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FORMATION AND PROPERTIES OF EMULSIONS IN HEAVY OIL PRODUCTION

Tálita Coffler Botti,
M. J. B. Moura,
M. S. Carvalho
Pontifícia Universidade Católica do Rio de Janeiro, Department of Mechanical Engineering
Rua Marquês de São Vicente, 225, Gávea - Rio de Janeiro, RJ – Brasil. CEP: 22451-900
talita@lmmp.mec.puc-rio.br; maria@lmmp.mec.puc-rio.br; msc@lmmp.mec.puc-rio.br

Abstract. *Emulsion formation is a challenge when transporting heavy crude oil. Due to high viscosity, electric submersible pumps (ESPs) at the wellhead have been used to improve production. ESPs provide high shear rates to the flow consequently contributing to increase the formation of emulsions. The main challenge is that these emulsions have higher effective viscosity, increasing the pressure drop and hindering the flow. This work investigated the formation of emulsions of a North Sea heavy crude oil and of a model oil (with added surfactant), with similar rheological properties, in a Stirred Tank under high shear rates. Several aspects of these emulsions were studied: the continuous phase of the emulsion for different oil/water concentrations, the effective water concentration of the emulsions formed, the droplet size distribution, and the coalescence rate of the emulsions. It was observed that the emulsions formed by both oil phases studied are water-in-oil emulsions. Also part of the water is not emulsified for water concentrations above 65%. This effect decreases the viscosity of mixture significantly and can improve the transport. Different from the model oil emulsions, the crude oil emulsions presented instability after days at rest. This study provides fundamental elements to better understand crude oil emulsion formation in rotating and high shear systems, such as ESPs.*

Keywords: *W/O emulsions, heavy crude oil, high shear system*

1. INTRODUCTION

Emulsions are fundamental to many different industries, such as food processing, pharmaceutical, cosmetics, and the petroleum industry. In the oil industry, initially the water and the crude oil phases are found separately, but due to turbulence, mixing, as well as agitation through downhole wellbore, surface chokes, valves, pumps and pipes, emulsions are formed (Fingas et al., 1993).

In general, there are three kinds of emulsions: oil-in-water emulsions (O/W), water-in-oil emulsions (W/O), and multiple emulsions (O/W/O or W/O/W). These emulsions are illustrated in Fig. 1.

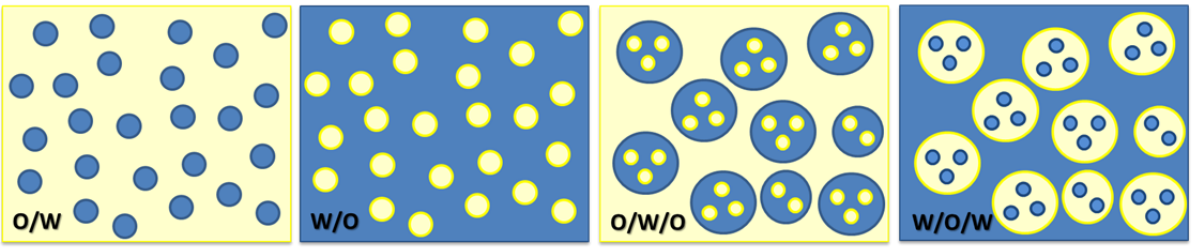

Figure 1. Illustration of the different types of emulsions that can be formed. From left to right: oil-in-water, water-in-oil, oil-in-water-in-oil, and water-in-oil-in-water.

Due to the high viscosity of heavy crude oils, electric submersible pumps (ESPs) at the wellhead have been used to improve transportation, and consequently production. In this system, the phases are subjected to high shear rates, and the water produced together with oil is emulsified. Heavy crude tends to form stable W/O emulsions (Rodionova et al., 2014), resulting in an increase in the viscosity of the mixture, making it even more difficult to transport. Fingas et al., (1993) reported that while the viscosity of an oil is on the order of a few cSt, the viscosity of a produced emulsion can reach about one hundred thousand cSt. As the water content of the emulsion increases its viscosity also increases. It is observed that, in general, at a certain water concentration the inversion of the emulsion occurs, leading to an abrupt decrease in the viscosity of the emulsion. This effect can improve the production.

