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Advances in green hydrate inhibitors

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Abstract

Gas hydrate blockage is a major issue that the production and transportation processes in the oil/gas industry faces. The formation of gas hydrates in pipelines results in significant financial losses and serious safety risks. To tackle the flow assurance issues caused by gas hydrate formation in the pipelines, some physical methods and chemical inhibitors are applied by the oil/gas industry. The physical techniques involve subjecting the gas hydrates to thermal heating and depressurization. The alternative method, on the other hand, relies on injecting chemical inhibitors into the pipelines, which affects gas hydrate formation. Chemical inhibitors are classified into high dosage hydrate inhibitors (thermodynamic hydrate inhibitors (THI)) and low dosage hydrate inhibitors (kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAs)). Each chemical inhibitor affects the gas hydrate from a different perspective. The modern-day inhibitors are majorly synthetic, expensive and lead to environmental pollution, therefore, there is need for less expensive and environmentally friendly inhibitors. This article reviews recent advances in the use of locally sourced bio-degradable materials to effectively inhibit gas hydrate formation. The inhibition efficiency of plant materials will be validated side by side with synthetic hydrate inhibitors. The performance of these green inhibitors will provide effective techniques for gas hydrate management.

Keywords: Hydrate Formation; Temperature; Pressure; Gas; Chemical Inhibitors

1. Introduction

Millions of dollars are spent annually in the oil and gas industry to inhibit the production of gas hydrates in the pipelines to assure an uninterrupted flow of natural gas in the pipelines. Gas hydrates are considered among the most catastrophic problems that face the flow of natural gas in the pipelines. Significant economic losses and severe safety threats are caused by gas hydrate formation in the pipelines. The formation of gas hydrates in the pipelines may occur during the production, processing, or transportation of hydrocarbons, depending on the thermodynamics of the surrounding environment. Thus, their production inhibition is a necessity for a more efficient natural gas production process. Gas hydrates are ice crystalline-like structures consisting of gas and water molecules. The water molecules form a cage-like crystal lattice structure via hydrogen bonding, and the gas molecules occupy the interstitial vacancies (cages) in the lattice without possessing a lattice position. These guest molecules include the small-sized hydrocarbon molecules by nature (e.g., CH4, C2H6, C3H8, etc.), as well as H2S, N2, and CO2. There are three fundamental gas hydrate structures that have been identified so far, based on the structure and the number of hydrate cavities and the size of the guest molecule, and include cubic structure I (sI), cubic structure II (sII), and hexagonal structure H. Gas hydrates are stable at low temperatures and high-pressure environment. Gas hydrates can efficiently contain gas molecules, since they are non-flowing crystalline solids.

Gas hydrate formation causes disastrous issues. Hence, their removal is a must. 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

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emphasis on the use of LDHIs is a common practice in the remote and offshore environment. But these mitigations are very costly to sustain and possesses environmental consequences. Subsequently, researchers are now shifting towards obtaining eco-friendly LDHIs for better gas hydrate management.

2. Experiments With Agro-Based Hydrate Inhibitors

Elechi et al (2019) investigated Plant Family Costaceae Extract as Gas Hydrate Inhibitor in a Simulated Offshore Environment. They prepared Costaceae extract from freshly cut stems and subjected it to phytochemical screening. The experiments were conducted in a mini flow hydrate apparatus at varying weight percentages of 1wt%, 2wt% and 3wt% of the extract inhibited hydrate formation. According to Virtue et al (2019), 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 (Figure 1). Their result indicated that 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), Virtue et al (2019) stated that it should be considered and developed as an inhibitor for gas hydrate in favour of MEG which is expensive and toxic to both humans and the environment.

