COB-2021-0275

INFLUENCE OF THE PRESSURE ON THE ETHANE HYDRATES KINETICS

Ana Carolina Guimarães Alves Rebello
Gustavo A. B. Sandoval
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, RJ, 22451-900, Brazil
anarebello@yahoo.com.br
gsandoval@puc-rio.br

Mônica F. Naccache
Paulo R. De Souza Mendes
Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, RJ, 22451-900, Brazil
naccache@puc-rio.br
pmendes@puc-rio.br

Adriana Teixeira
Leandro Valim
Petrobras Research Center (CENPES), Petrobras Av. Horácio Macedo 950, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ 21941-598, Brazil
adriteix@petrobras.com.br
leandro.valim@petrobras.com.br

Abstract. *In offshore oil and gas production and transportation a variety of issues can occur, which hinder or fully stop the flow within the pipeline. Production stoppage in this industry can cause huge financial costs and environmental commitments. Asphaltene precipitation, wax and sand deposition, and hydrate formation are some of the problems that can occur in the subsea pipeline. Hydrates, for example, are studied on a large laboratory scale due to the industry's interest in understanding them. They are crystalline water-based solids physically similar to ice, and form when guest molecules are trapped inside cages built by the water hydrogen bonds. These substances are stable under specific thermodynamic conditions of low temperatures and high pressures. Several chemical, thermal, and mechanical methods have been employed to solve hydrate formation problems over the years. However, these aforementioned methods are not successful in avoiding or controlling hydrates under certain thermodynamic conditions, or when there are specific cut-off levels of water present in the systems. One approach to study the kinetics of hydrate formation is through the rheological technique since chemical inhibitors and different thermodynamic conditions could be mimic on the rheometric pressure cells. Moreover, the rheological perspective is an essential complement regarding the understanding of hydrates because it allows an effective comprehension of hydrates fluidity in the production pipelines. Aiming to contribute with the study in this field, the main purpose of this work is to analyze the rheological behavior of ethane gas hydrates formed from water-in-model oil emulsions in a high-pressure system. The emulsions are composed of primol oil, span 80 surfactant and deionized water. The measurements are performed in a rotational rheometer using a vane geometry as a rheometric sensor. To keep the pressure cell constant and to make an accurate temperature control, a syringe pump and a thermostatic bath are used, respectively. The results are shown through viscosity and pressure curves as a function of the experimental time. The effects of pressure on the hydrate slurry rheology were analyzed. In addition, the amount of hydrates formed was determined and related to the slurry rheology.*

Keywords: *Rheology, Ethane gas Hydrates, High-pressure cell.*

1. INTRODUCTION

Gas hydrates are solid compounds that are formed when the water hydrogen bonds (hosts) encage and hold one or more guests molecules at particular thermodynamic conditions of high-pressure and low-temperature (Notz et al., 1996). The molecules that are usually captured are gases of low molecular weight as carbon dioxide, ethane, methane, and natural gas (Sloan et al., 2011). Hydrates are studied because its important applications in fields like refrigeration, gas storage, energy source, and as a principal concern due to their formation inside the pipelines during the production and transportation of hydrocarbon fluids in offshore operations (Sum, 2012). This latter application is the main motivation of this work.

The structures formed by the hydrates depend on the arrangement between the water and the guest molecules as well as on the thermodynamic conditions in which hydrates constituents form (Carroll, 2003). The most common crystal structures formed are structure I (formed from methane, ethane, and carbon dioxide guests) and structure II (formed from propane, hydrogen, and natural gas guests). The structure formed of Type sI is the simplest one. It consists of 46 water molecules. The Type sII hydrate structure is more complex than the Type sI, and the structure contains 136 water molecules (Webb, 2014). Both structures occur when one unique guest molecule is captured by the hydrogen bonds, but in the case of sII crystal, large cages are occupied.