In view of this scenario, a thorough characterization of heavy oil emulsions can provide valuable information about the formation and separation of these emulsions, which can help improve and predict transportation. Different techniques can be used to characterize an emulsion: droplet size distribution (DSD), stability tests, point-of-inversion tests, and others. Recent studies (Anisa et al., 2010, Rodionova et al., 2014) discuss that different parameters can influence the properties of crude oil emulsions, one of the most sensitive parameter being the DSD. If the DSD decreases due to the use of different rotation rates, the viscosity of emulsion will increase for the same oil phase and the same water content.

Model oils are formulated to mimic crude oils properties and can be used in several different applications (McLean et al., 1997, Mohammed et al., 1993, Rodionova et al., 2014):

- Tests where large volumes of fluid are required, such as pipeline tests;
- Imaging tests, because crudes are too dark for visualization;
- Tests to study different compositions of oils, for example a model oil, that mimics a crude, can have specific changes in the concentrations of asphaltenes, resins, and others to study the effect of each component independently;
- Laboratory tests, because of environmental and laboratory safety.

Rodionova et al., 2014 developed a model oil to mimic a North Sea heavy crude oil based on experimental data obtained from a rheometer. Their objective was modeling a separation profile of W/O emulsions, rheological properties, and pipeline flow behavior. For both oils they performed rheology tests, DSD measurements (via NMR and FBRM probe), emulsion stability tests, and pipeline flow tests. They observed a similar behavior for both oil phases. Their focus was on low shear rates (130-500 s^{-1}), because they studied laminar flow in pipelines.

In this work we study emulsions of the model oil proposed by Rodionova et al., 2014 produced in a Stirred Tank under high shear rates (17,732 and 30,145 s^{-1}), in an analogous environment to an ESP. Emulsions of a North Sea heavy crude oil were also investigated. Studies of stability of the emulsions, DSD (via FBRM probe), microscopic characterization of the emulsions, water concentration and point-of-inversion were performed. Two different rotations rates were tested to study the influence of the rotation rate on the emulsions´ characteristics. Developing a better understanding of how these emulsions are formed in rotating and high shear systems and their characteristics/properties is important to provide fundamental elements to realistic systems (ESPs), since experiments in real systems are complex and involve high costs.

2. EXPERIMENTAL PROCEDURE

The phases used were: model oil and sodium chloride solution 3.5% w/v. The model oil composition´s is (Rodionova et al., 2014): primol 352 mineral oil (98.5 wt%), polyisobutylene (Mw 500,000; Mn 200,000; Mv 420,000) (0.5 wt%), and hydrophobic nonionic surfactant SPAN 83 (1 wt%). The HBL of this surfactant is 3.7, suitable for obtaining W/O emulsions (Ushikubo et al., 2014), in agreement with the North Sea heavy crude oil emulsions. The measured kinematic viscosity of model and North Sea heavy crude oil is 43 and 36 mm^2/s, respectively, at 60°C. Tests with the North Sea heavy crude oil were also performed and compared with the model oil results.

The emulsions were prepared using an IKA ULTRA TURRAX T25 Basic rotor-stator mixer with the rotor head S25N – 18G – ST. The conditions of preparation were: constant temperature of 60°C (controlled through a water bath with a magnetic stirrer and hot plate) and 100 ml of total volume of fluids. Two rotation rates were tested: 8,000 and 13,600 rpm (shear rates of 17,732 and 30,145 s^{-1}). In general, mixing the fluids for 15 minutes was sufficient to reach a steady state, though in certain cases a longer period of time was required. The experimental set-up is shown in Fig. 2. The tests were performed for various water concentrations.

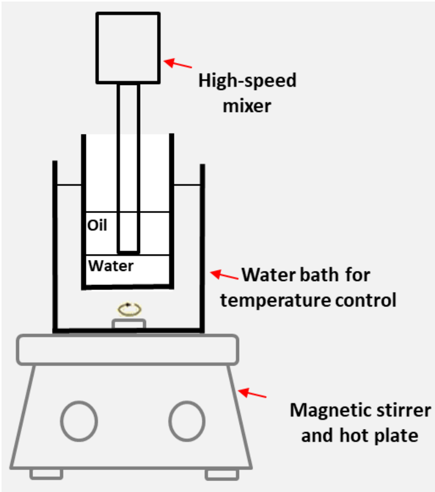

Figure 2. Experimental set-up: the water and the oil phases are mixed at a controlled temperature.

