SPE Brazil Flow Assurance Technology Congress
Rio de Janeiro, Brazil, November 15 – 18 2022

Methane Hydrate: Thermodynamic and Kinetic inhibitor evaluation in PVT apparatus with image analysis

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Abstract
The present study evaluated methane hydrate formation in a PVT apparatus using R.G.B. (Red, Green and Blue) image analysis system. The experiments were performed at 4ºC increasing pressure from atmospheric to 5145 psi with 15 psi/min rate. Pictures were recorded during the experiment every 5 second. From the pictures, Red, Green and Blue components were obtained as a function of the experiment time, which all components were able to show the moment that methane hydrate was formed. For methane-water system, gas hydrate appeared during pressurization at around 3740 psi. The method has also shown to be reproducible with a very low standard deviation, being equal to 82 psi. In addition, an anionic Rhamnolipid biosurfactant obtained by cultivating Pseudomona *aeruginosa* was evaluated as low dosage hydrate inhibitor, LDHI. As a matter of comparison, monoethyleneglycol (MEG) as thermodynamic inhibitor was also evaluated. The results showed that methane hydrate was formed after 84 minutes at 5145 psi using 1000 ppm of Rhamnolipid added to methane-water system. For MEG, the gas hydrate appeared at 4356 psi.

Keywords
Gas Hydrates; Inhibition; Natural Gas

Introduction
A major problem in offshore oil production is gas hydrate formation due to the low temperatures and high pressure, especially in subsea context with high depth of water. Most of the problems are due to solid deposition in safety valves and pipelines. These problems lead to productivity reduction and different kinds of losses. Indeed, gas hydrate formation is one of the main concerns in flow assurance. [1]
Gas hydrates is a solid solution, visually similar to ice. Gas clathrates, also called gas hydrates, are crystalline structures formed by small gas molecules enclosed in hydrogen-bonded water cages. The interaction between the water and the gas molecule (usually low molecular weight hydrocarbon, i.e., methane) occurs through Van der Waals forces. [2]
Due to the increasing amount of petroleum production, research on how to inhibit gas hydrates formation has been growing exponentially. Some common inhibition methods are heating and/or insulating the tubes, as well as the addition of chemical inhibitors. [3]
There are two classes of chemical inhibitors according to the literature: thermodynamic inhibitors and LDHI (low dosage hydrate inhibitors). Thermodynamic inhibitors are generally inorganic salts, alcohols, and glycols which act reducing water activity and, therefore, shifting the phase equilibrium curve to higher pressure and lower temperature. Unlike thermodynamic inhibitors, which prevent the formation of gas hydrates, LDHI do not change the pressure and temperature equilibrium values for gas hydrate formation. These types of inhibitors include two categories: (i) kinetic inhibitors (KI) and (ii) antiagglomerants (AA). The KI inhibitors delays hydrate formation and growth. Instead, AA prevent the aggregation of the small hydrate crystals that may block production stream. The molecules interact with water, avoiding cage formation that traps gas molecules. It is noteworthy to mention that LDHI concentrations are quite small, being on the order of parts per million (ppm). [3,4]
In this work we propose a method to evaluate gas hydrate formation in a PVT apparatus. In addition, two inhibitors were evaluated: a thermodynamic inhibitor (monoethyleneglycol, MEG) and LDHI inhibitor (biosurfactant obtained by cultivating Pseudomona aeruginosa, so-called TF32).

Methodology
A PVT (Pressure, Volume and Temperature) apparatus from Vinci Technologies “Fluid Eval PVT” was used to study gas hydrate formation and inhibitor evaluation. The equipment works up to 15,000 psi and temperatures ranging from -20 ºC to 200 ºC. For this gas hydrates study, 4 ºC was

chosen as representative Brazilian pre-salt ocean bottom temperature.

Methodology was optimized to reduce the differences related to the stochastic nature of gas hydrate formation. For that, similar induction times should be obtained for reproducing the same experiment. Ultrapure water and methane (99,9995%) were used in this study.

Accordingly with the experimental precure, the PVT temperature was first adjusted to 4 ºC while the cell volume was set to 45 mL. In this condition, methane was added to obtain 150 psi of pressure in the chamber. The cell volume was then set to 75 mL and 30 mL of H_2O was added. This procedure allows the evaluation of methane solubility in pure water or in the presence of an inhibitor.

Finally, a pressure increase ramp was set to be at 15 psi/min to reach 5145 psi. Pressure, temperature and volume are recorded during the evaluation.

The head of the PVT cell is equipped with a sapphire transparent window that allows the visual evaluation of fluid phenomena. The experimental conditions used were optimized to visualize fluid interface between methane and water. Images of the entire process were recorded with the aid of a high-resolution camera.

The images obtained were treated to evaluate the values of their R.G.B. (Red, Blue and Green) components which provide an indication of the beginning of the gas hydrate formation process.

After reaching 5145 psi, the pressure is kept for 10 minutes for stabilization. Then, the stirring at 150 rpm starts.

MEG and biosurfactant TF32 were evaluated separately as gas hydrate inhibitors. The experiments were conducted with 30 mL of water for both samples. When 10 wt.% of MEG, 34 mL of solution was added to the cell. For the biosurfactant TF32, 30 mL of a solution with 1000 mg L^{-1} was used.

