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RHEOLOGICAL STUDY OF GAS HYDRATES FORMED FROM CARBON DIOXIDE MOLECULES

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Abstract. *Hydrate concern have been the focus of attention in offshore oil production since the conditions for its formation are found in the deep subsea flowlines. Several works have been realized to understand this phenomenon and try to prevent and control it, but nowadays mechanisms related to its formation (nucleation including subcooling processes, growth) and decomposition are still not well understood. In this study, a high pressure cell is used to analyse rheologically the gas hydrate formation from water-in-crude oil emulsions. The viscosity behaviour of the hydrate slurry is measured during the dissolution, formation and dissociation. When hydrate is formed the hydrate slurry viscosity increases abruptly with time and the pressure decreases as a consequence of the gas consumption. Finally, it is shown how the subcooling degree influences the induction time under certain conditions.*

Keywords: *Gas hydrates, Water-in-Oil Emulsions, Pressure Cell, Carbon dioxide*

1. INTRODUCTION

Natural gas hydrates are crystalline solids composed of water and gas. They are formed when the water hydrogen bonded (host) encaged and hold one or more gas molecules (guests) if typical thermodynamic conditions of high pressure and low temperature is attained. As reported by Sloan (2003) and Makogon (2010), natural gas hydrates have several applications in different areas, as: Energy recovery, climate change, transportation of gas and flow assurance. The latter issue is the most problematic phenomenon present in the oil and gas industry (Sum *et al.*, 2009). Due to solid crystalline structure of gas hydrates, they are substances that do not flow. This situation must be considered when drilling and extracting oil and gas, or during well maintenance when the passage of oil has to be stopped, because the formation of hydrates plug flow lines causing expensive production shutdowns sometimes for as long as months, while the hydrates are dissociated. The oil industry would like to maintain production processes outside the gas hydrate-formation stable range. However the usual temperature conditions in ultra-deep waters, associated with high pressures from the economic production demands are into the hydrate formation region (Sloan, 2003). The strategy usually taken by the oil industry is to continue working in the thermodynamically favorable range to stability of the crystalline structure of solid hydrate with add of thermodynamic inhibitors (TIs) and LDHIs (low-dosage hydrate inhibitors). TIs such as methanol, glycol and saline solutions act changing the hydrate equilibrium curve. That is to say, the equilibrium temperature of hydrate formation is reduced for a certain pressure, shifting the chemical potential of water. By the other hand, LHDIs affect the kinetics of the process, since they delay the crystal growth and avoid the agglomeration, what makes them time dependent. Different proposed mechanisms of inhibition are presented by Kakati *et al.* (2016) and by Sun and Firoozabadi (2015). In the literature, most of the rheology studies have been applied to the oil industry or refrigeration. Some of them have been conducted in experimental loops (Andersson and Gudmundsson, 2000; Sinquin *et al.*, 2004; Delahaye *et al.*, 2008) and with the aid of high pressure rheometers, as the published by Camargo *et al.* (2000); Rensing *et al.* (2008); Webb *et al.* (2012, 2013, 2014). However, the majority of rheology studies concerned with hydrate slurries has been realized with

liquid hydrate former such as cyclopentane and tetrahydrofuran at atmospheric conditions, see Leopércio *et al.* (2016); Ahuja *et al.* (2015); Peixinho *et al.* (2010). This allows the study of hydrate formation processes without the added experimental difficulties of dealing with elevated pressure.
The goal of the present work is to rheologically analyze the gas hydrate formation in a rheometric geometry, through a pressure cell. With this device, it is possible to study the emulsion under low, medium and high pressures and several temperatures.

2. EXPERIMENTAL PROCEDURE

A high pressure system was utilized to supply the gas volume and pressure to make a live crude oil, that is, with light hydrocarbons. The system, illustrated in Fig. 1 is composed by the gas storage cylinder where pressurized CO_2 (guest molecule use in this study) come out until a booster, equipment that allows increasing above of 400 bar the initial pressure established in the cylinders. Depending of the experimental pressure studied, sometimes the booster is not required. After that, the pressurized gas is conducted to a serpentine pipe configuration to guarantee a constant rate of gas volume in the pressure cell. The maximum volume provides is 712 ml and the admissible pressure of the cell is 420 bar at 80 ^oC. The experimental pressure is controlled and setting up in a regulating valve before entering to a measure cell. The diameter of stainless steel pipes are of 6.35 mm (1/4 in). When the experiments have finished, the gas inlet valve of the pressure cell and the regulating valve are closed and the remaining gas in the duct is released through a relief valve. The