Different tests were performed to analyze the behavior of the emulsions. First, to identify which phase was the continuous phase the drop test and the conductivity test were performed for each water concentration. The drop test consists of putting a drop of emulsion in a recipient with each phase and observe in which phase the drop spreads. The conductivity of the samples was measured using a Oakton™ PC 700 pH/Conductivity Meter. Next, the effective water concentration of the emulsion was quantified by separating the amount of water that was not emulsified after the preparation. Finally, the DSD was determined by the focused beam reflectance method (FBRM) using a Particle Track G400 probe. The probe's lowest particle size limitation is of approximately 1 μm. These measurements were done after the preparation of the emulsion, using a magnetic stirrer to promote the motion of the sample. For the samples of water-in-oil emulsions we simply switched the mixer for the probe to perform the measurements. In the case where there was the appearance of free water, as will be explained in the next section, the free water was removed and then the DSD of the emulsion was measured.

Microscope images of the emulsions were also performed to compare with the FBRM probe measurements and to visualize the microstructures. An inverted microscope (Axiovert 40 MAT, Carl Zeiss) with different magnifications (10x and 20x) and the software AxioVision Rel. 4.9 (Carl Zeiss) were used to capture the images. As the emulsions prepared were too concentrated to allow the visualization of the droplets with the microscope they were diluted in a mineral oil with a lower viscosity than the oil phase, the EXXSOL D60 (1.81 mm^2/s at 25°C). The procedure consists of placing a drop of emulsion in a vial with EXXSOL D60 and mixing it manually to dilute it. In addition, the Petri dish used to make the images of the emulsions was treated hydrophobically. Because the water droplets are denser than the oil they tend to migrate to the bottom. This treatment avoids the water droplets in the emulsion to spread when they come in contact with the glass surface.

3. RESULTS AND DISCUSSION

3.1 Model Oil

The first experiments showed that these emulsions exhibit no inversion point, that is, the emulsions formed are always of W/O, independent of the water concentrations. However, at a critical water concentration not all the water phase is dispersed and a free water volume is observed. When this phenomenon occurs the viscosity of the solution decreases considerably during the mixing.

The experiment begins with 100% oil and water is added gradually in quotas of 10%, as shown in Fig. 3 (here the model oil is transparent and the water phase was colored red, for visualization purposes). It is observed that for a water concentration between 10-60% the water is completely emulsified, causing an increase of the effective viscosity of solution. At water concentrations between 60-70% an abrupt change in the color of the mixture is observed due to the appearance of free water in the system, as a consequence the effective viscosity of solution while stirring decreases significantly. When the mixer is turned off the free water immediately separates from the emulsion, as shown in the last image of Fig. 3. The results were similar for both rotation rates studied.

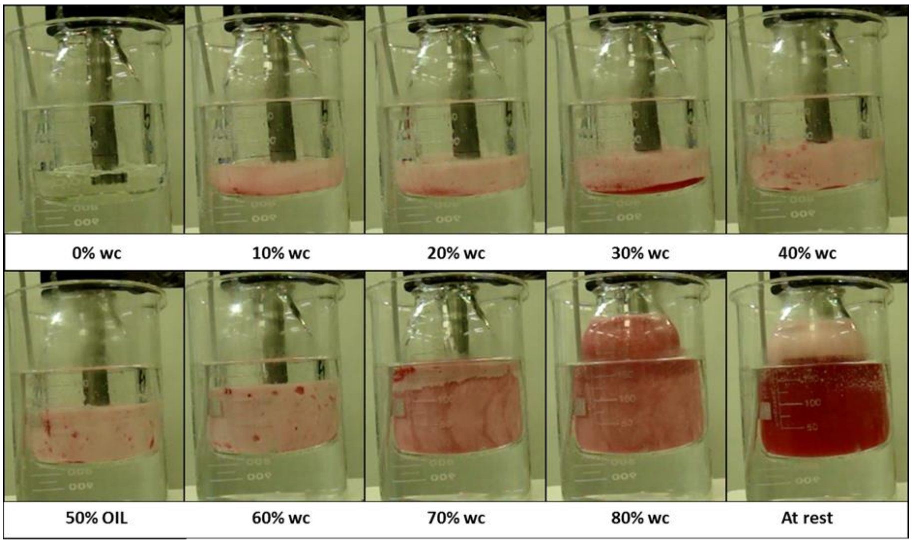

Figure 3. Increase of water concentration (wc), from 0% to 80%, for a rotation rate of 8,000 rpm. In this experiment the model oil is transparent and the water phase was colored red, for visualization purposes.