As a result of the solid crystalline structure of gas hydrates, they are substances that do not flow. This situation must be considered in some circumstances, such as in drilling and extraction of oil and gas processes or when the production of oil or gas is interrupted, because the formation of hydrates can plug the flow lines, causing expensive production shutdowns. In fact, this is one of the main problems faced by oil and gas industries (Sum, 2009), because many oil reserves are located in ultradeep waters, where the usual pressure and temperature conditions (approximately 4 °C and 100 bar) are in the hydrate formation zone (Camargo et al., 2004).

One strategy usually taken by the oil industry to overcome this problem is to operate outside of the stable hydrate zone, using insulation, heating, dehydration, or thermodynamic inhibitors (THI). Insulation or heating of the pipe in strategic areas can keep the system out of the hydrate equilibrium temperature, and the thermodynamic inhibitors such as methanol and ethylene glycol can be added to shift the thermodynamic boundary for hydrates formation to higher pressure/lower temperature conditions. However, for high water cuts in the system, the insulation method is not appropriate and high doses of thermodynamic inhibitors are required to avoid hydrates formation. These high amounts of chemical agents, turns the inhibitor method too expensive, and environmentally unfriendly choice (Brown et al., 2020). Another strategy is to continue working in the thermodynamically favorable hydrate formation zone and introduce low-dosage hydrate inhibitors (LDH) to avoid hydrate agglomeration (Anti-agglomerants) or delay the time for hydrate formation (Kinetic hydrate inhibitors – KHI) (Sandoval et. al., 2018).

Kinetic hydrate inhibitors (KHIs) delay the formation of hydrates, ensuring the transportation of hydrocarbons in a specific period. Application of Anti-agglomerants permits hydrates to form in the pipeline, but the chemical additives decrease the cohesion among the particles and its adhesion to the pipe walls, allowing the hydrates to flow as a slurry until the pipeline reaches higher temperature and, lower pressure conditions, and the hydrates dissociate back into their constituent components (Anklam, 2008; Gao, 2009).

The main objective of the present study is to analyze the rheological behavior of ethane gas hydrates formed from water-in-model oil emulsions in a high-pressure system. The experiments are conducted in an assemble composed by a high-pressure cell and a shear stress-controlled rotational rheometer. The results are exhibited through viscosity and pressure curves as a function of time, and it is possible to quantify the amount of water converted to hydrate.

2. EXPERIMENTAL PROCEDURE

The tests were conducted in a shear stress-controlled Rheometer Haake Mars III (Thermo Fischer Scientific). The rheometer is connected to both a syringe pump and a thermostatic bath. The syringe pump maintain the pressure constant in the cell, and the thermostatic bath helps to keep the temperature control of the sample during the experiments.

The pressure cell consists of a rotor, which is the vane geometry (that has 4 blades, forming a projected diameter of 35 mm with a blade height of 93 mm), and the stator. The rotor is supported by two sapphire bearings, so it was necessary to perform a calibration of the system under analysis to discount the friction caused between the geometry and the bearings from the total torque generated by the rheometer. The geometry is placed inside the cell together with the emulsion, and the geometry is rotated using the magnetic field created by an external propulsion magnet coupled to the rheometer. The gap between the vane and the geometry cup is 2 mm. The stator consists of the cup and a top cover to seal the system. At the top of the cup, there are three connections, for a safety valve, inlet of pressure transducer, and for the gas inlet. The pressure transducer is used to monitor the internal pressure in the cell during the experiments. As the experiments are conducted with the system closed, there is a needle valve on the gas inlet connection to cut off the ethane inlet.

3. METHODOLOGY

Our experiments were carried out with a water-in-model oil emulsion, which is placed in the cell before running each test. The main components of our emulsions are mineral oil, deionized water, and Span 80 as a stabilizer agent. The oil used was Primol oil that is highly refined, composed of saturated aliphatic hydrocarbons. This oil is stable, colorless and odorless, its density is in the range of 870 kg/m³ at 20 °C and the pour point temperature is -18 °C. Our deionized water was purified through reverse osmosis and obtained from the Gehaka OS 10 LX system. Span 80 is a non-ionic oil-soluble surfactant with a hydrophilic-lipophilic balance of 4 ∓ 1. Karanjkar et al. (2016) reported that Span 80 acts as an anti-agglomerant agent for hydrates. So, it is important to consider this property of Span 80 as a hydrate inhibitor. Even with this premise, Span 80 was used since this surfactant is an excellent stabilizer of water-in-model oil emulsions. In the tests, an amount of 0.08% of Span 80 was employed in the emulsion. The water-in-model oil emulsions were prepared using the following methodology:

1) Weigh the required masses of Span 80, deionized water and Primol oil;
2) Magnetic homogenization of Span 80 with Primol oil at a speed of 1000 rpm for 5 min;
3) Addition of deionized water in the mixture of Span 80 and Primol oil;
4) Homogenization of the components obtained in step 3 on the Turrax mechanical stirrer (model IKA T25, rotor 18G), at speed of 10000 rpm for 3 min and 12000 rpm for 2 min.

The emulsion has a characteristic white color and stability of approximately 2 hours. The gas selected to conduct the experiments was ethane, since this gas allows hydrates to form at moderate pressures, which facilitates their study at laboratory scale. Ethane, with chemical formula C_2H_6 is an aliphatic component that is in a gaseous state under normal conditions of pressure and temperature, see the saturation curve inserted in Figure 1. As shown in the equilibrium curve, a subcooling of roughly 8 °C is attained if the system is submitted to a thermodynamic condition of 20 bar and 4 ºC.

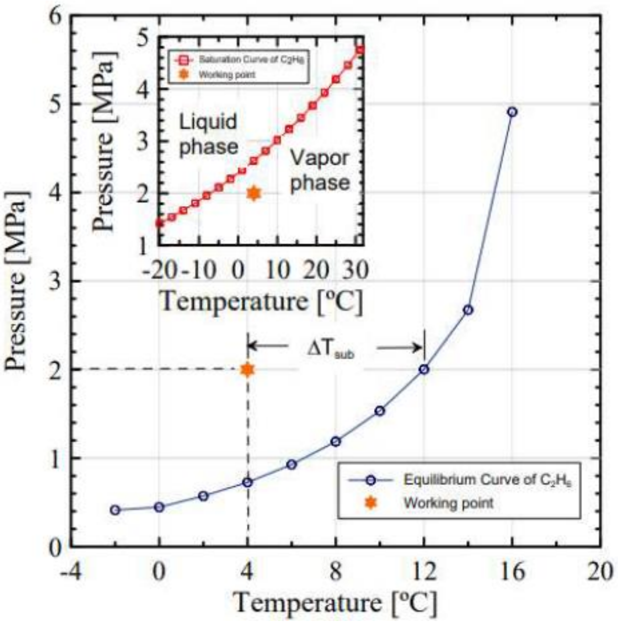

Figure 1. Ethane equilibrium curve for hydrate formation (blue). Ethane saturation curve (red). Figure taken from Sandoval et al., 2020.

In this work, the experiments were conducted in a closed system, that is, the needle valve is closed at some point of the test, then, the pressure varies throughout time as gas is consumed during the process. Henceforth, the conditions of hydrate formation could be different in the experiments.

Once the cell is sealed and placed in the rheometer, the ethane gas line and the pressure sensor are connected to the cell, and the syringe pump is actioned to pressurize the system until the desired pressure (a picture of our system is shown in Figure 2). Subsequently, the thermostatic bath is switched on and programmed to make a temperature control during the dissolution, cooling, and period for hydrate formation. The dissolution of the gas in the emulsion was performed at 25 ºC and lasts 4 hours. During the cooling step, a temperature ramp from 25°C to 4°C at a rate of 0.4 °C/min was conducted, this final temperature of 4°C remains constant until the end of the experiment. Our experiments were conducted with closed system after the dissolution period, so once the temperature ramp starts, the needle valve is closed and thus no more gas enters the cell until the end of the test. The shear rate imposed is kept constant throughout the test.

