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Abstract

The effects of corrosion and hydrate formation on carbon steel pipeline is a major challenge to the oil and gas industry. These hydrates are often encountered during multiphase flow of fluid and the problem is more significant in transient operations. Different types and grades of inhibitors (both thermodynamics and kinetic) are applied to the pipelines to avoid hydrate formation, especially when the pipelines are operated under high-pressure and low-temperature conditions. However, these thermodynamic and kinetic inhibitors are quite expensive and are not environmentally friendly. In this paper, the inhibition performance of a local inhibitor Saccharum Officinarum (SAOF) on X-65 carbon steel in deaerated environment were evaluated at varying conditions using a flow loop. Experimental results obtained were recorded and analyzed to determine the efficiencies of the inhibitors used at varies conditions of temperature, pressure and concentrations. The results obtained shows that the local inhibitor perform extremely well compared to the conventional inhibitor, and are found to be very effective in reducing the hydrate formation of X65 carbon steel compared to the conventional inhibitor at the specified conditions and concentrations. Consequently, It was noted that the optimum inhibition capacity occurred at 0.05 wt. % and prevented hydrate formation at declined temperature of 6.5°C.

Key words: Gas hydrate, Inhibitor, carbon steel, mono-ethylene glycol, concentrations.

1. Introduction

Carbon steel pipelines are required to transport oil and gas products from the well, sometimes over long distances. In addition to oil/or gas, It is common that wells produce other products that are likely to cause corrosion, such as water (H_2O), carbon dioxide (CO_2), hydrogen sulphide (H_2S) and acetic acid (CH_3COOH). Pipeline failures due to corrosion could be very costly in terms of safety, cost or environmental damage [1]

The processing and transportation of this gas is hindered by corrosion due to water content and formation of gas hydrates in pipelines. Water can condense along the pipeline due to temperature gradients between the source and process plant, and this can lead to more corrosion and gas hydrate formation [2]. Similarly to ease the flow of gas, MonoEthylene glycol is usually injected into the pipeline as an antifreeze and anticorrosion agent. In most gas production system, thermodynamic hydrate inhibitors are applied to prevent the formation of hydrates that can block the pipelines. More importantly, MEG is used in inhibitor prevention because it is less toxic than methanol and has low density [3-6]. Also, MEG has corrosion inhibition properties, but the corrosion inhibition of MEG is normally inadequate to protect the carbon steel used in the construction of oil and gas pipeline [5].

Several mitigation measures have been developed to reduce the corrosion rate in such pipelines to acceptable limits, which includes Injection of corrosion inhibitors or stimulating the growth of protective corrosion film [7, 8]. Wong and Park [9] explored the interactions of iron carbonate with three corrosion inhibitor generic actives (quaternary amine monomer, imidazoline, and phosphate ester. It was observed that the presence of quaternized amine monomer increases the precipitation rate of iron carbonate scale. They also reported that the presence of phosphate ester and imidazoline at concentrations above 25ppm prevents the growth of iron carbonate scale. Evidence suggests that iron and phosphate ester interact to form a more protective film on the surface [9]. Bilkova and Gulbrandsen in their studies established that the CO_2 corrosion inhibition was composed of two processes, a rapid process connected to hydrophobically driven adsorption of the inhibitor leading to inhibition of the anodic part reaction, and a slower process leading to a reduction in the corrosion rate through inhibition of the cathodic part reactions. They clearly stated that the performance of CO_2 corrosion inhibitors in many cases was hindered when the steel corroded before inhibition. However, the corrosion deposit may reduce access of the inhibitor to the steel surface and inhibitor performance might differ significantly from what is seen on bare carbon steel surfaces [10]. McMahon [18] noted that corrosion inhibitor performance is being affected by the use of hydrate inhibitors.

