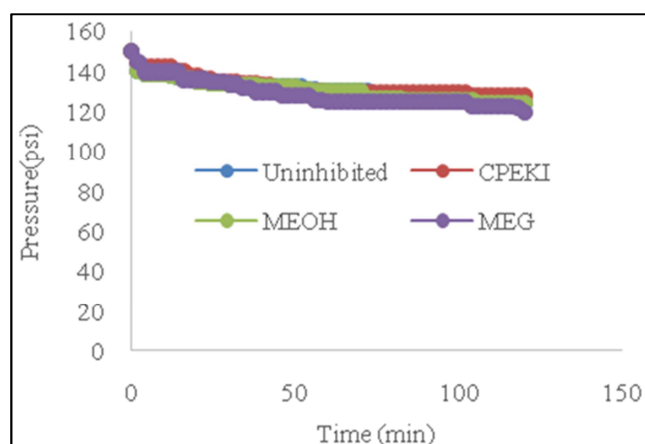


Figure 3. Pressure as a function of time for 2nd concentration of MEG, MEOH, CPEKI and Uninhibited.

Similarly, Figure 4 shows the relationship of CPEKI, MEOH, MEG and uninhibited as a function of time. From the Figure (Figure 4), It can be seen that CPEKI again prove to be a better inhibitor for the pressure of 3rd concentration for MEOH, MEG, CPEKI and uninhibited against time. CPEKI shows better inhibitory effect with 0.03wt. % concentration at a pressure decline from 150psi to 125psi in 106 minutes against MeOH and MEG with high weight percentage concentrations of 3wt. % each respectively. MEG competed with CPEKI which shows hydrate inhibition at pressure drop of 121psi in 100minutes of the experiment. MEOH have a pressure drop of 110 psi.

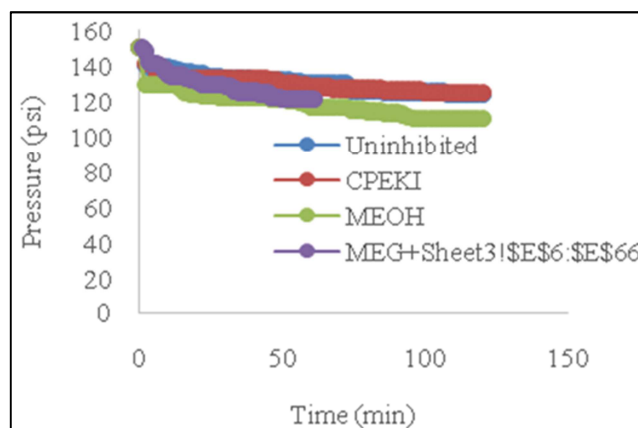


Figure 4. Pressure as a function of time for 3rd concentration of MEG, MEOH, CPEKI and uninhibited.

Figure 5 shows the plot of pressure against time for 4th concentration of MEOH, MEG, CPEKI and the uninhibited. As expected, it can be seen that CPEKI had a better inhibition performance as compared to MEOH and MEG. In Figure 5, It can be observed that CPEKI for the 4thconcentration with 0.04wt. % performed more accurate than MEOH and MEG with high concentration of 4wt. % each. The trend in loop pressure decline was from initial pressure of 150psi to 128psi which shows good inhibitory capacity in 80minutes of the experiment and further declined to 127psi after 38minutes. However, the delay in pressure drop made CPEKI a good inhibitor. MEG inhibited the system at pressure drop of 115psi in 106 minutes, while MEOH have a pressure drop of 104 in 86minutes.