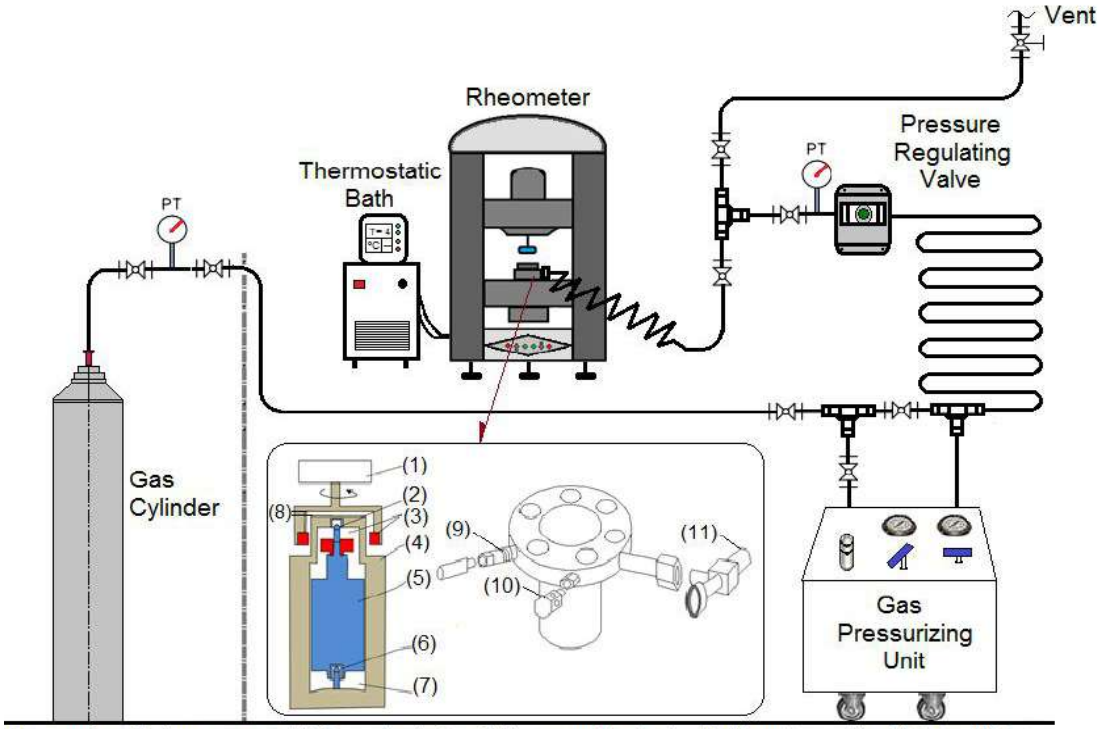

Figure 1. High pressure system using in the experiments

measurements were made with a commercial rheometer Haake Mars II, manufactured by Thermo Scientific, Germany. The geometry used is a concentric cylinders PZ35 for pressure cell, as illustrated in the Fig. 2. The device consists of two parts. The outer part, which is composed by the cylinder base of the pressure cell and the magnetic coupling, and by the measuring geometry (rotor), which is supported by two sapphire bearings, located at top and bottom within the pressure cell. The rotor drive is done by the magnetic field created by the two magnets, indicated in red in the Fig. 2. The inner magnet is located at the top of the measuring geometry, while the external magnet is coupled to the measuring head of the rheometer. The shaft of the rheometer is conducted with compressed air supplied by an oil-free compressor. The air is used to lubricate the bearings of the measuring head, allowing it to rotate with minimum friction. The sample temperature control is done through a thermostatic bath type Thermo Haake Phoenix II P1-C50P model, also provided by Thermo Scientific. All experiments are automatically controlled and the results are extracted with the aid of HAAKE RheoWin program. The amount of sample used for each test is 50 ml, which is deposited between the rotor and the inner wall of the pressure cell. Our waxy crude oil extracted from the (presalt) well was supplied by the Brazilian Oil Company (Petrobras). Initially with 10% of water, it was dehydrated by the gravitational method of the volumetric flask.

