Investigation of Plant Family Costaceae Extract as Gas Hydrate Inhibitor in a Simulated Offshore Environment

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Abstract - Formation of gas hydrates during oil and gas production especially in the deep offshore (having limited access) with low temperatures and very high pressures is inevitable. These crystalline solids plug the pipelines, valves, transmission lines and chokes giving rise to shut-downs and Non-Productive Times (NPT) which cost the oil and gas operators billions of dollars to remEDIATE. Its safety concerns are also an issue in oil and gas production. The Costaceae plant family is a medicinal plant family widely spread across the tropics of Africa, America and Asia that possess anti-oxidation capacity. Extract was prepared from freshly cut stems and subjected to phytochemical screening. Anti-oxidation capacity had to do with phenolic compounds present in it. Using a mini flow hydrate apparatus as experimental set-up, and varying weight percentages of 1, 2 and 3, the extract inhibited hydrate formation. The weight percentage of the Costaceae Family Extract (CFE) with the highest inhibition capacity was 2wt% with pressure drop of 107 psia as compared with the conventional Mono Ethylene Glycol (MEG) that had pressure drop of 105 psia. The CFE showed inhibitory capacity in all weight percentages and performed favorably well when compared to MEG. Presence of bioactive compounds like phenols, tannins, alkaloids, flavonoids and saponins could be responsible for the anti-oxidation and inhibitory performance of the CFE. Given the fact that Costaceae Family Extract (CFE) is locally available and gotten from Plant family, that makes it cost effective and environmentally friendly (in the sense that it is biodegradable), it should be considered and developed as an inhibitor for gas hydrate in favor of MEG which is expensive and toxic to both humans and the environment.

Keywords - Gas Hydrates, Costaceae Family Extract (CFE), Mono Ethylene Glycol (MEG), Mini Flow Loop Apparatus, Phytochemical Screening

I. INTRODUCTION

Gas Hydrates are glass-like solids which form when gases such as Methane, Ethane, Propane and Butane and impurities or non-hydrocarbon gases such as Carbon dioxide, Hydrogen Sulfide or Nitrogen mix with water under very low temperatures (0-40°C) and high pressure (>200psig) [1][2]. They are crystalline structures whose building blocks are gas and water molecules [3]. Three types of hydrate structures are known, sI, sII and sH hydrates and the formation of anyone is dependent on the size and type of gas molecules that is encaged by the water molecules. sI molecules are formed by Methane, Ethane and Carbon dioxide gas molecules while sII is formed by larger gas molecules such as Propane and normal Butane although Nitrogen which is a small molecule can also form sII structure. SH structures are formed by Pentanes, Paraffins and Cycloalkanes [4].

One of the flow assurance problems which is considered to be perennial is gas hydrate formation in pipelines. About 70% of the operating expenditure used for flow assurance is used on hydrates. Its accumulation plugs oil and gas pipelines and disturbs hydrocarbon flow along sides its inherent safety concerns [5][6]. Flow assurance problems such as paraffin wax deposition and hydrate formation are major problems that cost the industry billions of dollars in lost production and cleaning operations [7]. Hydrate removal in pipelines transmitting hydrocarbons leads to about a million per day shut downs[1], and hydrate prevention methods and techniques cost the oil and gas industry about one billion U.S. dollars yearly [8]. Gas hydrates can be prevented by water removal or dehydration, pressure reduction or depressurization, thermal heating and chemical injections [5]. Chemical injection is considered more economical especially in deep offshore environment where accessibility is limited [2][9]. Chemicals used for the prevention of hydrates are divided into various categories such as:

1) Thermodynamic Hydrate Inhibitors (THIs): they function by shifting the hydrate equilibrium curve to lower temperatures and higher pressures. They require large concentrations (10–50 wt% of water cut) examples are Methanol and Glycols.

2) Low Dosage Hydrate Inhibitors (LDHIs) are so named because they are applied in very small concentrations (<2wt%). They are subdivided into:

- Kinetic Hydrate Inhibitors (KHI) whose action is to delay the onset of hydrate formation and growth rate. They
are water soluble compounds examples are PolyVinylPyrrolidone (PVP) and Poly Vinyl Caprolactam (PVCap). The kinetics of KHI evaluation is problematic [10] [11], exclusively with KHI because its process of evaluation is dynamic and complex [12].

- **Anti-Agglomerants (AAs):** These are surface acting chemicals that modify the hydrate crystals [13]. And prevent their agglomeration. Example is Berol 26.