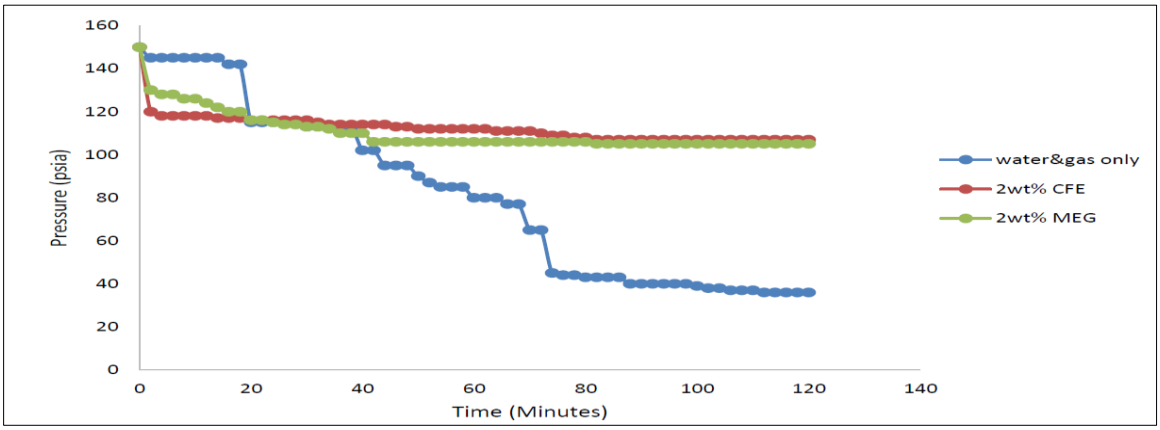

Figure 1 Pressure versus Time for 2wt% Costacaea Family Extract (CFE) and Mono Ethylene Glycol (MEG)

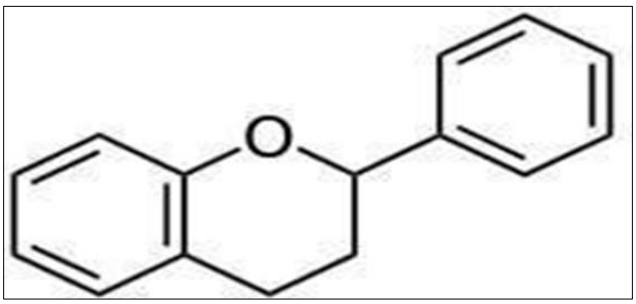

Figure 2 Chemical structure of Flavonoids (Elechi et al 2019)

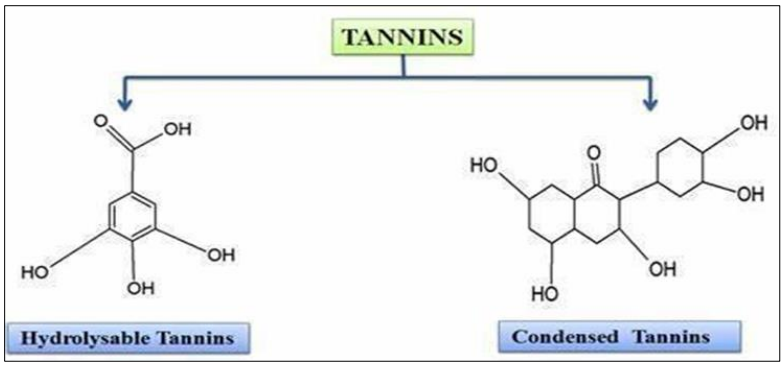

Figure 3 Chemical structure of Tannins (Elechi et al 2019)

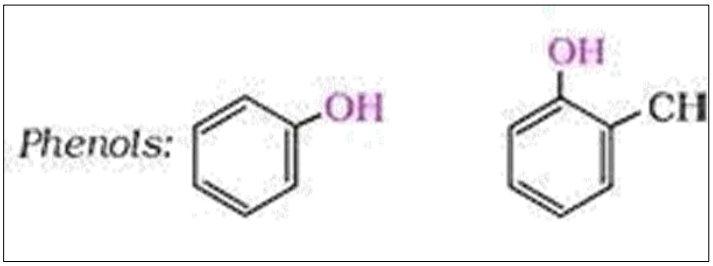

Figure 4 Chemical structure of Phenols (Elechi et al 2019)

Okon et al (2018) experimentally studied Locally Formulated Inhibitor from Agro Waste for Gas Hydrate Inhibition in a Mini Flow Loop. They compared 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 (Figure 5). The LFKHI is eco-friendly and biodegradable since it is produced from agro waste-based starch. It is cheap and water-soluble. Okon et al (2018) recommended LFKHI for field trial.