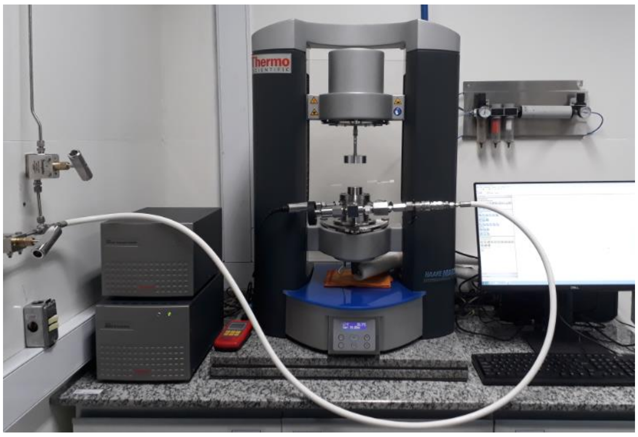

Figure 2. Rheometer Haake Mars III with pressure sensor and gas line connections.

4. DISCUSSION AND RESULTS

All our experiments are presented through viscosity and pressure curves varying with time, as seen in Figure 3. Figure 3 shows the typical rheological curves of hydrate formation obtained from our experiments. The first step of the experiment is the dissolution of the gas, then, the temperature remains constant during the first 4 hours of testing as represented by the red curve in Figure 3. Concurrently, the pressure inside the cell is kept constant with add of the syringe pump (in this case, 28 bar). In this step, the viscosity of the sample decreases due to the dissolution of the gas in the sample, until achieve a stable value, indicating, probably a total saturation of the sample emulsion-gas. Once the saturation step ends, a cooling step is performed from 25°C to 4 °C at a rate of 0.4 °C/min. This final temperature remains constant until the end of the experiment. As a consequence of the cooling step, the pressure is reduced, and the viscosity is increased. For this experiment, the pressure is reduced around 7.5 bar during the cooling step, then, the subcooling is around 8 ºC under these thermodynamic conditions.

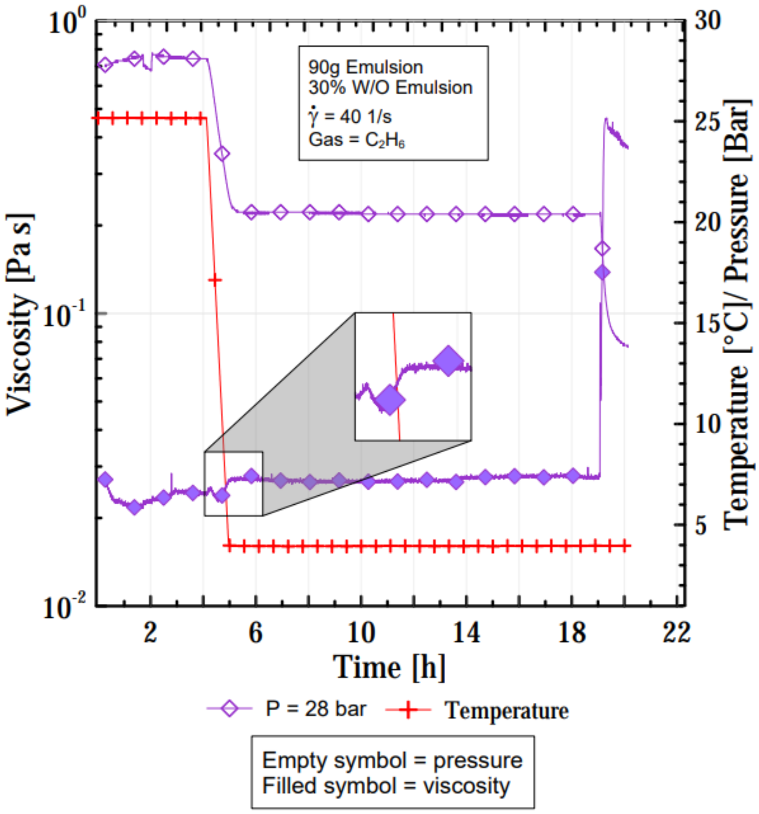

Figure 3. Viscosity, pressure, and temperature curves varying with time.