Results and Discussion

Figure 1 shows the R.G.B. values obtained during the experiment of water-methane in the PVT apparatus. It can be noted that there is a variation of all components during the experiment, which is due to pressurization and water level rising followed by the decrease of gas volume (PVT cell images are also shown in Figure 1). However, there is a very important signal drop for all components when the system reaches 3850 psi. This result shows methane hydrate formation during pressurization process.

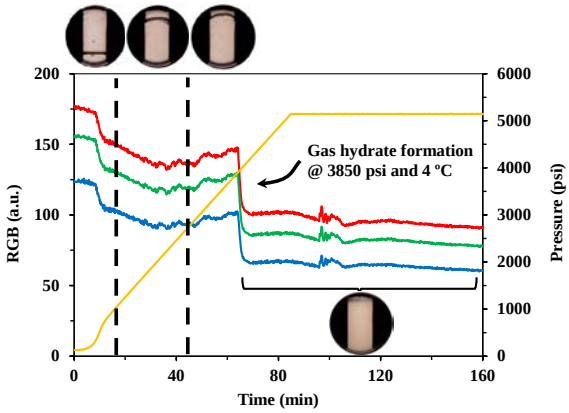

Figure 1. Red, Green and Blue components and Pressure as function of time for gas hydrate formation in methane-water system, with images of the PVT cell window during the experiment.

To evaluate reproducibility, the experiment was carried out three times. Since all RGB components displayed the same kind of result for hydrate formation, the red component for all experiments is shown in Figure 2.

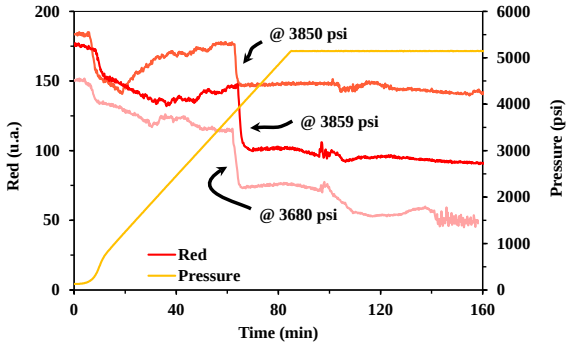

Figure 2. Red component for three experiments conducted at 4 ºC for methane-water system.

As can be seen, methane hydrate formation occurred at similar conditions. The formation occurred at 3850, 3859 and 3680 psi, respectively. The average pressure was 3780 psi. Indeed, the stochastic features related to gas hydrate formation seems to be reduced. In our case, the reproducibility may be given to the equipment used. The PVT apparatus measures and controls temperature, pressure, and volume in a strict manner.

The results for the system methane-water+MEG is displayed in Figure 3. The gas hydrate formation occurred at 4356 psi average, considering 3 experiments. As expected, gas hydrate formation occurred in a higher pressure.

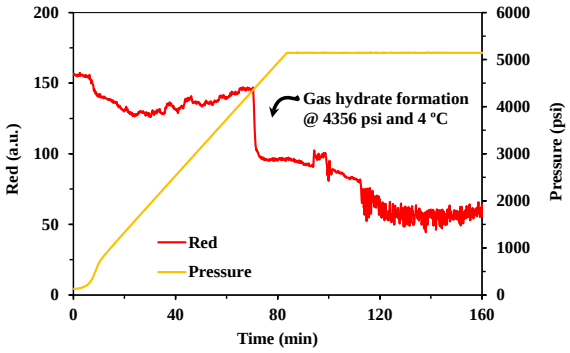

Figure 3 Average of Red component and Pressure as function of time for gas hydrate formation in methane-water+MEG system

Interesting results were obtained using a product consisting of amphipathic molecules, an anionic biosurfactant of the Rhamnolipid type (kinetic inhibitor). Figure 4 shows the average values of the red component for methane-water+TF32 system. In this case, the system not only reached 5145 but no gas hydrate was observed for an average time of 84 minutes after reaching this pressure. It should also be noted that stirring at 150 rpm was started after 10 minutes when 5145 psi was reached. Indeed, Rhamnolipids act by reducing the surface tension of water, probably stabilizing its molecules avoiding cage formation. This factor directly affects the gas hydrates formation.

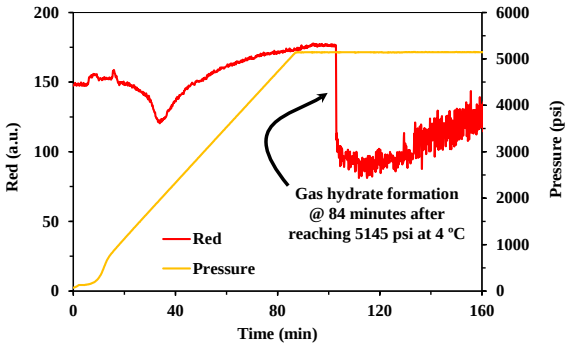

Figure. 4 Average of Red component and Pressure as function of time for hydrate formation in methane-water+TF32 system

Conclusions

The present study presented insights into a new methodology for evaluating gas hydrate formation, employing a method developed in a PVT apparatus. A biosurfactant, Rhamnolipid type, was much more efficient than the use of monoethyleneglycol 10wt.%. Based on the results of this present work, some additional investigations may be considered such as evaluating a mixture of gases simulating natural gas, effect of biosurfactant concentrations and the use of brines.

Acknowledgments

The authors acknowledge FAPERJ - Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro for supporting this project

Responsibility Notice

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