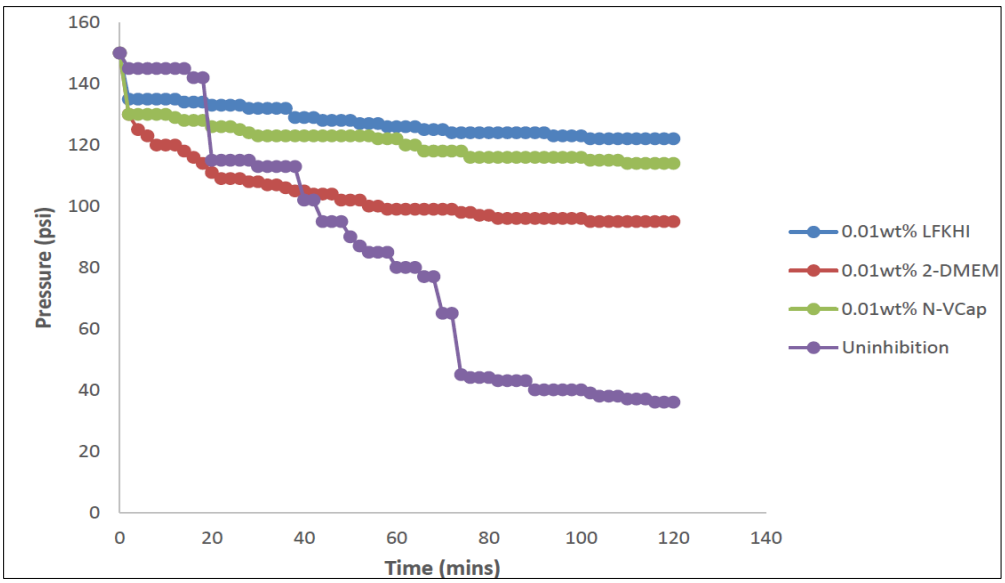

Figure 5 Pressure versus time for 0.01wt% LFKHI, 2-DMEM, N-VCap and Uninhibition

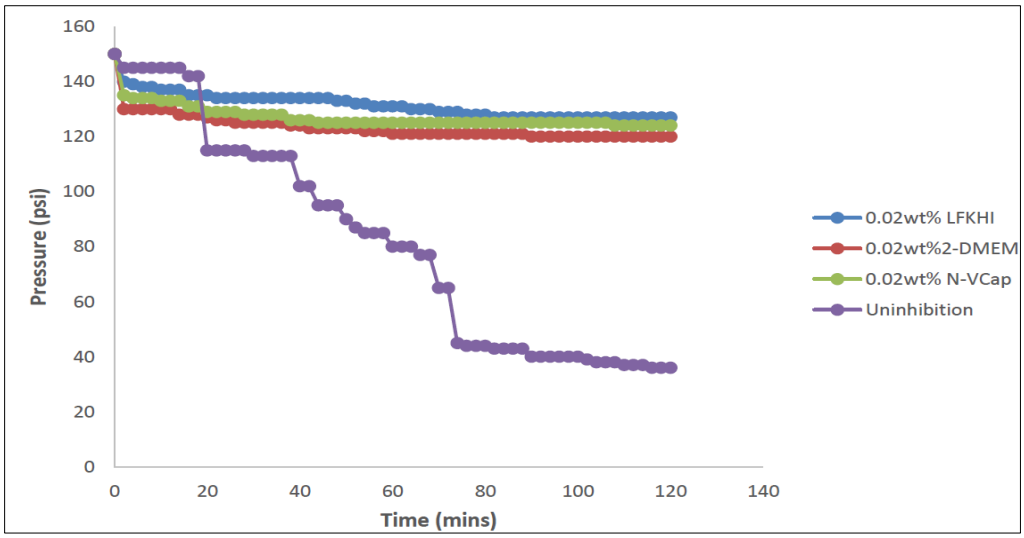

Figure 6 Pressure versus time for 0.02wt% LFKHI, 2-DMEM, N-VCap and Uninhibition

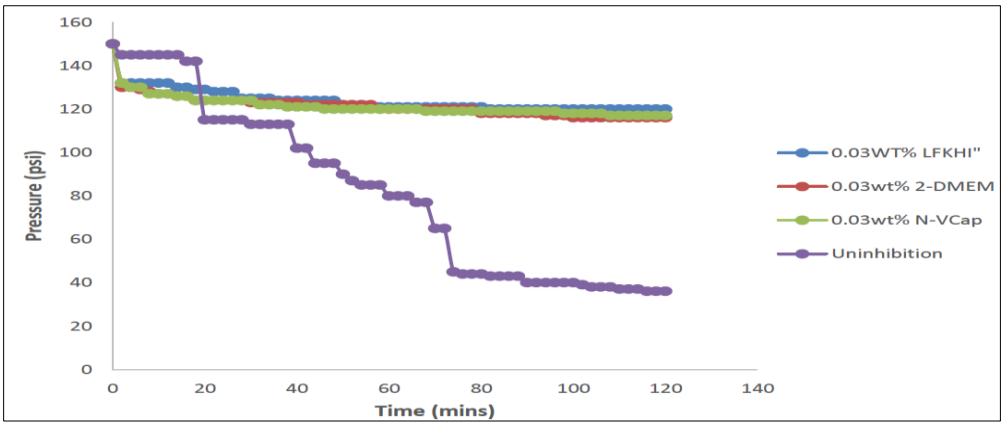

Figure 7 Pressure versus time for 0.03wt% LFKHI, 2-DMEM, N-VCap and Uninhibition

Odutola et al (2019) experimentally investigated modified starch from white corn as a kinetic inhibitor of gas hydrate. They modified the starch from white corn by oxidation and applied in low dosages (0.01wt%, - 0.05wt %) in a constant volume experiment conducted in a laboratory hydrate flow loop used to simulate subsea pipelines. The pressure time profile (Figure 8) of the experiments conducted was evaluated based on the gas dissolution time, nucleation time and hydrate growth time. The effectiveness of the modified starch was indicated by how much gas was used up in forming hydrates during the experiments conducted. 0.04wt% of modified starch was the optimal dosage of inhibitor in this study as it showed less reduction in pressure implying less gas was used. When the performance of modified corn starch was compared with the performance of similar experiments done in the same equipment using polyvinylpyrrolidone (PVP), N-vinylcaprolactam (PVCap), and 2-(dimethylamino)ethylmethacrylate (DMEM) as hydrate inhibitors, Modified starch performed best. Odutola et al (2019) recommended modified corn starch as an efficient, inexpensive and environmentally friendly hydrate inhibitor.