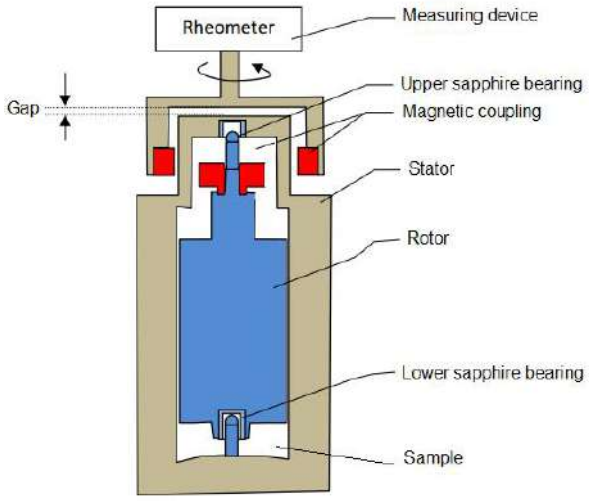

Figure 2. Geometry PZ35 for Pressure Cell

The residual water content was then measured by Karl Fischer titration technique indicating 0.3%. This dehydrated oil is used as a reference for all our experiments. The emulsions were prepared rigorously following the procedure described below: Initially the oil and deionized water were heated to 80 ^{o}C in closed bottles for 1h. After that, the samples were cooled down spontaneously at the room temperature. Finally, when the samples reached the ambient temperature, they were mixed manually, and subsequently, for 3 minutes at 10000 rpm in a CAT X360 homogenizer to obtain the emulsion. Before deposited the prepared sample in the geometry of the pressure cell, it was stirred again manually for 3 minutes. The emulsion was pressurized with CO_2 using the high-pressure system explained above. In an attempt to fully saturate the oil phase with CO_2, the pressure cell was heated up to 80 ^{o}C. This temperature was retained for 8 h, keeping the rotor of the pressure cell at constant angular velocity. Next, the pressure cell was cooled until 4 ^{o}C, the working temperature. The great majority of the tests was conducted at constant temperature, pressure and rotor angular velocity. Specifically, the pressure and temperature were, respectively, fixed at 60 bar and 4 ^{o}C.

3. RESULTS AND DISCUSSION

Before performing a hydrate formation experiment, is necessary calibrate and validate the pressure cell as a rheometric geometry. The first step to calibrate de geometry and pressure cell used in the experiments is to determine the optimal gap between the outer magnet and the cover of the stator. Then, the torque is analyzed as a function of the angular velocity for standard Newtonian fluids as well as a water-in-oil emulsion of 30%, a water volume fraction typically used in the hydrate formation tests in this study. The results are shown in Fig. 3 for a concentric cylinders geometry. As it can be observed, the measured points for the soybean oil (Newtonian fluid) are very similar for the different gaps studied. The same occurs for the emulsion. The torque obtained for the emulsion is higher than the other oils due to its high viscosity, measured at 4 ^{o}C, temperature at which hydrates are formed. An intermediary gap of 2.9 mm was selected to realize the experiments, since this gap helps to levitate the rotor between the sapphire bearings. If the gap is greater than 5 mm, the magnetic field is weakened and the outer magnet does not manage to drive the rotor. On the other hand, if the gap is very small, there can be some interference among the pieces, caused by condensed water droplets, for example. Once the optimal gap is determined by means of the previous test, see Fig. 3, the same curve is used to compute the friction correction parameters. This is realized using a linear curve fit model in the Rheowin data program. From the fitting model are obtained three parameters which must be manually filled in the geometry dialog box. By means of these parameters, the program discounts from the original measured torque the value of the friction fraction between the sapphire bearings and the rotor. This calibration is carefully performed following the instruction manual of the pressure cell given by the provider company. In the present research, the calibration is realized frequently for each material studied at the test temperature. Fig. 4 shows the viscosity function measured in the rheometer for the soybean oil with and without friction factor calibration and compared with a referential value obtained in a Canon Fensk viscometer. We can notice that the results obtained when the friction factor correction is applied are closer to the values measured by the Cannon-Fenske viscometer, what justifies the importance of the calibration.