Kowata and Takahashi [11] did a research on corrosion inhibition at steel surfaces covered with corrosion product layers. They reviewed the work done on rusted surfaces, and showed that some inhibitors are able to penetrate deep into the rust layer. Hausler [12] in his research considered inhibition of CO_2 corrosion under conditions where $FeCO_3$ films predominated. The concept of interphase inhibition has also been developed to describe inhibition in porous corrosion product layers as opposed to interface inhibition at bare surfaces [13]. Al-Maslamani et al [14] conducted a test on how well corrosion inhibitors perform under high velocity flows or flows containing solid particles. They noted that in some cases, inhibitors may be stripped from the surface they are supposed to protect by hydrodynamic forces or by the impingement of solid particles. For inhibitor that depends on the formation of a corrosion product for maximum efficiency, it may be the scale that is destroyed by erosive forces. Jasinski [15] found that commercial filming amine corrosion inhibitors transformed the morphology of the corrosion product scale that forms in CO_2 saturated systems into a more compact form. Based on his findings, corrosion rate was found to be related to the morphology of the scale with the denser scales corresponding to the lower corrosion rates. It was speculated that the denser corrosion scales formed when an inhibitor is present are more erosion resistant than scales formed without benefit of inhibitor. This means that using an inhibitor may also offer a means of controlling erosion-corrosion. Consequently, more researches had been carried out on the benefit of using corrosion inhibitors to reduce the corrosion rate of steel in CO_2 environment, but so far little literature have been reviewed about the use of local inhibitor on X-65 carbon steel deaerated environment.

In this study, two CO_2 corrosion inhibitors (phosphate ester and an oleic imidazoline salt) would be used to study the interaction of MEG and HAc on mild steel in CO_2 environment.

2. GAS HYDRATE INHIBITION USING GRAMINEAE SACCHRUM OFFICINARUM

Sugarcane (Graminae saccharum officinarum) is cultivated in considerable quantities in tropical countries. In 2017, about 1.84 billion tons of sugarcane were produced worldwide. It is used in sugar mills and alcohol mills. But it cannot be consumed entirely by those mills as about 30% pulpy fibrous residue is produced after being utilized in those mills. These residues are called bagasse.Sugarcane bagasse is a fibrous material that's left over after sugarcane is processed to extract the sugar. Sugarcane bagasse is usually treated as a waste product, but it has a wide range of potential uses, including as a biofuel, a compost material, and as a feedstock for bioplastics. It's also being studied for its potential to inhibit gas hydrate formation.

Sugarcane bagasse may have the potential of inhibiting gas hydrate formation by acting as a kinetic inhibitor. Kinetic inhibitors don't prevent gas hydrates from forming, but they slow down the process so that it takes longer for the hydrates to form. This gives operators more time to take action to prevent hydrate formation or to remove existing hydrates. Sugarcane bagasse is thought to work as a kinetic inhibitor by adsorbing onto the surface of water molecules, preventing them from binding with gas molecules to form gas hydrates

Sugarcane bagasse is a promising material for gas hydrate inhibition for several reasons. First, it's abundant and readily available, since it's a waste product of sugar production. Second, it's composed of cellulose and hemicellulose, which can interact with water molecules to prevent them from combining with gas molecules and forming gas hydrates. And third, it's biodegradable and has a low environmental impact. All of these factors make it a promising option for preventing gas hydrate formation.

3. INHIBITORY EFFECTS OF SACCHARUM OFFICINARUM

Saccharum officinarum (sugarcane bagasse), aside from being a byproduct of sugar production, finds various applications. It is utilized in paper and pulp production, as a biofuel for energy generation (Chinnadurai 2017), and even in construction materials. It is also used in the production of bio-based materials like compostable packaging and disposable tableware. Additionally, in agriculture, bagasse is employed as a mulching agent and soil conditioner, enhancing water retention and soil fertility. Overall, these diverse uses showcase the potential of sugarcane bagasse in contributing to eco-friendly and sustainable practices.

Specifically, in the oil and gas industry, saccharum officinarum has gained attention for its potential as a gas hydrate inhibitor. It's ability to alter the thermodynamic conditions of hydrate formation makes it valuable in preventing hydrate blockages in pipelines and equipment, ensuring smooth oil and gas flow (. Saccharum officinarum exhibits inhibitory effects on gas hydrate formation through its bioactive components. Its polyphenols and other organic compounds interfere with the nucleation and growth of hydrate crystals, disrupting the formation process. This inhibition potential makes sugarcane bagasse an interesting candidate for environmentally friendly approaches in managing gas hydrates in various industrial application (Gao et al., 2014).