3) **Ionic (Imidazolium based) Liquids (ILs):** Research on the need for a better and safer environment is ongoing due to the health risk of some KHI such as PVP and Poly Ethylene Oxide (PEO) reported to have some cancer causing material which poses severe health issues for human health although PEO is less carcinogenic than PVP [14]. Ionic Liquids which are mostly Imidazolium based have also been subjected to test as gas hydrate inhibitors. It functions well and is more efficient when used alongside KHIs and THIs and is dual functional in nature.

Its research was initiated by Xio and Adidharma [15] who found out that Imidazolium based Ionic Liquids have dual function. Ionic liquids are molten state salt and has the ability to exhibit electrostatic interactions forming hydrogen bond with water molecule which enhance their crystalline surface adsorption capacity and ability through the retardation of hydrate nucleation process. The use of high pressure cell to evaluate Pyrrolidinium‐ and Morpholinium based ionic liquids such as N-hydroxethyl-N-methyl pyrrolidinium chloride ([HEMP][Cl]), N-hydroxethyl-N-methyl pyrrolidinium tetrafluoroborate ([HEMP][BF$_4$]), N- butyl-N-methyl pyrrolidinium bromide ([BMP][Br]) and others has been carried out. It was found that the hydrate nucleation time was delayed better than PVP anion/cation present in ionic liquids affect how effective it is [17][18]. When used as a synergist with and PVCap at 0.1, 1 and 10wt% [16]. The type of PVCap, its kinetic impact of inhibition was increased [18]. The use of tetrathylammonium hydroxide (TMAOH) was investigated by Khan et al. [5][19] and was reported to be effective as THI for both carbon dioxide and methane hydrate, having suppression temperatures (AT) of 1.53 and 2.23°C respectively. Khan et al. [19] further did a study on the kinetic assessment of carbon dioxide and methane and binary mixture of methane and carbon dioxide hydrate formation and found that the presence of TMAOH delayed the induction time for systems of carbon dioxide, methane and mixed binary gases (CO$_2$ + CH$_4$), reduced total gas consumption and initial hydrate formation rate in most of the systems studied.

Odutola et al. [20] compared the effect of ionic inhibitors calcium chloride, sodium chloride, potassium chloride salts and Thermodynamic inhibitors methanol and mono ethylene glycol combination on gas hydrate inhibition. This was done through temperature depression using Hammerschmidt and Ostergaard equations. It was observed that THI dosage was reduced by 14% when used with ionic inhibitors. The blend of methanol and sodium chloride saved the use of the THI by 34%. They concluded that this approach will help to reduce the amount of methanol/glycol used based on water salinity.

Talaghart [21], in his research on gas hydrate using a mini flow apparatus found out that increase in pressure in the system under study, led to gas consumption rate increment and decrease in induction time. He also noted that the extent of hydrate formation decreased in the presence of inhibitors. L-Tyrosine as a gas hydrate inhibitor performed better than Poly Vinyl Pyrrolidone (PVP) in all the systems studied. Comparison of the effect of methanol and mono ethylene glycol on gas hydrate inhibition during gas expansion using Colorado School of Mines (CSM) Gem software was studied by Odutola et al. [22]. It was observed that methanol performed better than mono ethylene glycol. In all of these studies, synthetic based gas hydrate inhibitors were used. These inhibitors though are shown to be effective on gas hydrate mitigation, pose environmental concerns to human, terrestrial and aquatic lives. There is a need to use local materials that are readily found and available in our environment which pose less threat to lives and the environment. The use of local materials as enhance oil recovery (EOR) agents have been investigated by several authors. Irvingia Gaboneensis seed, Lecithin and Palm Bunch Ash (PBA) has been used by Ojukwu et al. [23] to enhance oil recovery from unconsolidated beach sand having porosity of 29.25% saturated with oil. These flooding agents were used individually and also in combination with concentrations 15g/L, 10g/L and 1g/L of the Alkaline Surfactant and Polymer (ASP) respectively. It was concluded that local ASP had the capacity to enhance oil recovery and also in synergy they performed better. This was so because the ASP worked by reducing interfacial tension between oil and water and also increased the viscosity of the displacing fluid. Ojo [24] also studied the relationship between the viscosities of ASP solution and oil recovery in heterogeneous porous medium. Twenty-four (24) ASP flooding tests were conducted using artificial models having different permeability variations coefficients so that ASP floods in heterogeneous and homogeneous reservoirs where captured using local materials instead of conventional materials used by the oil and gas industry. They concluded that increased viscosity of ASP (1.06cp) above that of water (1.05cp) increased residual oil recovery. There also exists a maximum ASP viscosity (2.56cp) at which residual oil recovery began to diminish. Particle size has a lot to do with oil recovery as larger particle size gave better recovery than smaller ones and decrease in heterogeneity lead to increase in oil recovery.