Fig. 5 shows the hydrate slurry viscosity behaviour and pressure profile with respect to time during the temperature variation for a water-in-oil emulsion. The shear rate of 200 s^{-1} is constant throughout the experiment. In this specific test the pressure cell valve was closed after the cooling. At the initial of the test, in the dissolution stage the measured

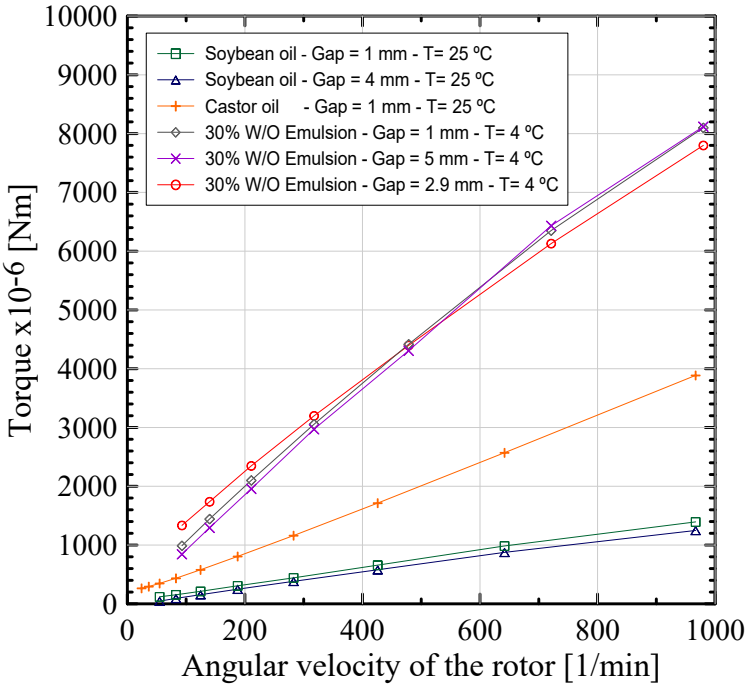

Figure 3. Influenced of the gap in the measurement torque.

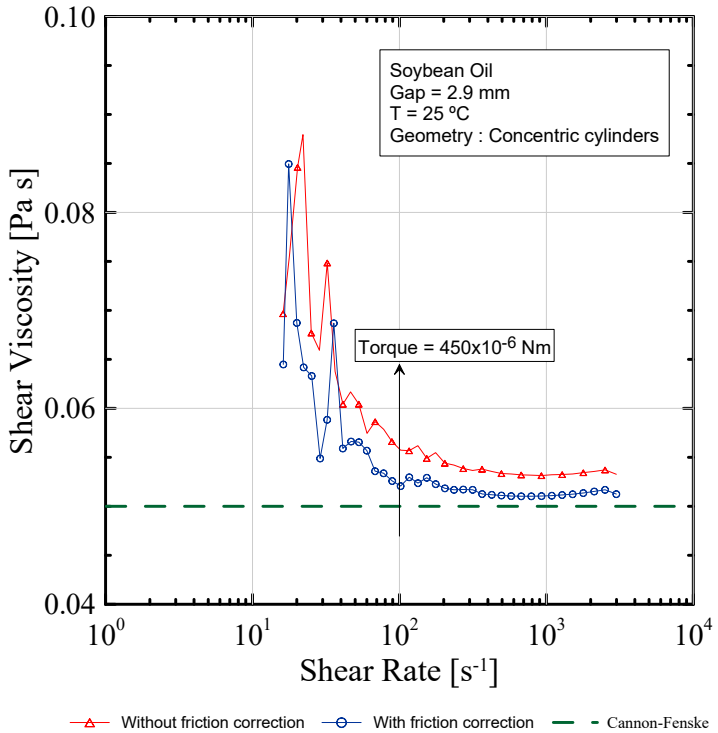

Figure 4. Comparison between viscosity values of soybean oil obtained in the rheometer with and without friction correction and with Canon Fensk viscometer.