4. MATERIALS AND PROCEDURE

The test specimens used throughout this study are X-65 carbon steel having a surface area of 8.11cm^2 with chemical compositions shown in Table 1, and 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 experiment, 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 inlet valve until it achieves a pressure of 25psi. The water is removed with an outlet valves 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 CO_2 bottle is turn on and then valve opened while orifice are enabled to build pressure to 150psia after closing down the valves and orifice. Varying quantities of the local inhibitor 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.

Table 1: Chemical composition of X-65 carbon steel used for the experiment (wt. %).

Comp.	C	Si	Mn	S	P	Sn	Cr	Ni	Mo	Cu	Al
Val. %	0.08	0.25	1.54	0.001	0.019	0.008	0.04	0.03	0.01	0.12	0.038

Fig. 1. Hydrate circulation flow loop used the experiment. (Odutola T.O., 2017)

5. RESULTS ANALYSIS

5.1 Analysis of Local Inhibition and Uninhibited Plots (Base Solutions)

In the process of this work, experimental data have been reviewed and different plots were made for the various experiments conducted for both inhibited and uninhibited solutions

Figure 2 shows a plot of pressure and temperature as a function of time for base solution or 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 2, it is observed that the pressure decreases from 151psi to 120psi in the first 2 minutes of the experiment and remained steady till after 10 minutes when the pressure decrease to 114 psi. Consequently, there was a corresponding decrease in temperature from 35ºC to 20ºC. At the end of the experiment (120 mins), the pressure declined to 98psi and corresponding temperature of 7ºC 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.

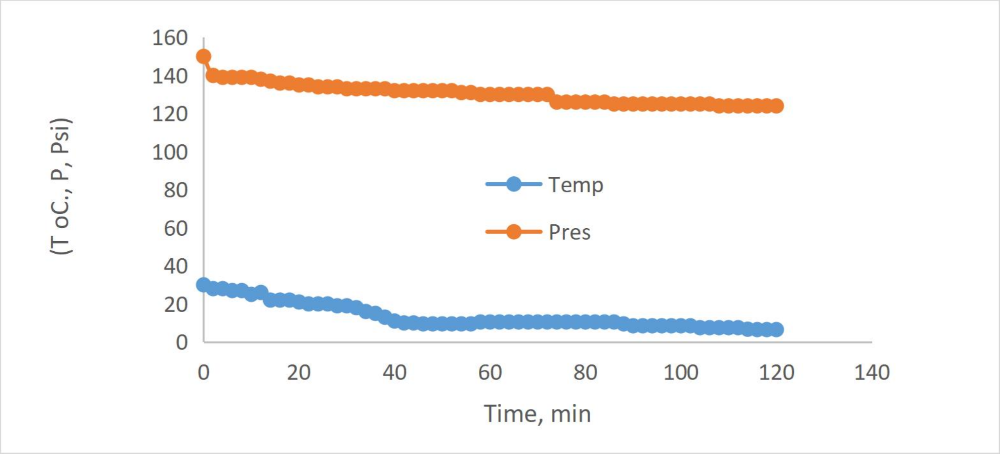

Fig. 2. Plot of pressure and temperature as a function of time for uninhibited fluid.

In order to determine the inhibitory effect of Saccharum Officinarum (SAOF), a comparison has been made with conventional inhibitors (MEOH, MEG) for various weight percentage concentrations for each of the inhibitors used and base experiment against time as can be seen in **Figure3** – **Figure 7**.

Figure3 shows the relationship between pressure of 1st concentration for MEOH, MEG, SAOF and uninhibited against time. 0.01w% of SAOF was used while that of MEOH and MEG were 1wt. % each respectively. From the plot (**Figure 3**), 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 3**, SAOF 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 attributed to an increased pressure from 110psi to 118psi based on agitation in flow that could have form hydrate. MEOH had a decrease in pressure of 105psi.