When the working temperature is attained (4 ºC), both the viscosity and the pressure remain constant with time, until the moment of hydrate formation, which is detected by two simultaneous events, a random increase in viscosity during the 19th hour for this test, and a decrease in pressure. The pressure drop is caused by the gas consumption by the water hydrogen bonds during the process of hydrate formation. The increment in viscosity is related to both, a change from liquids drops to small solid particles of hydrate and to the agglomeration of these particles. The viscosity increment is noted until achieving a maximum value, due to the cohesion forces among the hydrate particles, then, the viscosity decays because the shear forces imposed by the flow field break the agglomerates. Finally, a steady state regime is attained when these forces are in equilibrium. Despite hydrates formation be a stochastic phenomenon, the induction period could give interesting insights about its kinetics. The induction period is the time that elapses from the instant that the system cross the hydrate equilibrium curve, until the moment where hydrate formation is detected.

The following set of tests carried out was made with 30% of water cut, with constant shear rate of 40 1/s, and varying the pressure in each experiment. Thus, it was possible to observe the range of the pressure where ethane hydrates form in an experimental time of 24 h. As indicated before, this pressure was applied at the beginning of each experiment and remained constant for 4 h until the end of the dissolution step.

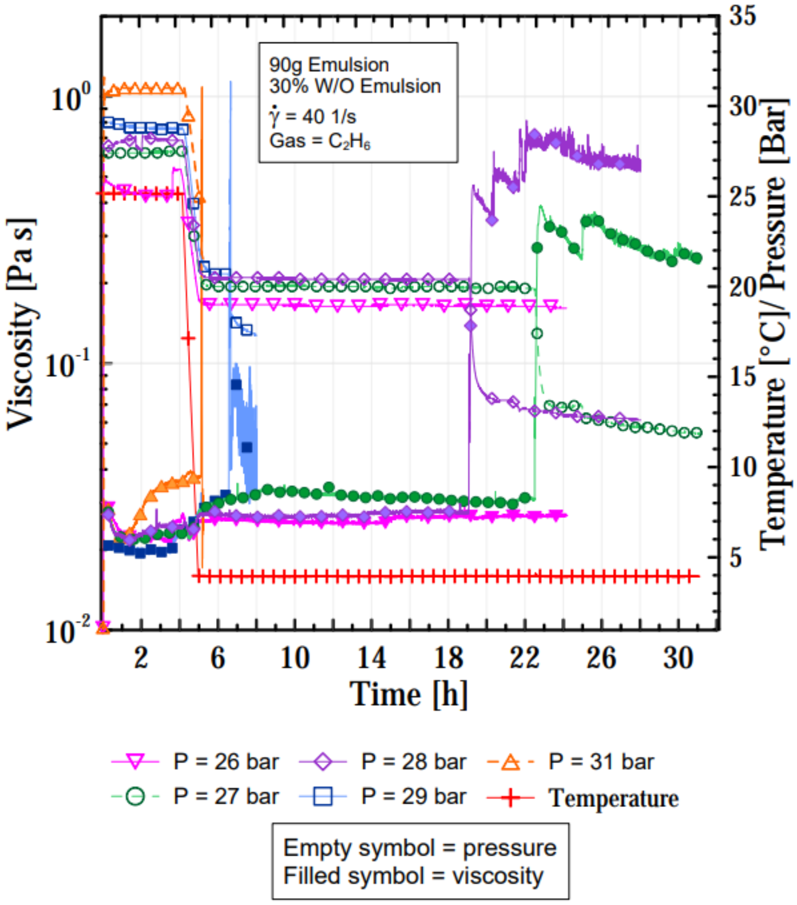

Figure 4. Figure of pressure variation with constant shear rate.

Initially, we conducted an experiment with 31 bar – represented by the orange curve in Figure 4, but once the cooling step ended, hydrate formation was so strong that the maximum allowable rheometer torque was achieved, and the experiment must be stopped. As a result of this severe hydrate formation, a rapid spike in viscosity is observed during the experiment, following by a sudden fall of it. This fall happens because the impeller magnet inserted in the pressure cell loses its magnetic communication with the external propulsion magnet. For this sort of experiments is not further possible to determine the water consumption during hydrate formation, since the data related to the final state of viscosity and pressure drop are not possible to be acquired. This same behavior of severe formation was exhibited by the experiment conducted with a pressure of 29 bar, as shown in the blue curve of Figure 4.