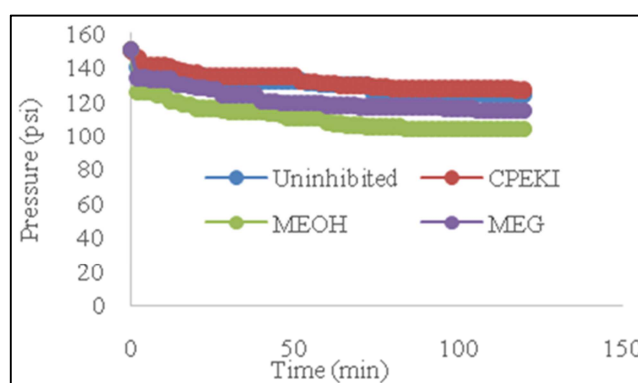


Figure 5. Pressure as a function of time for 4th concentrations of MEOH, MEG, CPEKI and uninhibited.

A similar trend was also observed in Figure 6for the plot of pressure against time for the 5th concentration of MEOH, MEG, CPEKI and the uninhibited. As can be seen from Figure 6, it is worthy to note that CPEKI performed credibly well when compared to MEG and MEOH. It is noted that 0.05 wt. % of CPEKI gave good inhibitory effect more than MEOH and MEG with concentration as high as 5wt. % each. CPEKI inhibited the system at decline pressure from 150psi to 131psi in 56minutes of the experiment and maintained steady decline till the end of 120minutes. MEG had a pressure drop of 120psi, while MEOH encountered a drastic drop of 90psi.

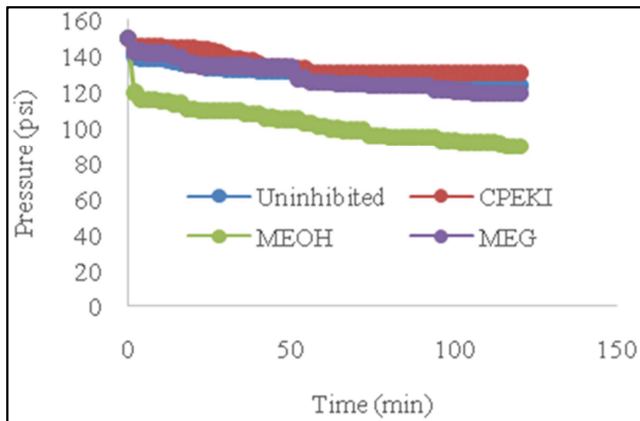


Figure 6. Pressure as a function of time for 5th concentrations of CPEKI, MEG, MEOH and uninhibited.

4.2. Analysis of Optimum Weight Percentage of Inhibitors Used

The optimum weight percentage of all the inhibitors used were determined and different plots were made for the different concentrations.

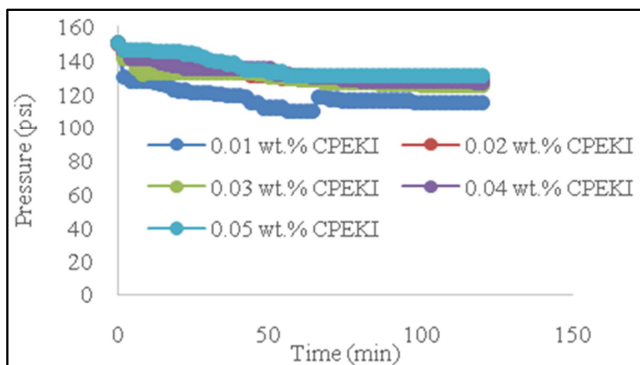


Figure 7. Pressure as a function time for different concentrations of CPEKI.

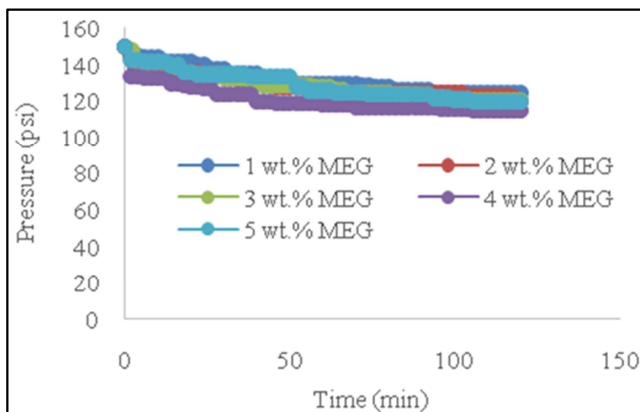


Figure 8. Plot of pressure against time for different concentrations of MEG.