The water content in the W/O emulsions was calculated by subtracting the volume of water that was no emulsified from the total volume of water added in the mixture. Figure 4 shows that from 0 to 60% of initial water concentration, all water is emulsified for both rotation rates. Above 60% of initial water concentration a part of this water does not emulsify. The curves in Fig. 4 are an average over three experiments and the error bar is the standard deviation. Note that there is no significant difference between the emulsions produced at different rotation rates.

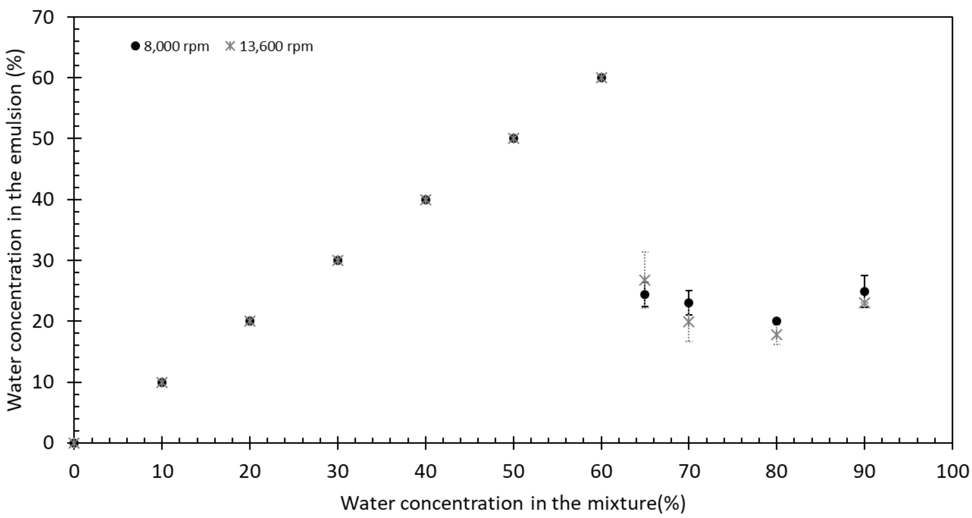

Figure 4. Graph of the final water concentration in the model oil emulsion versus the initial water concentration.

The stability of the emulsions was studied over a few days. The emulsions were prepared and left at rest in a graduated cylinder for 5 days at the temperature of preparation, 60°C. Figure 5 shows the results for the rotation rate of 8,000 rpm. Similar results were obtained for the higher rotation rate. No coalescence was observed for these samples. It is possible to see only gravitational segregation of the oil on the top of the cylinder, but the amount of water on the bottom remained constant.

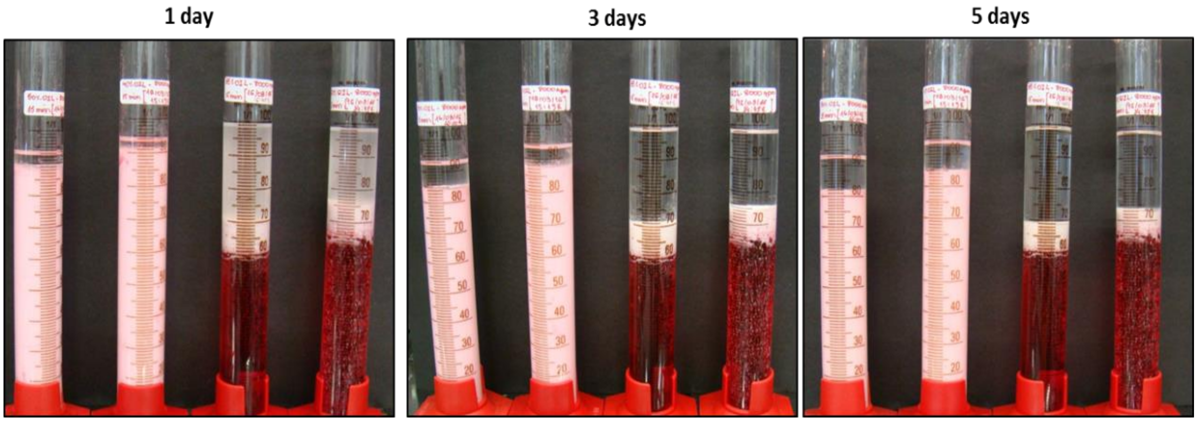

Figure 5. Model oil emulsions with different water concentrations: 50%, 60%, 65%, and 70% (from the left to the right). For this experiment the water phase was colored red and the model oil is transparent.