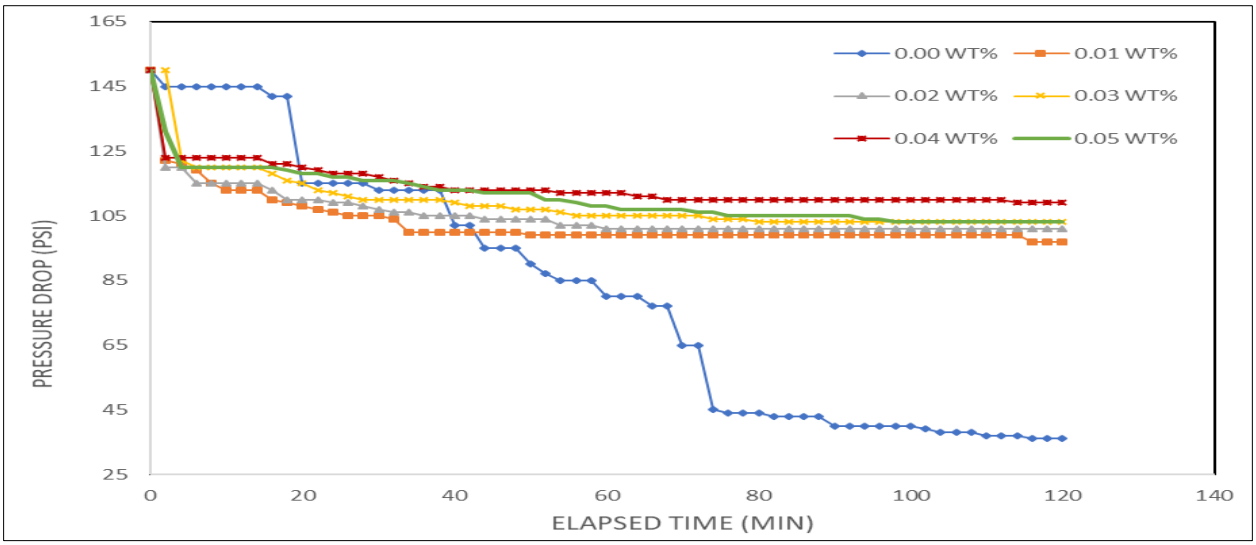

Figure 8 Comparative analysis of pressure drop versus elapsed time for 0.00wt % - 0.05wt% of modified starch

Elechi et al (2022) investigated the influence of a Plant Extract (PE) on the phase behaviour and equilibrium of structure I (SI) gas hydrate and its inhibition efficiency. The PE was screened using a mini flow loop. From the pressure-temperature phase diagram, the various weight percentages of the PE were able to disrupt the thermodynamic equilibrium conditions of the water and gas molecules to lower temperatures and increase pressures, which caused a shift in the equilibrium curve to an unstable hydrate formation zone. The pressure versus time plot (Figure 9) as well as the inhibition efficiency plots for the PE and Mono Ethylene Glycol (MEG) were evaluated. Overall, the inhibition efficiency of the PE was higher than that of MEG for 1 wt% (60.53%) and 2 wt% (55.26%) but had the same efficiency at 3 wt% (73.68%). The PE at 1 wt% had the greatest inhibition effect and adjudged the optimum weight percent with a well-regulated phase equilibrium curve. This shows that PE is a better gas hydrate inhibitor than MEG, which is toxic to both human and aquatic life; therefore, Elechi et al (2022) recommended this solution for field trials.