Figure 7 shows that CPEKI maintained pressure decline of 131psi at the end of 120minutes which steadily delayed decrease in pressure and prevented hydrate crystals from forming. From the plot (Figure 7), it can be noted that the optimum inhibitory capacity was gotten at 0.05 wt. %. It can also be seen in Figure 8 that CPEKI prevented hydrate formation at decline temperature

of 6.5°C in 106minutes. From the results analysis, CPEKI is seen as a better inhibitor in hydrate prevention when compared with the conventional MEG and MEOH which are toxic to humans and aquatic life. CPEKI prevention raise in system loop temperature which would have resulted to hydrate nucleation and growth [30, 32]. Hence it is not toxic, eco-friendly and locally available.

In Figure 9, it is observed that the highest concentration for MEG is 1wt. % at pressure drop of 125psi which is the optimum percentage of inhibition. This implies that the optimum dosage for MEG is 1wt. % which is quite economical. The plot of pressure, temperature of 1wt. % of MEG against time indicate that as loop pressure declined to 125 psi, there was a drastic temperature reduction of 7°C.

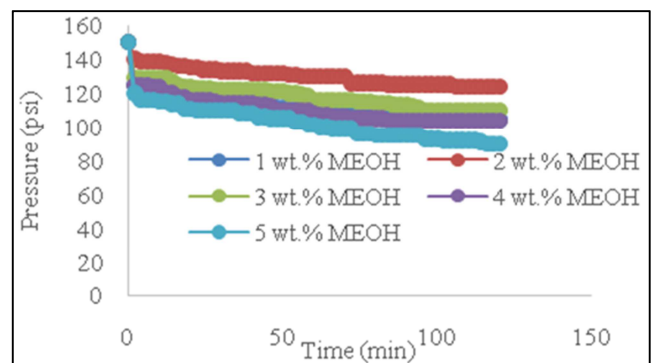


Figure 9. Plot of pressure against time for different concentrations of MEOH.

5. Conclusion

The study of hydrate treatments in gas pipeline using locally sourced material as green inhibitor has been carried out in this work. Different plots have been made and results analysed. From the results analysis, the following conclusions can be deduced:

- 1) A gas hydrate inhibitor termed caricaceae plant extract kinetic inhibitor (CPEKI) was developed from a locally sourced material.
- 2) Gas hydrate can be mitigated using optimal concentration of the local inhibitor.
- 3) The CPEKI inhibitor is environmental friendly which implies that it cannot be harmful to human and aquatic life.
- 4) The CPEKI can be used as an alternative to conventional inhibitors like that of MEG and MEOH.
- 5) As the experimental results clearly shows that CPEKI performed better with low concentration compared to the conventional inhibitors (MEG and MEOH), it implies that it will inhibit hydrate formation effectively and should be given a field trial.