The droplet size distribution was obtained using the FBRM probe for different water phase volume percentages: 10%, 30%, 50%, and 70%. Note that the mixture with initial water concentration of 70% produces free water. For this case, the procedure was to separate the emulsion sample and then measure its DSD. It is important to note that the effective water concentration of this emulsion is around 20%, as shown in Fig. 4.

Figure 6(a) shows the DSD, obtained with the FBRM probe, for the rotation rate of 8,000 rpm. Each curve in the graphs represents an average over three experiments for each concentration. Initially, at a water content of 10% the DSD was dominated by small droplets, exhibiting mainly two peaks at ~1 and ~5 μm. As the water content was increased to 30% and then 50%, both peaks decreased and the number of drops with size between 10 and 100 μm increased. At a water content over 60% the appearance of free water occurred. Therefore, at 70% the effective water concentration in the emulsion decreased, which explains the similarity between curves of the emulsions with 70% and 10% water content. Fig. 6(b) shows that the DSD for the two rotation rates for a water concentration of 10% exhibit the same behavior. For each water concentration similar curves were observed for the two rotation rates.

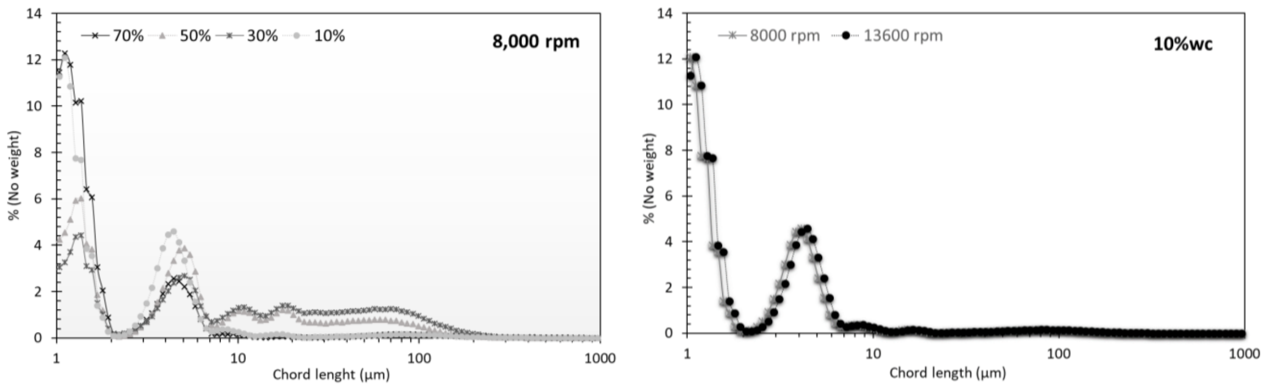

Figure 6. (a) Droplet size distribution (DSD) of model oil emulsions with water concentrations of 70%, 50%, 30% and 10%. The emulsions were prepared with a rotation rate of 8,000 rpm and 15 minutes of mixing time. (b) Comparison between the DSD of model oil emulsions with 10% water content (wc) prepared with two different rotation rates.

The microscope images in fact illustrate the FBRM probe and the previous tests results. Figure 7 shows microscope images of emulsions as the water concentration increases. Initially, with a low water concentration (10%), the emulsion is mostly populated with small drops. As the water concentration increases, the drops increase in size. As presented before between 60-65% of water content occurs the appearance of free water. Therefore, for water concentrations higher than 65% the droplet sizes decrease, as the effective water concentration in the emulsions decreases.