viscosity data have most dispersion that in the other stages, that is because the torque required to keep the specific shear rate is very small, close to the lower measuring window of the rotor (PZ35b). The small values of viscosity $(6.8 \pm 2mPa)$ in this period of dissolution are due to the imposed thermodynamic conditions, which are selected taken into account the field operations. After dissolution time, the temperature begins to reduce producing the subsequently viscosity augment, this increment is most notably when the sample temperature cross the equilibrium temperature, which for our experiments conditions is 9 ^{o}C, at pressure of 60 bar. When the temperature of 4 ^{o}C is reached, the material viscosity remain in the value attained for a certain time, this time known as induction time is function of the shear rate, among other variables, and is the time taken for hydrates to be detected macroscopically (Sloan Jr and Koh, 2008). In this time the hydrate

does not form because the metastability. After the induction time, hydrate growth occurred, and then is observed a rapid increased with time in the viscosity, since solid structures are formed, probably with aggregation between them. When the maximum spike in viscosity is attained, the material structure begins to break down and consequently the viscosity decreases with time. Other possible explanation of the decrease viscosity is the disaggregation, since the viscosity only reduce 0.02 Pa.s during 60 h of experiment. Is hypothesized that the viscosity behaviour during the experiment is related to competitively forces between shear forces created by the rheometer through the rheometric geometry and the structure forces associate to the material, responsible to cause the particle aggregation. One way to confirm the hydrate formation is monitoring the pressure behaviour in the cell during the test, which decreases due to gas consumption as observe on the right of the Fig. 5. In the dissolution process and during the cooling, gas also is consumed, but is not observed because the cell valve is open to keep the pressure in the cell constant. Due that the hydrate formation is an exothermic process, the temperature in the cell must be increase, but is not possible to observe that behaviour in our cell, since the temperature is measured in the jacket located at the base of the rheometer, instead of in the fluid, and the jacket temperature remains constant by the thermostatic bath.

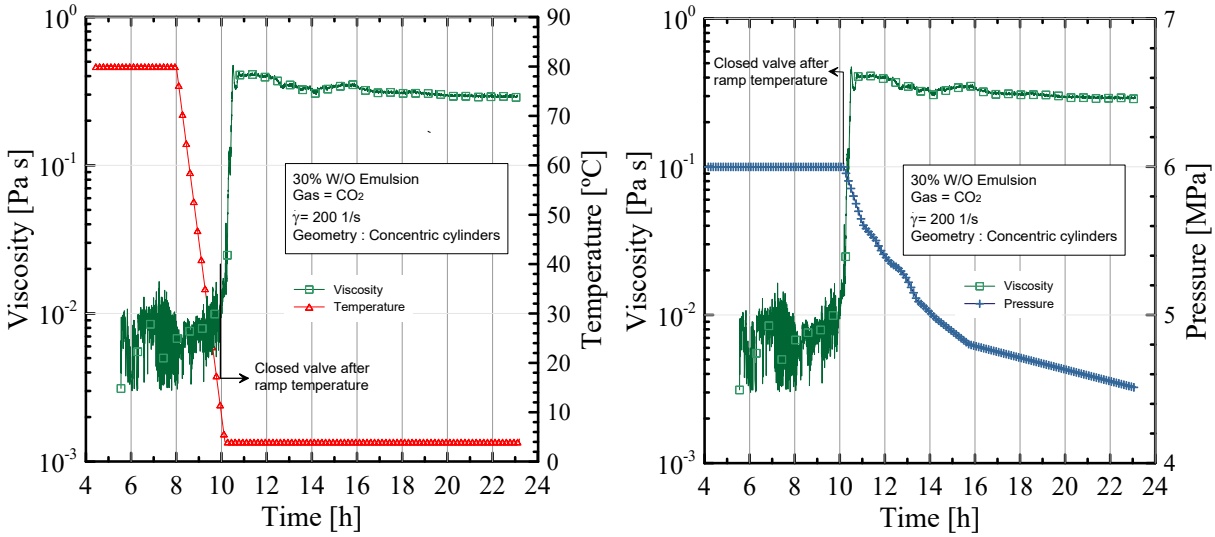

Figure 5. Viscosity and pressure behaviour during hydrate formation for a W/O emulsion