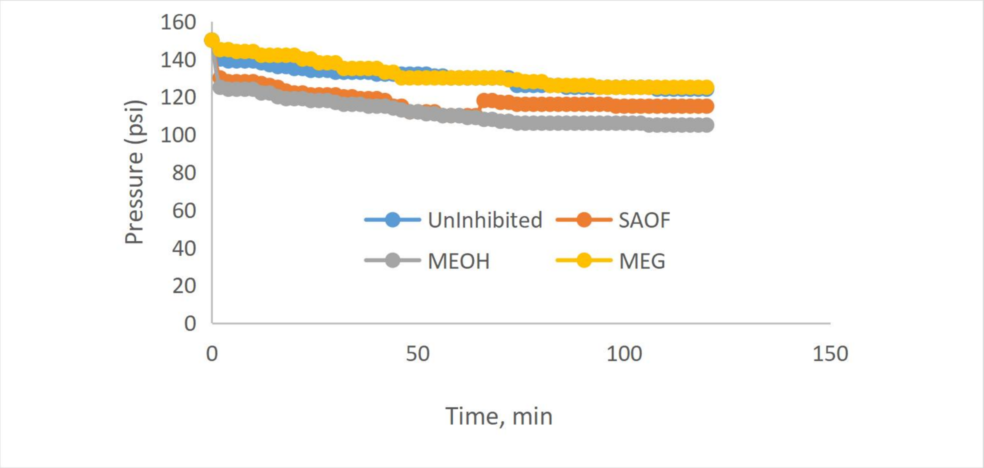

Fig. 3. Pressure as a function of time for 0.01 concentrations of SAOF, MEG and MEOH and uninhibited.

Again, **Figure 4** present results of pressure for 2nd concentration of MEOH, MEG, SAOF and uninhibited as a function of time. From the plot (**Figure 4**), It is observed that SAOF with 0.02wt.% concentration had a good inhibition performance at decrease 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.

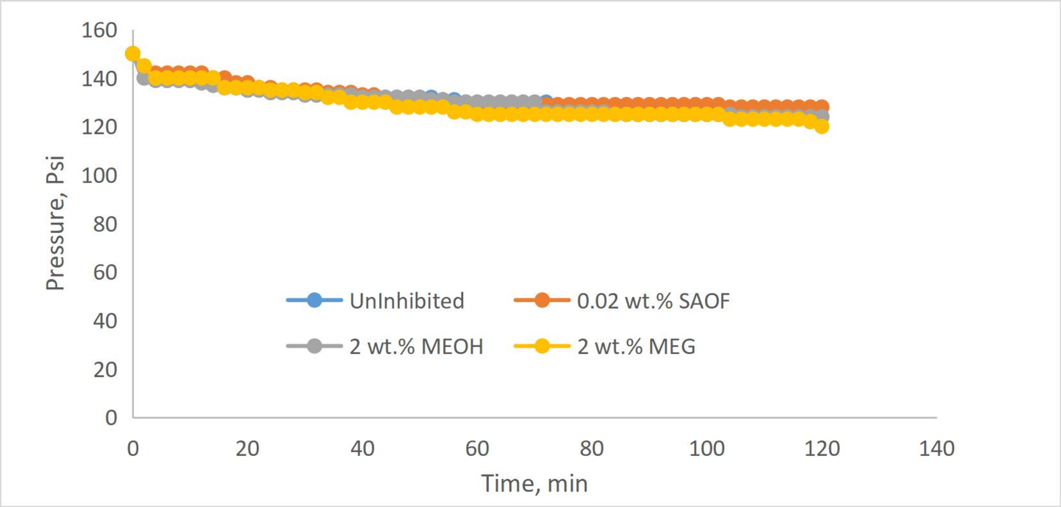

Fig. 4. Pressure as a function of time for 2nd concentration of MEG, MEOH, SAOF and Uninhibited

Similarly, **Figure 5** shows the relationship of SAOF, MEOH, MEG and uninhibited as a function of time. From the Figure (**Figure 5**), It can be seen that SAOF again prove to be a better inhibitor for the pressure of 3rd concentration for MEOH, MEG, SAOF and uninhibited against time. SAOF 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 SAOF which shows hydrate inhibition at pressure drop of 121psi in 100minutes of the experiment. MEOH have a pressure drop of 110 psi.