A study carried out by Nwugo et al. [25] investigated the use of extract from the plant family Palmae as a corrosion inhibitor. In their study, the Gas Chromatography-Mass Spectrometer (GCMS) showed the active ingredient to be oleic acid, palmitic acid and stearic acid with Carbonxyl group and double bond which aided in the extract being a good corrosion inhibitor as a result of the hydrogenation of the double bond. Fourier Transform Infrared Red (FTIR) showed the presence of tannins, alkaloids, flavonoids and Saponins which contributes to it being a good corrosion inhibitor. Elechi et al. [26] did a study using plant extract as gas hydrate inhibitor in a mini flow loop using weight concentrations of 1, 2 and 3wt%. A comparison was made with the conventional gas hydrate inhibitor Mono Ethylene Glycol (MEG). The plant extract was found to also contain the above-mentioned bioactive
compounds. They concluded that the presence of these bioactive compounds aided in the plant extract being a better hydrate inhibitor as compared to MEG.

The role of some medicinal plants valued for their anti-diabetic, anti-oxidative, anti-microbial, anti-arthritis and anti-inflammatory has been investigated by many authors in the area of medical pharmacology. One of such plants is of the family Costaceae. This plant has over a hundred species which are widely distributed in the tropics of America, Africa and Asia and contain bioactive compounds such as phenols, tannins, alkaloid, flavonoid and saponins [27]. Not much has been done on the use of plant families as gas hydrate inhibitors. This study is to assess the effect of the extract from the Costaceae family as a gas hydrate inhibitor as compared with the conventional inhibitor Mono Ethylene Glycol (MEG).

II. MATERIALS AND METHOD

The materials used for this study are, water, ice blocks, Compressed Natural Gas (CNG) of specific gravity 0.5, containing 98.44% methane and 1.50% carbon dioxide, local inhibitor from the costaceae extract & Mono Ethylene Glycol. The constituents of the plant extract are shown in Table 1. Flavonoids are polyphenolics found in plants and are powerful anti-oxidants which act to prevent the action of reactive oxygens. Tannins are high molecular weight polyphenolics and are found to be most abundant in nature as condensed tannins which act to prevent the action of reactive oxygens. Tannins are high molecular weight polyphenolics and are found to be most abundant in nature as condensed tannins which act to prevent the action of reactive oxygens. Phenols are a class of natural compounds produced by living cells found in nature [29]. Alkaloids are synthesized by both plants and animals and prevent coagulation.

<table>
<thead>
<tr>
<th>Bioactive components</th>
<th>Quantity present in extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tannins</td>
<td>+</td>
</tr>
<tr>
<td>Saponins</td>
<td>++</td>
</tr>
<tr>
<td>Flavonoids</td>
<td>++</td>
</tr>
<tr>
<td>Phenols</td>
<td>++</td>
</tr>
<tr>
<td>Alkaloids</td>
<td>++</td>
</tr>
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Key: + means present in small quantity, ++ means present in appreciable quantity

Saponins are surface active foamy agents that prevent agglomeration with foams and bubbles giving it good stability [29].

Apparatus: the apparatus used is a mini-hydrate flow loop shown in fig. 1. It is made of 316 stainless steel having an internal diameter of half inch (1/2) enclosed in a four (4) inch diameter Poly Vinyl Chloride (PVC) pipe that is skid mounted on an external metal frame work. It functions as a constant volume batch process set-up. The experimental set up has pressure gauges for measuring the inlet, outlet and differential pressures of the system, Temperature gauges for reading the inlet and outlet and also temperature of the cooling unit used to mimic the marine environment which in this case is a refrigerator. A mixing vessel is used to mix the water and the weight percentage of the inhibitor to be used. It is also fitted with a CNG bottle which supplies gas to the system with valves and orifices. Three pumps are connected to the system which helps to pump the water and inhibitor into the inner line, draw and circulate water into the PVC pipe and also cause proper mixing of the fluids and ensure continuous flow of the fluid around the loop. A Control Panel houses the switches for the pump and power button for the system.