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References

- [1] Amir H. Mohammadi, Dominique Richon, (2010). "Gas Hydrate phase Equilibrium in the presence of Ethylene Glycol or methanol aqueous solution Industrial & Engineering chemistry Research. Vol. 49, No. 18, pp. 8865-8869.
- [2] A. Mohammadi, Manteghian (2014). "The induction time of Hydrate Formation from a carbon dioxide-Methane Gas Mixture; Petroleum Science and Technology. Vol. 32. No 24. Pp. 3029-3035.
- [3] Bai, Y., Bai, Q., (2005) Subsea Pipelines and Risers, Second ed. Elsevier Science Ltd.
- [4] Boyun Guo, Shanghong song, Jacob Chacko, Ali Ghalambor, (2005). Flow Assurance, Offshore pipelines, pp. 169-214.
- [5] Bei Liu, Weixin Pang, BaoziPeng, Changyy Sun, GuangjinChe (2011). "Heat Transfer Related to Gas Hydrate Formation/Dissociation" Developments in Transfer.
- [6] Camargo, R. and Palermo, T. (2002). Rheological Properties of Hydrate Suspensions in an Asphaltic Crude Oil. Proceedings of the 4th International Conference on Gas Hydrates, May 19-23, 2002. Yokohama Symposia, Yokohama, Japan.
- [7] Carroll, J. J (2009). Natural gas hydrates: a guide for engineers. Amsterdam, Elsevier XVII 276s.
- [8] Chaudhari, P. N (2015), Department of Hydrate risk quantification in oil and gas production, Ph.D Dissertation, Colorado School of Mines.
- [9] Deaton, W. M. and Frost, E. M. Gas Hydrates and their Relation to the Operation of Natural Gas Pipelines, U.S. Bureau of Mines Monograph, 1946, 8, 101.
- [10] Dyke, V. K (1997). "Fundamentals of petroleum, Petroleum Extension Service, Austin, Texas.
- [11] E. M Reyma, S. R. Stewart (2001)," Case History of the Reward of a Hydrate plug formed during deepwater Testing". SPE/ADC Conference.
- [12] Edmonds B., R. A. S. Moorwood & R. Szczepanski (2001); "Controlling, Remediation of Fluid Hydrates in Deepwater Drilling Operations", *Ultradeep Engineering Supplement to Offshore Magazine*, March 2001, pp. 7-10.
- [13] Elechi, V. U., Ikiensikimama, S. S., Ajenka, J. A., Akaranta, O., Onyekonwu, M. O., Odutola, T. O. and Okon, O. E. (2018): Gas Hydrate Inhibition in a Simulated Offshore Environment using Local Inhibitor. SPE Paper 193439 presented at Nigeria Annual International Conference and Exhibition, held in Lagos Nigeria.
- [14] Freer, F. M and Sloan E. D (2000) Ann N. Y Acad. Sci 912, pp 651-657.
- [15] Fulong Ning, Ling Zhang, Yunzhong Tu, Guosheng Jiang, Maoyong Shi (2010). "Gas Hydrate Formation, agglomeration and inhibition in oil-based drilling fluids for deep-water drilling. *Journal of Natural Gas Chemistry*, vol. 19, No. 3. Pp. 234-240.
- [16] Giavirini, C and Hester, K (2011). Gas Hydrate: Immense Energy Potential and Environmental Challenges, London: Springer London.
- [17] Kelland, M. A. (2006): History of the Development of Low Dosage Hydrate inhibitors. *Energy fuels*, 20 (3), 825-847.
- [18] Khan, M. S., Parlool, C. B., Lal, B., Mellon, N. B. (2017): "Influence of Tetramethylammonium Hydroxide on Methane and Carbon Dioxide Hydrate." *Phase Equilibrium Conditions. Fluid Phase Equilibra*. Vol. 440, pp 1-8.
- [19] Lederhos, J. P., Long J. P., Sum, A., Christiansen, R., and Solan Jr., E. D. (1996): "Effective Kinetic Hydrate Inhibitors for Natural Gas Hydrates", *Chemical engineering science*, Vol. 51, No. 8, pp. 1221-1229.
- [20] Mogbolu, P. O. and Madu, J., 2014, August. Prediction of Onset of Gas Hydrate Formation in Offshore Operations. In SPE Nigeria Annual International Conference and Exhibition. Society of petroleum Engineers.
- [21] Mujis, H. M, Beers, N. C, Van Om N. M, Kind, C. E and Anselme, M. J (1990): Pat. 2036, 084.
- [22] Nwigbo, S. C., Okafor, V. N. and Okewale, A. O. (2012): "Comparative Study of ElaeisGuiniensis Exudates (Palm wine) as a Corrosion Inhibitor for Mild Steel in Acidic and Basic Solutions." *Research Journal of Applied Science, Engineering and Technology*. Vol 4, No 9 pp 1035-1039. ISSN: 2040-7647.
- [23] Nasheed, O., Sabil, K. M., Lal, B., Ismail, L and Jafaar, A. J. (2014): "Study of 1- (2-hydroxyethyl) 3-methylimidazolium halide as Thermodynamic Inhibitors." *Applied Mechanics and Materials*, Vol. 625, pp 337-340.
- [24] Odutola, T. O., Ajenka, J. A., Onyekonwu, M. O. and Ikiensikimama, S. S. (2017): "Design, Fabrication and Validation of a Laboratory Flow Loop for Hydrate Studies." *American Journal of Chemical Engineering*. Vol 5, No. 3-12, pp 28-41. doi: 10.11648/j.ajche.s.2017050301.14.
- [25] O. Urdahl, A. Lund, P. Mark, T. N Nilsen (1995). *Chemical Engineering Science*. Vol. 50, pp 863-870.
- [26] Peng B-Z, Sum C-Y, Liu P, Liu Y-T, Chen J. Chen G. J. (2009). Interfacial properties of methane (aqueous VC-713 Solution under hydrate formation condition. *Journal of Colloid and Interface Science*. 336 (2): 738-42.
- [27] Reijnhout, M. J, Kind. C. E, Klomp, U. C (1993): Eur. Pat. 526,929. Sami. N. A, Sangwai, J. S & Balasubramanian. N. (2013). Gas hydrate applications and problems in oil and gas industry. *International Journal of scientific & Engineering Research*. 4, pp. 1-4.
- [28] Sloan, E. D and Koh C. A., (2008). "Clathrate Hydrates of Natural Gases, Tgird edition CRC Press, Taylor and Francis Group. Boca Raton, Florida, USA pp. 319-341.
- [29] Singh, P., Venkatesan, R., Folger, H. S and Nagarajan, N., (2000). Formation and aging incipient thin film Wax- oil Gels *AIChE Journal*. 46 (5), pp 1059-1074.
- [30] Sum, A. K., (2013) October. Prevention management, and remediation approaches for gas hydrates in the flow assurance of oil/gas flowlines. In OTC Brasil. Offshore Technology Conference.
- [31] Talaghat, M. R. Enhancement of the Performance of Modified Starch as a Kinetic Hydrate Inhibitor in the Presence of Polyoxides for Simple Gas Hydrate Formation in a Flow Mini-Loop Apparatus. *J. Nat. Sci. and Eng.*, 2014, 18, 7-12.