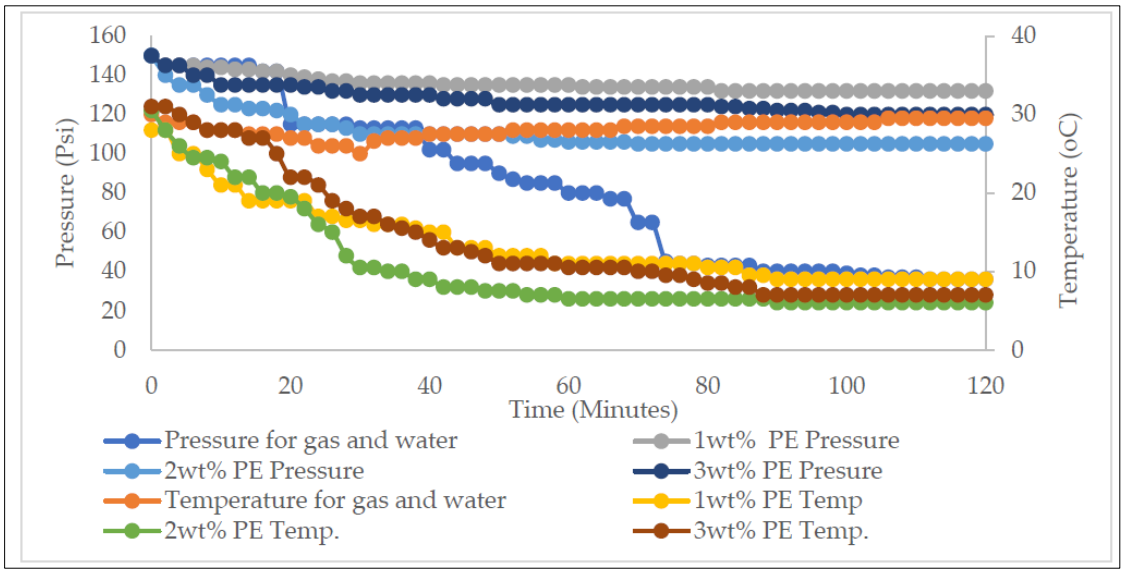

Figure 9 Pressure and Temperature versus Time for 1, 2 and 3 wt% Plant Extract (PE)

Elechi et al (2018) experimentally studied the influence of bio-degradable gas hydrate inhibitor from locally sourced materials as compared to a conventional hydrate inhibitor Mono ethylene glycol (MEG). Experiments were conducted using a mini flow loop. It involved mitigating hydrate formation using varying weight percentages of the inhibitor (1wt%, 2wt% and 3wt %) and then evaluate their effect on hydrate inhibition in the mini flow loop. Sensitivity charts (Figure 10) of pressure, temperature and time for both the local inhibitor and MEG were made. From the analysis, 1 and 2 weight percentages of the local plant extract (PE) showed better inhibitory capacity than MEG while 3 weight

percentages of plant extract (PE) and MEG had a close match. Based on the result obtained, Elechi et al (2018) recommended PE for field trial.

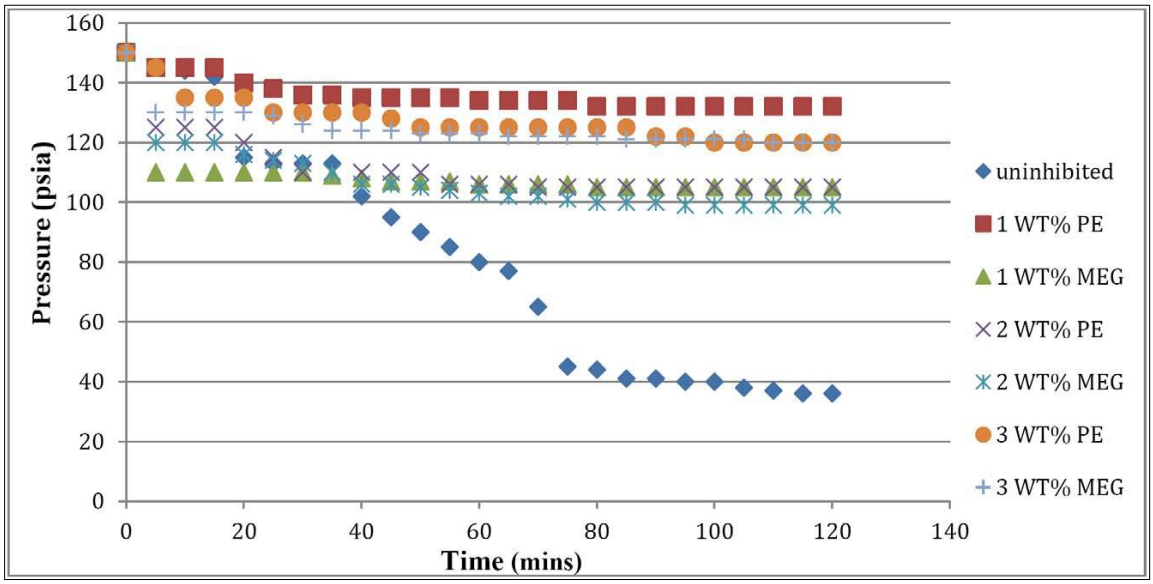

Figure 10 Plot of Pressure and Time for uninhibited, 1wt%, 2wt% and 3wt% of PE and MEG