In order to obtain a hydrate slurry where the steady-state regime can be captured by the rheometer, three more tests were done at lower pressures equal to 26, 27, and 28 bar. For the test conducted with 26 bar, hydrates formation was not observed even after approximately 20 h with the system under the equilibrium region. Then, in another different experiment, the pressure was increased to 27 bar and hydrates formation was noted after 17 h of induction time. Hydrates formation was also noted for another test with 28 bar. However, in this case, the induction time was around 13 h and the final steady-state of viscosity was larger than that of the experiment of 27 bar. It is important to point out how the increment in pressure of only 1 bar changes the kinetic of ethane hydrates formation. For example, hydrate formation was not observed for 26 bar, but was noted to 27 bar in the assessed period of 24 h. As noted in the experiments exposed before, the induction time is reduced with the increment in pressure, probably, this time is influenced by the degree of subcooling imposed in the test. Our tests have a hydrate formation window where the phenomenon can be analyzed. When the pressure is lower, no hydrates are evinced, and for larger pressures, a severe formation is noted but the experiment must be stopped due to equipment limitations.

After the experiments with pressure variation, the next step is to analyze the amount of water converted into hydrates. This information is evaluated through the data collected in the tests with pressure of 27 bar and 28 bar (pressures inside our measurement window). This conversion analysis is possible due to the application of the equation of the state in two points, a moment before hydrates formation, and at the end of the test, when the pressure achieves a constant value. Therefore, the initial and final pressure values are used for the calculation, as well as temperature, pressure cell volume, universal gas constant, gas compressibility factor, ethane mass and the number of moles of ethane gas. The results obtained are show in Figure 5.

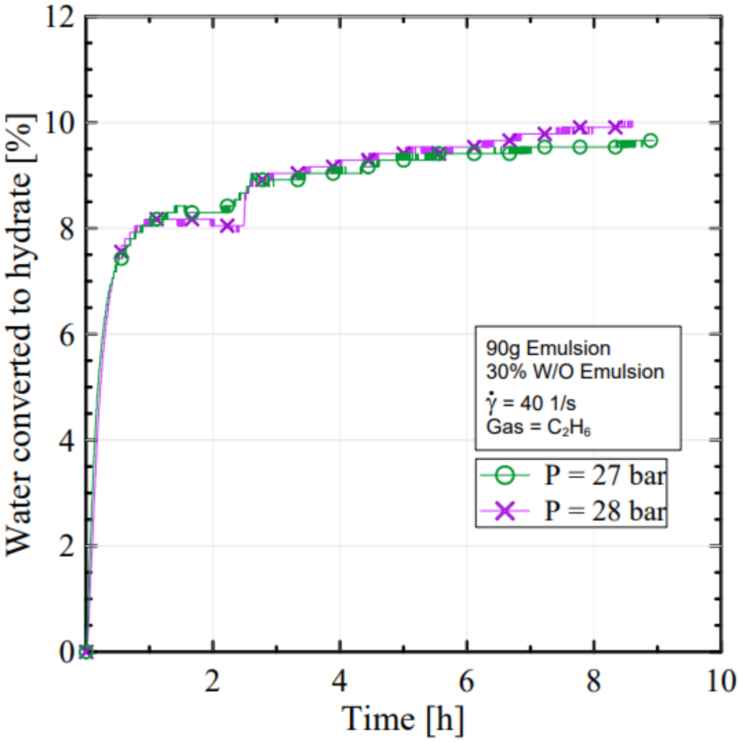

Figure 5. Water converted to hydrate as a function of time.