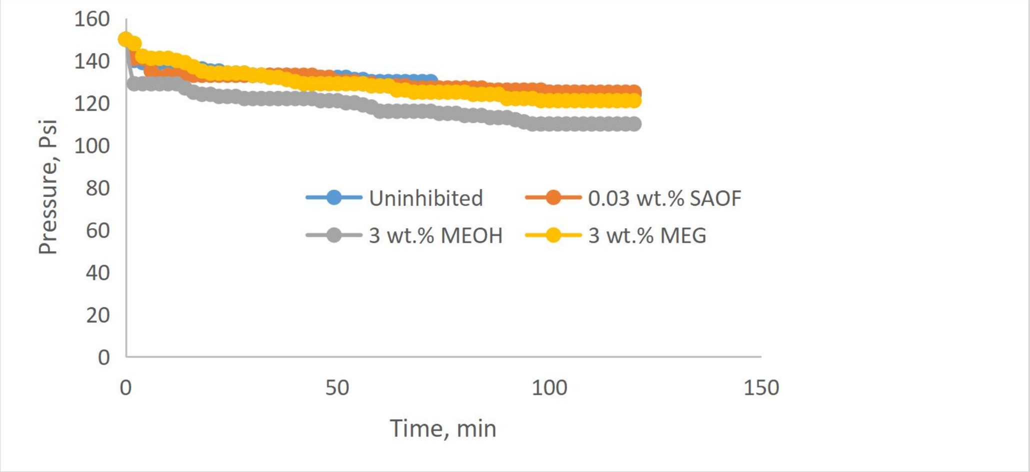

Fig. 5. Pressure as a function of time for 3rd concentration of MEG, MEOH, SAOF and uninhibited

Figure 6 shows the plot of pressure against time for 4th concentration of MEOH, MEG, SAOF and the uninhibited. As expected, it can be seen that SAOF had a better inhibition performance as compared to MEOH and MEG. In **Figure 6**, It can be observed that SAOF 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 SAOF 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.

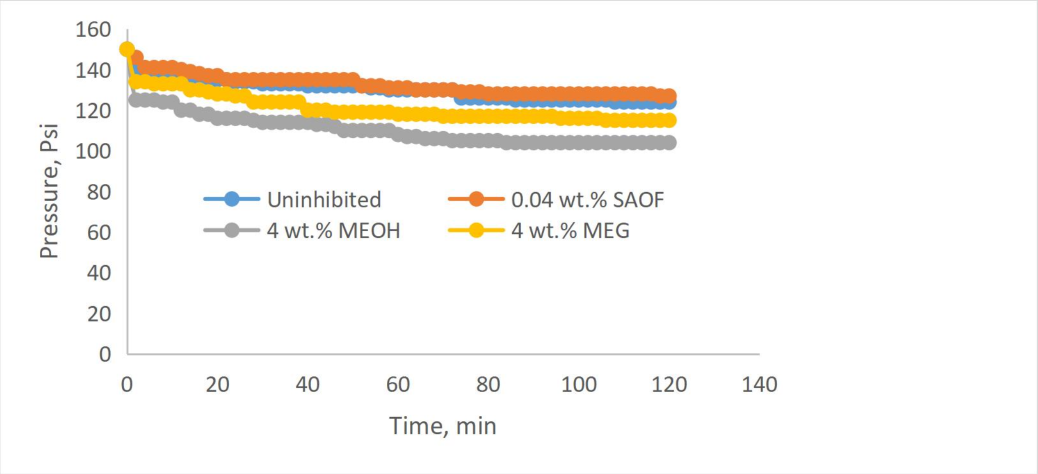

Fig. 6. Pressure as a function of time for 4th concentrations of MEOH, MEG, SAOF and uninhibited

A similar trend was also observed in **Figure 7** for the plot of pressure against time for the 5th concentration of MEOH, MEG, SAOF and the uninhibited. As can be seen from **Figure 7,** it is worthy to note that SAOF performed credibly well when compared to MEG and MEOH. It is noted that 0.05 wt. % of SAOF gave good inhibitory effect more than MEOH and MEG with concentration as high as 5wt. % each. SAOF 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.