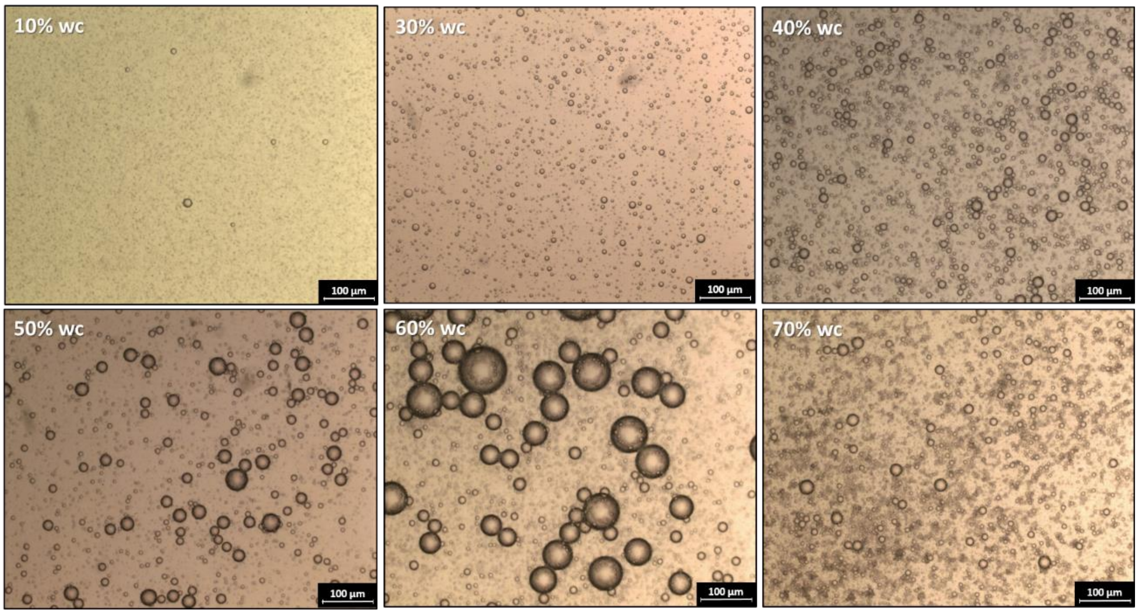

Figure 7. Microscope images of model oil emulsions with different water a water concentrations (wc), prepared at 13,600 rpm.

3.2 Crude Oil - Model Oil Comparison

A limited amount of crude oil was available for testing therefore tests were performed with the model oil to set up a methodology to analyze the North Sea heavy crude oil and to provide insight into the crude oil emulsions´ behavior under high shear systems, such as the Stirred Tank. For all experiments performed the results were similar for the model oil and the North Sea heavy crude oil. The range of water concentration at which the appearance of free water occurs is 60-65% for both oils. Because of the color of the crude oil it was not possible to obtain images of the water and oil mixing process similar to Fig. 3. The drop test and the conductivity test verified that the North Sea heavy crude oil emulsions are W/O emulsions, same as the model oil.

An important difference observed for the two oils was the stability of the emulsions over days. For the North Sea heavy crude oil emulsions coalescence was observed after a few days of rest (at the preparation temperature of 60°C). The image on the right of Figure 8 shows the increase in the amount of water on the bottom of the cylinder over a period of three days. On the other hand, coalescence was not observed in the model oil emulsions, as shown in the image on the left of Figure 8. This behavior was observed for every water concentration studied, Figure 8 just shows two examples of emulsions of two different water concentrations.

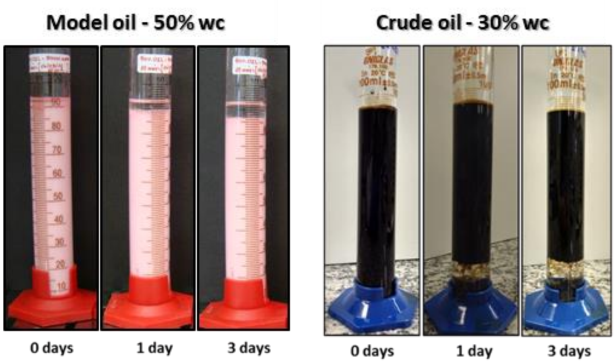

Figure 8. Stability test: on the left, emulsions with the model oil (transparent) and the water phase (colored red). On the right, emulsions with the North Sea heavy crude (black) and the water phase (transparent). The emulsions were prepared with 13,600 rpm and 15 minutes of mixture. They were left at rest for 3 days at 60°C to observe coalescence.