![Figure 1. Process Diagram of the Mini Flow Loop Apparatus for Hydrate Studies [29]](image-url)
A. Procedure

Preparation of Plant Extract: The stems of Costaceae family were collected fresh from their natural habitat behind the World Bank Center of Excellence, University of Port Harcourt, Rivers State. Samples were prepared by removing the outer skin and then pounded/crushed mechanically and strained with a sieve to get out the fresh juice and used immediately after extraction.

Experimental Runs: Before the commencement of each experiment, the loop is flushed to get rid of rust or debris that may be in the loop. This process is initiated by drawing water into the inner line from the mixing vessel by opening Valve 4 until a pressure of 25 psi is reached (after turning on Pump 3, after which it is turned off). The water is removed using Valves 5, 6 or 7 and the process may be repeated as many times as possible to ensure that the debris is flushed out. The same procedure is followed for the hydrate formation experiment but here after attaining the pressure buildup of 25psia, the CNG bottle is turned on and then Valve 1 and Orifice are opened to build up the pressure to 150 psia after which the Valves and Orifice are shut off. Water is drawn into the refrigerating and allowed to circulate inside the 4 inch Poly Vinyl Chloride (PVC) pipe by turning on Pump 2. Circulation and proper mixing of gas and water is achieved by turning on the variable screw pump (Pump 1) set at 150V. To reduce the temperature of the water in the system quickly to hydrate formation temperature, ice blocks are added into the refrigerating unit and then the temperature and pressure of the system are recorded every two minutes for 120 minutes which is the duration of the experiment.

Key indicators of hydrate formation in the mini flow apparatus are rapid rise in loop temperature, rise in differential pressure of the system, plugging of the sample point quarter (1/4) inch sample test point valve (Valve 5), colour of effluent from the test point and increase in the loop pressure [30]. In the case of hydrate mitigation, varying weight percentages of the inhibitors in relation to water is poured into the mixing vessel and the same procedure is applied with temperature and pressure readings taken for duration of 120 minutes at an interval of two minutes.

III. RESULTS AND DISCUSSIONS

Plots of pressure and temperature for the system with water and gas alone was done and used as a control for the systems with gas, water and the various weight percentages of the inhibitors (both conventional and local) used. Figs. 2 to 4 show different plots of the water and gas system. Fig. 2 shows the experimental run with water and gas alone at 150 psia. The initial pressure dropped from 150 psia to 115 psia in the first twenty minutes of the experiment. This is attributed to the rapid drop stage of hydrate formation which occurs as a result of gas dissolution in liquid phase, in this case water. This pressure drop of 115psi was maintained for about 10 minutes before another decline in pressure to 113 psia. Further reduction in pressure to 80 psia was observed after about an hour of the experimental run. This stage is the hydrate nucleation phase (induction of nucleation) or stable phase [31]. After this a rapid decline in pressure is noticed from 80 psia to 36 psia in the next 60 minutes of the experiment which is an indication of the second rapid stage of hydrate formation [31][32]. This rapid decrease is as a result of growth in the hydrate crystal as more gas is being used up in the system [31][32].

Temperature reduction was observed as shown in Fig. 3 from 30°C to 28°C after about twelve minutes into the experiment. It reduced to 27.5°C and was maintained for about 4 minutes after which there was a further decrease to 25°C in another 8 minutes. Temperature began to raise from 25°C to 27.5°C and after 60 minutes into the experiments, it increased to 28°C then further increased to 29°C in the next 22 minutes. At the end of 120 minutes the final temperature reading was 29.5°C. This temperature decrease is an indication of hydrate formation because heat is being given off to the surrounding being that hydrate formation is an exothermic reaction.

Fig. 4 shows pressure and temperature versus time for the system with water and gas alone, the induction time for this system is recognized by the point at which there is a drastic drop in loop pressure and it is accompanied by a corresponding sudden spike in the loop temperature. This indicates the onset of hydrate formation.

Pressure versus time and Temperature versus time for the varying weight percentages (1, 2 and 3 wt.%) of the local inhibitor from the Costaceae Family Extract (CFE) were plotted to see their effect on hydrate inhibition as shown in Figs. 5 and 6 alongside the basic case.

From Fig. 5, all the weight percentages of the CFE did very well in reducing the pressures of the system gradually as compared with that of water and gas system. 2 and 3wt% of CFE had almost the same pressure reduction trend while 1wt% was least in pressure reduction. From Fig. 5, it is seen that there was hydrate inhibition in the system using the various weight percentages. Fig. 6 also showed the same trend in Temperature reduction as in Fig. 5. The temperature of the system was gradually reduced for each of the weight percentages and they had almost the same trend. There was no sudden temperature increase in the system, which shows that there was hydrate mitigation unlike in the water and gas system were there was a sudden spike in the system temperature, and temperature increased to 29.5°C at end of the experiment which is an indication of hydrate formation.