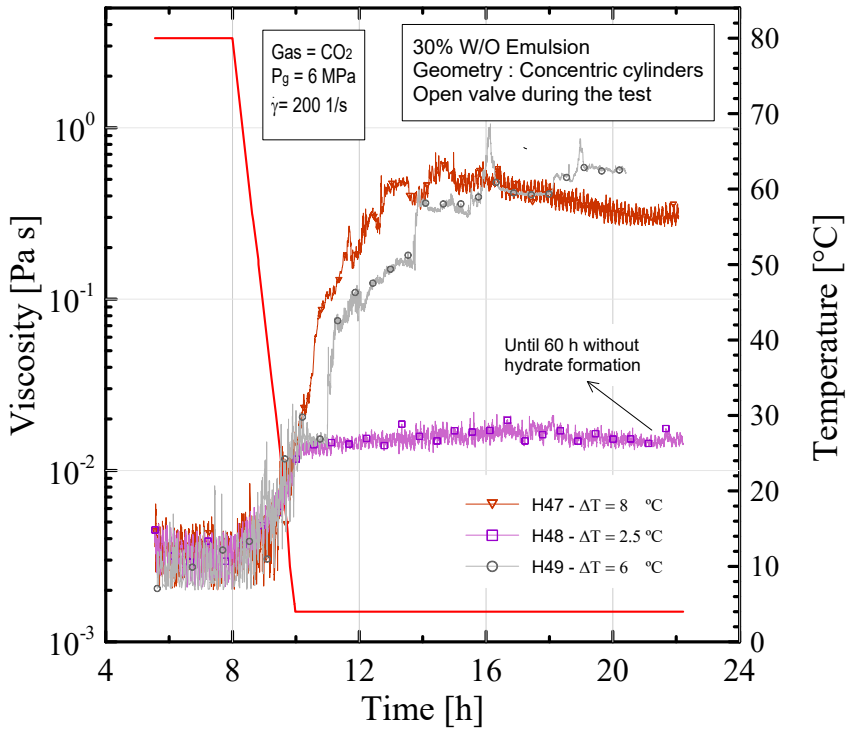

Figure 6. Hydrate slurries viscosity under different supercooling degrees

Fig. 6 shows the viscosity behaviour of a three different emulsions of 30%. In this case the pressure keeps constant throughout the experiment, that is to say, the cell valve remained open allowing the continuous injection of gas. The tests were conducted to analyze the influence of the supercooling on the phenomenon of hydrate formation. Supercooling (also known as subcooling) is defined as the difference between the system temperature and hydrate dissociation temperature at a given pressure (Tohidi *et al.*, 2012). The supercooling is directly related to the driving force of nucleation, which is defined as the difference between the chemical potentials of the old (aqueous water with dissolved gas) and new phase (hydrate). In fact, Arjmandi et al. (2005) noted that the subcooling could be used solely to represent the driving force for hydrate formation (Sloan Jr and Koh, 2008) above 20 MPa for a methane-water system. Fig. 6 depicts experiments with different subcooling degrees; 2.5, 6 and 8 ^{o}C and is observed how the hydrate formation is delayed when the subcooling degree is smaller. Indeed, for subcooling degree of 2.5 ^{o}C hydrate did not form after 60 h of test, in this test the viscosity remained constant over time at temperature of 4 ^{o}C. When the supercooling begins to increase the induction time was reduced. As noted, the time required for hydrate formation was about one hour for the test of 6 ^{o}C of subcooling, and for the test of 8 ^{o}C the hydrate growth starts as well as the temperature of 4 ^{o}C was reached (with any induction time). That is, bigger subcooling degrees, lower the induction time. Is important to note that the asymptotic viscosities attained when the hydrate is formed are very similar, close to 0.5 Pa s. As the induction time appears to be depending of several variables as: apparatus (surface area generated by the rheometric geometry, time and velocity of the sample agitation to prepare the emulsion), shear rate, foreign particles, gas consumption among others, the results obtained are restricted to the conditions employ in this experiments, however the curves shown to be reproducible.

4. CONCLUSIONS

The evolution of viscosity hydrate slurries has been analysed during induction, formation and dissociation processes in a rotational rheometer. Before executing the main tests, the rheometric geometry has been calibrated using a Newtonian fluid. Tests to determine the optimal gap between the external magnet and the cap of the stator also have been realized. The viscosity increases abruptly when the hydrate is formed and subsequently begins to decrease due to disaggregation or break down of the structures formed. Simultaneously of the drastic increase in viscosity, the pressure in the cell drops, which also indicates hydrate formation as observed in Fig. 5. As noted in Fig. 6 at higher supercooling degrees, the induction time becomes lower. However, this kind of result are aparatus and experimental procedure dependent.

5. ACKNOWLEDGEMENTS

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