To study short term coalescence, which could influence the DSD measurements, images of North Sea heavy crude oil emulsions were taken over the period one hour, Figure 9. For this test a sample was left on the microscope and a sequence of photos were taken at multiple time intervals. Over a period of time of one hour no significant coalescence was observed. Hence, the instability of the North Sea heavy crude oil emulsions was observed only over a long period of time, not influencing the short-term morphological characterization of the emulsions.

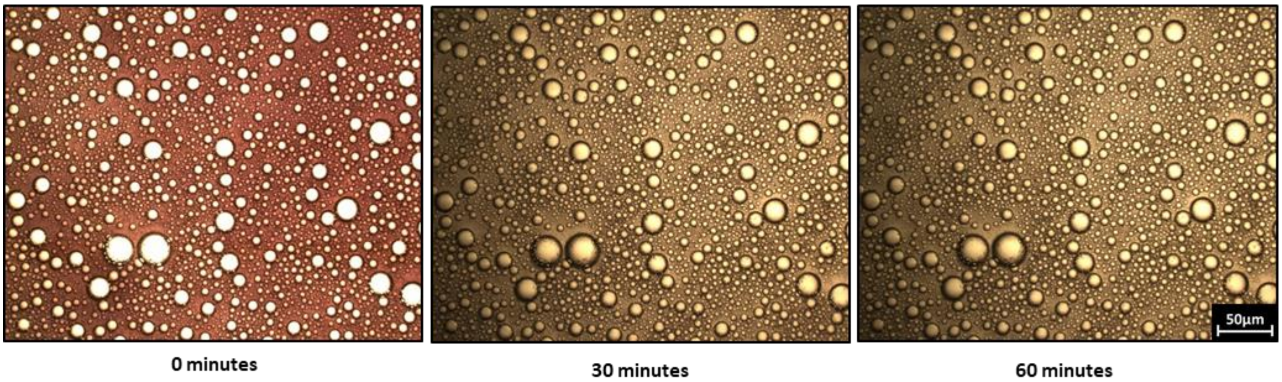

Figure 9. Short-term stability test of North Sea heavy crude oil emulsion with microscope images. The emulsion sample was prepared with 50% water content, at 13,600 rpm, and mixed for 30 minutes.

Figure 10 shows the DSD obtained with the FBRM probe for three different water concentrations and the same rotation rate. Due to the limited amount of the North Sea heavy crude oil only one experiment for each water concentration was performed. For the lowest water content, 10%, it is possible to observe two peaks in the region between 1-10 µm and almost no drops with size larger than 10 µm. As the water concentration increased the amount of small droplets decreased. At the water content of 50% the two peaks decreased significantly and many more drops with size larger than 10 µm appeared.

Figure 11 shows a comparison between the DSD curves of the model oil and the North Sea heavy crude oil emulsions for two different water contents and same rotation rate. At 10% water content both oil phases exhibit two peaks and most chord lengths smaller than 10 µm. At 50% water content a wider distribution of chord lengths is observed as a result of an increase in drop size. As a whole both oil phases presented similar DSD distributions for each water content.

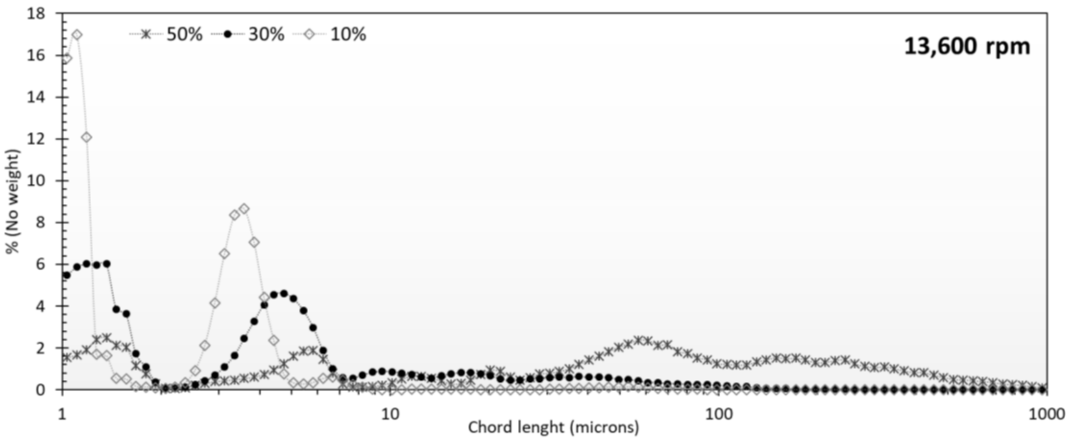

Figure 10. DSD of North Sea heavy crude oil emulsions with water concentrations of 50%, 30% and 10%. The emulsions were prepared with a rotation rate of 13,600 rpm and 15 minutes of mixing time.