Figure 5 shows that both curves are very similar independent of the pressure used for hydrates formation. In this case for 27 and 28 bar. Notwithstanding, the experiment conducted with pressure of 28 bar attained a higher viscosity level during hydrate formation in comparison to the test conducted with pressure of 27 bar (see Figure 4). It is to say, despite the viscosity curves show a large discrepancy in the steady state regime, it seems that the same amount of water was converted into hydrates. Therefore, the difference in viscosity would be due to a more agglomerated structure at higher pressures.

5. FINAL REMARKS

This study brings information about the subcooling degree influence on the kinetics of ethane hydrates formation. The experiments were conducted in an assemble composed by a high-pressure system, a stress-controlled rheometer, and a syringe pump. Hydrate formation is detected by a random abrupt increase in viscosity and a significant decrease in pressure. It has been observed that when certain subcooling degrees are achieved, the maximum torque value allowed by the rheometer is attained and the experiment must be stopped. The induction time seems to be also dependent of the subcooling degree since the induction time decreases with increasing the subcooling. Despite the ethane hydrates viscosity curves show different behavior whit the increment of 1 bar in pressure, the amount of water converted into hydrates seems to be the same.

6. ACKNOWLEDGEMENTS

These experiments and this research were only possible due to the contribution of Petrobras S.A, FAPERJ, Brazilian Research Foundation (CNPq) and Brazilian Graduate Education Foundation (CAPES).

7. REFERENCES

Anklam M., York J., Helmerich L.; Effects of antiagglomerants on the interactions between hydrate particles. Elsevier, 2008, 23, 2118-2121.

Brown, E. P., Turner D., Grasso G., Koh C. A.; Effect of wax/anti-agglomerant interaction on hydrate depositing systems. Elsevier Fuel 264 (2020) 116573.

Camargo, R. M. T.; Gonçalves, M. A. L.; Montesanti, J. R. T.; Cardoso, C. A. B. R.; Minami, K. A perspective view of flow assurance in deepwater fields in Brazil. Proceedings of the Offshore Technology Conference; Houston, TX, May 3−6, 2004.

Carroll, J.J. Natural Gas Hydrates: a Guide for Engineers. Elsevier Science. 286p. 2003.

Gao S. Hydrate risk management at high watercuts with anti-agglomerant hydrate inhibitors. Energy Fuels 2009;23(4):2118–21.

Karanjkar, P. U.; Ahuja, A.; Zylyftari, G.; Lee, J. W.; Morris, J. F.; Rheology of cyclopentane hydrate slurry in a model oil-continuous emulsion. Rheol Acta (2016) 55:235-243.

Notz, P. K., Bumgardner, S. B., Schaneman, B. D., Todd, J. L., 1996. Application of Kinetc Inhibitors to Gas Hydrate Problems. Offshore Tecnology Conference, Houston, Texa, EUA.

Sandoval, G. A. B.; Soares E. J.; Thompson R. L.; Siqueira R. N.; De Andrade R. M.; Campos F.; Teixeira A.; Analysis of CO2 Hydrates in Crude Oils from a Rheological Point of View. Energy and Fuels 2018, 32, 2733−274.

Sandoval, G. A. B., Rebello, A. C. G. A., Naccache, M. F., Mendes, P. R. D. S., Teixeira, A., Valim, L., Rheological study of ethane gas hydrates through a high-pressure cell. Brazilian Congress of Thermal Sciences and Engineering, 2020.

Sloan, E. D., Koh, C. A., Sum, A., 2011. Natural gas hydrates in flow assurance. Gulf Professional Publishing.

Sum, A. K.; Koh, C. A.; Sloan, E. D.; Clathrate Hydrates: From Laboratory Science to Engineering Practice. Industrial and Engineering Chemistry Research, 2009, 48,7457−7465.

Sum, A. K.; Koh, C. A.; Sloan, E. D. Developing a Comprehensive Understanding and Model of Hydrate in Multiphase Flow: From Laboratory Measurements to Field Applications. Energy Fuels 2012, 26, 4046−4052.

Webb, E. B.; Koh, C. A.; Liberatore M. W.; High Pressure Rheology of Hydrate Slurries Formed from Water-in-Mineral Oil Emulsions. Industrial and Engineering Chemistry Research, 2014, 53, 6998-7007.

8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.