Raimond et al (2010) experimentally showed that antifreeze proteins (AFPs) possess the ability to modify structure II (sII) tetrahydrofuran (THF) hydrate crystal morphologies by adhering to the hydrate surface and inhibiting growth in a similar fashion to the kinetic inhibitor poly-Nvinylpyrrolidone (PVP). The effects of AFPs on the formation and growth rate of high-pressure sII gas mix hydrate demonstrated that AFPs are superior hydrate inhibitors compared to PVP (Figure 11). These results indicate that AFPs may be suitable for the study of new inhibitor systems and represent an important step towards the development of biologically based hydrate inhibitors.

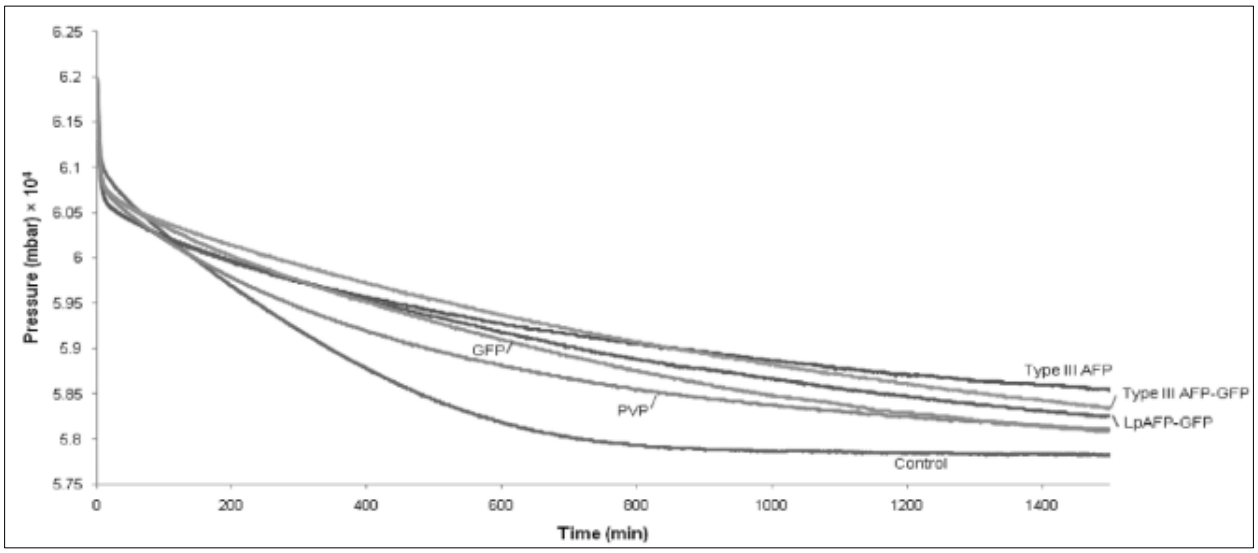

Figure 11 Pressure summary of sII methane/ethane/propane gas hydrate with 0.1 mM additives. Pressure trends plotted against time for Type III AFP, Type III AFP-GFP, LpAFP-GFP, GFP, PVP and control water samples. Absolute pressure drops are proportional to the quantity of moles of gas consumed

Morteza et al (2023) demonstrated that crystal growth inhibition (CGI) methods have been used to assess the KHI performance of aqueous food grade apple pectin for pure methane and a multicomponent natural gas, with results compared to the commercial biodegradable KHI polymer Luvicap Bio. Results show that Luvicap Bio can offer significant inhibition to high subcoolings (e.g 9.1°C for the complete inhibition region in the natural gas system). In contrast, data

show that pectin lacks the ability to significantly inhibit hydrate crystal growth, with it only showing some anti-nucleation properties, namely, through the ability to remove hydrate "history" (relic nuclei/water structuring). This analysis highlights why it is crucial to ensure the presence of seeds (nuclei/water structures) and ideally viable hydrate crystals, ahead of a re-cooling cycle for the reliable assessment of KHIs by CGI type methods. An inadvertent lack of such "seeding" could potentially result in misleadingly strong apparent inhibition performance results, as recently found in related studies of some commercial KHIs.