To ascertain the inhibitory capacity of the Costaceae Family Extract (CFE), a comparison with the conventional hydrate inhibitor Mono Ethylene Glycol (MEG) was made for the various weight percentages in terms of pressure and temperature of the systems. Fig. 6 is a plot of pressure versus time for 1wt% of CFE and MEG and water and gas only. From Fig. 7, the pressure of the CFE inhibited system decreased from 150 psia to about 103 psia in 40 minutes and further to 100 psia after about 60 minutes into the experiment. Slight decrease to 98 psia was observed and maintained till the end of the experimental run. The conventional inhibitor (MEG) inhibited the system and had its pressure decreased from 150 to 115 psia.
in 40 minutes and further to 110 psia in another 20 minutes. It decreased to 105 and maintained this value till the end of the experiment. Although CFE has a higher pressure drop when compared to MEG, the difference in pressure drop was about 5 psia which is not a bad one given the fact that CFE is cheaper, locally available and less toxic than MEG. In both cases hydrate formation was prevented as opposed to the system with water and gas alone.

Fig. 8 shows the plot of temperature against time for 1wt% of CFE and MEG. Temperature for both CFE and MEG followed the same trend as pressure as seen in Fig. 8. MEG had a better temperature drop as compared to CFE with a difference of 3°C temperature drop which gives CFE credit. Both were able to inhibit hydrate as there was not any unusual increase in the loop temperature when compared to water and gas temperature trend.

A plot of pressure against time for 2wt% of CFE and MEG is shown in Fig. 9. CFE had a higher-pressure value than MEG. For the first 40 minutes as seen in Fig. 9, CFE had a pressure drop of 114psia while MEG was 110. The next 40 minutes gave pressure drop of CFE as 107 which was maintained till the end while that of MEG was 105 psia up to the end of the experiment. Temperature followed the same trend of gradual reduction for both but MEG had a higher temperature value than CFE with difference in temperature of 3°C at the end of 120 minutes as seen in Fig. 10.

Fig. 11 shows pressure for 3wt% CFE and MEG. For the first 60 minutes, the pressure drop was from 150psia to 109 psia and 126 psia respectively after which it reduced to 105 and 121 in the next 40 minutes and finally maintained a pressure of 104 and 120 for CFE and MEG till the end of the experiment. In this weight percentage, MEG had a higher pressure at the end than CFE with a pressure difference of 6 psia. Both inhibitors prevented crystal agglomeration.

Fig. 12 shows that there was reduction in temperature from 29°C to 11°C for CFE while MEG had temperature drop from 30°C to 8.5°C in 60 minutes. Further decrease after 90 minutes was 7°C for both inhibitors and then to 6°C for CFE and 6.5°C for MEG. Both inhibitors curbed sudden rise in temperature which is a sign of hydrate nucleation and growth as seen in the run with water and gas alone.
Figure 3. Temperature versus Time for water and gas system alone

Figure 4. Pressure and Temperature versus Time for Water and Gas alone
Figure 5. Pressure versus Time for 1, 2 and 3 wt% of Costaceae Family Extract (CFE)

Figure 6. Temperature and Time for 1, 2 and 3 wt% Costaceae Family Extract (CFE)
Figure 7. Pressure versus Time for 1wt% Costaceae Family Extract (CFE) and Mono Ethylene Glycol (MEG)

Figure 8. Temperature versus Time for 1wt% Costaceae Family Extract (CFE) and Mono Ethylene Glycol (MEG)
Figure 9. Pressure versus Time for 2wt% Costaceae Family Extract (CFE) and Mono Ethylene Glycol (MEG)

Figure 10. Temperature versus Time for 2wt% Costaceae Family Extract (CFE) and Mono Ethylene Glycol (MEG)
IV. CONCLUSION

From the analysis given so far, Costaceae Family Extract (CFE) competed favorably well with the conventional hydrate Mono Ethylene Glycol (MEG) in all the weight percentages although it did slightly better than MEG in 2wt% which is considered the optimum for CFE with a pressure of 107 psi at the end of the experiment whereas MEG had a pressure value of 105 psi. Given the fact that Costaceae Family Extract (CFE) is locally available, gotten from Plant family, it will be environmentally friendly (in the sense that it is biodegradable), it should be considered and developed as an inhibitor for gas hydrate in favor of MEG which is toxic to both humans and the environment.
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