- [32] Turner, D. J., Mahadevan, G., Lachance, J., (2015) Hydrate stable start-up and restart of oil and gas production systems, article presented at the 25th International.
- [33] Urdahl O; Lund, A; Mork. P and Nilsen, T. N (1995): Inhibition of Gas Hydrate Formation by Means of Chemical Additives. Development of an experimental set-up for Characterization of Gas Hydrate Inhibitor Efficiency with Respect with Respect to Flow Properties and Deposition. *Chem Eng Sci.* 50 (5), 863-870.
- [34] Wu, M. Wang S, Liu H. (2007). A study on inhibitors for the prevention of Hydrate Formation in Gas Transmission pipeline. *Journal of Natural Gas Chemistry.* 16 (1): 81-85.
- [35] Xiaoyong FU, Chou-Hong Tann, T. K, Thiruvengadam, Jurning Lee, Cesar colon (2001). "A regioselective PCL5 Mediated dehydration for preparing 9, 11 corticosteroids" *Tetrahedrum Letters*, Vol 42, No. 14, pp2639-2642.
- [36] Lee, W.; Kim, K.-S.; Kang, S.-P.; Kim, J.-N. Synergetic Performance of the Mixture of Poly(N-vinylcaprolactam) and a Pyrrolidinium-Based Ionic Liquid for Kinetic Hydrate Inhibition in the Presence of the Mineral Oil Phase. *Energy Fuels* 2018, 32, 4932–4941.
- [37] Zheng, Z (2010) "Molecular Dynamics Simulations on Inhibition of Methane Hydrates" Master of Science. IOWA State University.