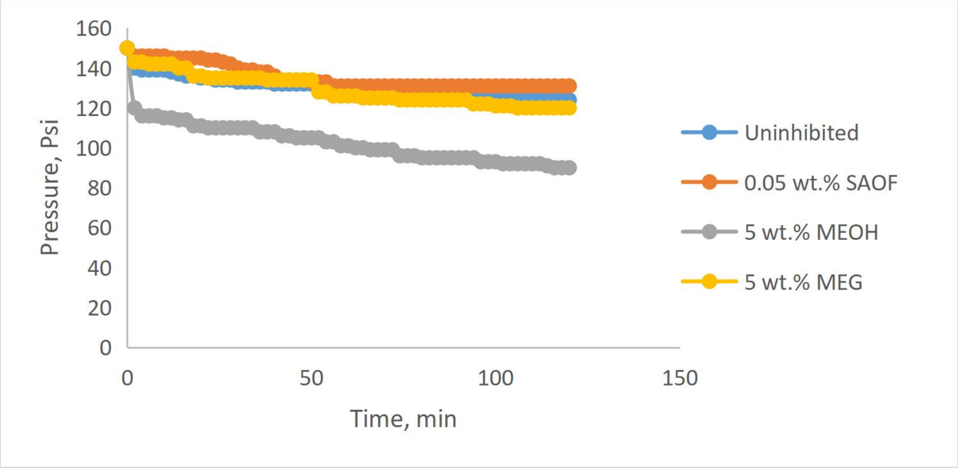

Fig. 7. Pressure as a function of time for 5th concentrations of SAOF, MEG, MEOH and uninhibited

5.2. Determination 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 8** shows that SAOF 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 8**), it can noted that the optimum inhibitory capacity was gotten at 0.05 wt. %. It can also be seen in **Figure 8** that SAOF prevented hydrate formation at decrease temperature of 6.5ºC in 106minutes. From the results analysis, SAOF 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. SAOF prevention raise in system loop temperature which would have resulted to hydrate nucleation and growth (Turner, 2005, Sun2013). Hence it is not toxic, eco-friendly and locally available.