Erfani et al (2020) conducted experiments to determine the performance of starch (Figure 2.1) in hydrate inhibition. They observed that the anhdroglucose segment of starch contains hydrate structure like that of hydrophilic pendant lactam group. They also stated that starch reacts with hydrogen in the water molecules during hydrate process. They concluded that the presence of starch generates significant force that inhibit hydrate formation.

Elechi et al (2021) experimentally investigated the effect of caricaceae plant (Figure 2.2) as gas hydrate inhibitor. The experiment was done in a locally fabricated hydrate loop. Pressure profile from the experimental runs were used to compare the inhibition efficiency of caricaceae extract (CE) and monoethylene glycol (MEG). The outcomes indicated that less gas was used up in the presence of caricaceae extract compared to that of monoethylene glycol. This is also evident in the pressure profile which indicated less reduction in the presence of carinceae extrat compared to that of monoethylene glycol. Elechi etal (2021) recommended the use of caricaceae extract as hydrate inhibitor in field applications.

Shurui et al (2016) experimentally investigated the inhibition efficiency of Es-PVCap-OH (addition of ester group and hydroxy group to the molecular chair end of polyringl caprolactam). Gel permeation Chromatography and Fourier transform infrared spectroscopy techniques were used to characterize both Es-PVCap-OH and PVCap. The inhibitor efficiency of both PVCXap and Es-PVCap-OH on methane hydrate formation was investigated. The characterizes of formed methane hydrate were determined with Cryogenic Scanning Electron Microscopy (Cryo-SEM), Powder X-ray diffraction and Raman Spectroscopy. The outcomes of the experimental investigation indicated that Es-PVCap-OH performed better than PVCap in inhibiting the methane hydrate. The results also showed that Es-PVCap-OH demonstrated higher maximum sub-cooling than PVCap at the same concentration levels. They said that Es-PVCap-OH particularly acted on specified hydrate crystal planes and weakens its growth capacity. They recommended the use of Es-PVCap-OH as hydrate inhibitors because of its ability to mitigate the number and impact of methane molecules in cases of hydrate lattice. According to Shurui et al (2016), Es-PVCap can change the microstructure of hydrates from submicron pores to a scaly cluster.

Abdolreza et al (2020) experimentally investigated hydrate formation and dissociation in a 4inch laboratory flow loop. The analysis was used to determine the impact of pressure, temperature, density and differential pressure on hydrate formation and dissociation. They also evaluated the effect of different velocities and liquid loading on hydrate formation and growth for 100% water cut. In the experiment, methane gas was used. A significant pressure drop was recorded during hydrate formation in the flow loop. It was observed that the pressure drop was affected by liquid loading and salt solution. The pressure drop was also observed to be directly proportional to the velocity.

3. Conclusion

From the analysis given so far, natural plant materials competed favourably well with the conventional synthetic hydrate inhibitors in hydrate management. Given the fact that these agro-based materials are locally available and can be obtained from Plant family, it will be environmentally friendly (in the sense that it is biodegradable). Less fund will be required to obtain and prepare local plant materials as hydrate inhibitors than the conventional synthetic hydrate inhibitors that are usually expensive to sustain. Some of the local plants with potential hydrate inhibitory are ignorantly abandoned to rot and which constitutes nuisance to our immediate environment. It should therefore be considered and developed as inhibitors for gas hydrate control in favour of conventional synthetic hydrate inhibitors which are toxic to both humans and the environment.

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