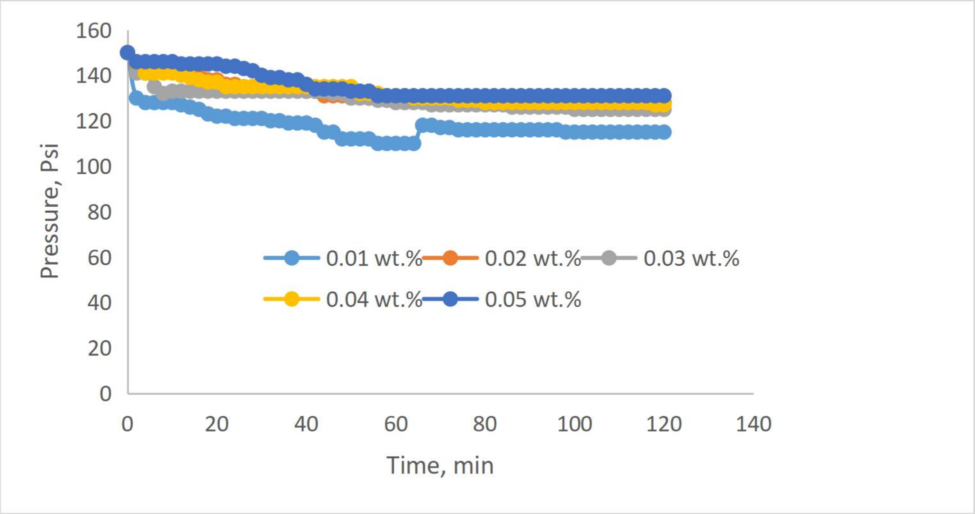

Fig. 8. Pressure as a function time for different concentrations of SAOF

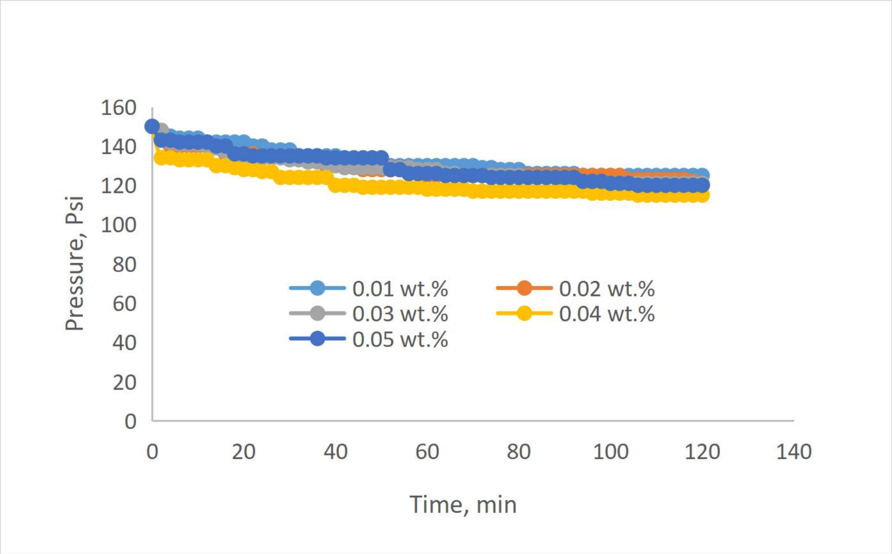

Fig. 9. Plot of pressure against time for different concentrations of MEG

In Figure 9, it is observed thatthe 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 quiet 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 7ºC.

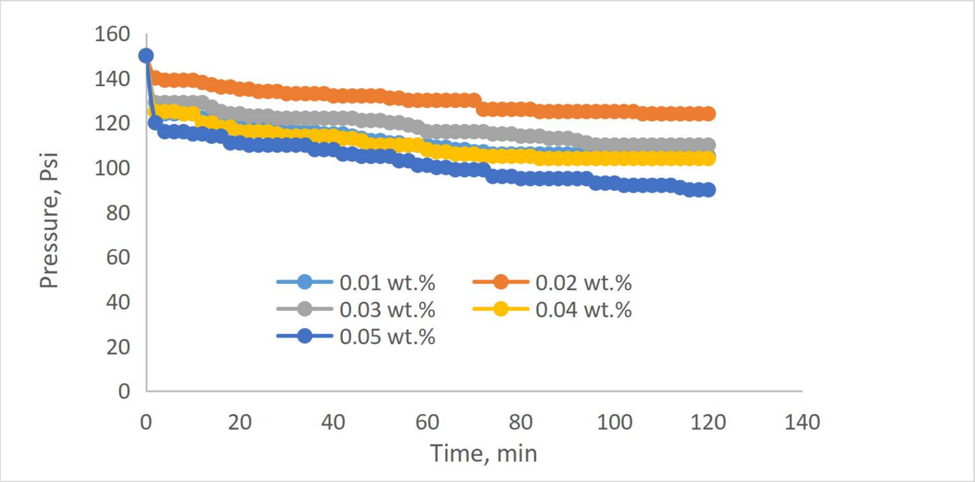

Fig. 10. 10 Plot of pressure against time for different concentrations of MEOH

4. Conclusion

The investigation of hydrate formation and treatments in gas pipeline using locally sourced material as green inhibitor has been carried out in a laboratory using a circulated flow loop. Experimental results have been obtained, recorded and analyzed. Different plots has also been made to determine their relationship. However, from the analysis of the results, it can be summarized as follows:

- A gas hydrate inhibitor, Saccharum Officinarum (SAOH) plant extract kinetic inhibitor was developed from a locally sourced material.
- Gas hydrate can be mitigated using optimal concentration of the local inhibitor, SAOH.
- The SAOH inhibitor is environmental friendly which indicates that it cannot be harmful to human and aquatic life.
- The SAOH can be used as an alternative to conventional inhibitors like that of MEG and MEOH
- As the experimental results clearly shows that SAOH performed better with low concentration at 0.05 et.% compared to the conventional inhibitors (MEG and MEOH). This implies that it will inhibit hydrate formation effectively and should be given a field trial.

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