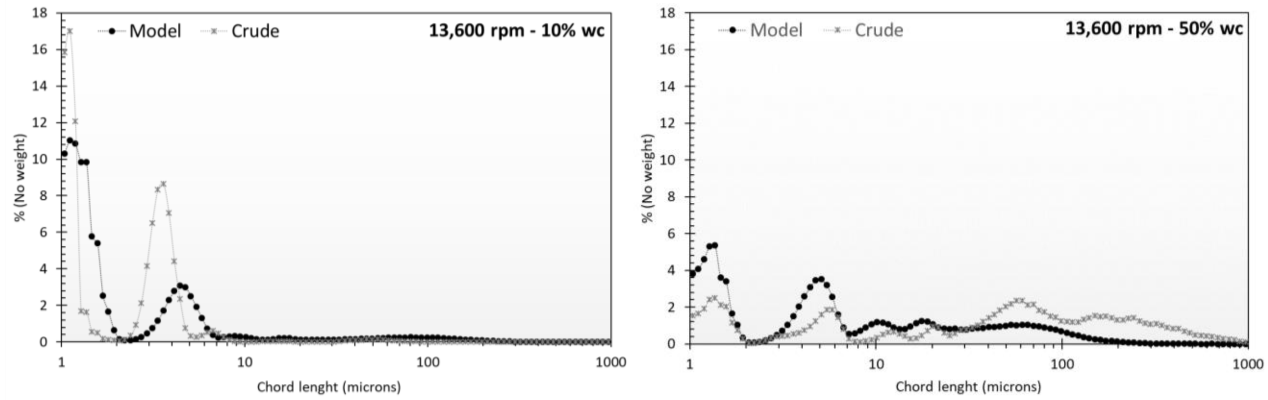

Figure 11. Comparison between the DSD of the model oil and the North Sea heavy crude oil emulsions. On the left emulsions with 10% water content (wc) and on the right with 50% wc. The emulsions were prepared with a rotation rate of 13,600 rpm and 15 minutes of mixing time.

4. CONCLUSIONS

Emulsions of a North Sea heavy crude oil and of a model oil (Rodionova et al., 2014) with similar rheological properties were produced in a Stirred Tank under high shear rates (17,732 and 30,145 s^{-1}). These emulsions were studied through several tests: water concentration, droplet size distribution, stability of the emulsions, and microscopic characterization. Similar results were obtained for both oil phases. It was observed that the emulsions formed with the model and the crude oil are always of water-in-oil, independent of the initial water/oil concentration. For both oil phases, at a water concentration between 60-65% there is an abrupt decrease in the solution's viscosity, due to the appearance of free water in the system. The droplet size distribution analysis shows that as the water concentration increases the number of small drops decreases for both oil phases, up to the water concentration at which the appearance of free water occurs. Above this water concentration, when the free water is separated, the water concentration of the formed emulsions was not higher than 30%, a fact that explains the decrease in the drop size. Microscope images confirmed these results and showed a large population of small droplets (<10 µm in size). No significant difference was observed between the emulsions produced with two different rotation rates, 8,000 and 13,600 rpms, for all the tests performed for both oil phases. One significant difference was observed between the emulsions of the two oil phases: the model oil emulsions are stable over a few days at rest, while the North Sea heavy crude oil emulsions exhibit coalescence.

The tests with the model oil were essential to set up a methodology to analyze the crude oil and to provide insight into the crude oil emulsions´ behavior under high shear systems, such as the Stirred Tank. It is interesting that the emulsions formed by the model and the North Sea heavy crude oils exhibit no inversion point. Rather, they are always water-in-oil emulsions independent of the water concentration. The appearance of free water is particularly interesting for industrial applications, because that decreases the viscosity of the mixture, making it easier for electric submersible pumps (ESPs) to transport the crude oil.

5. ACKNOWLEDGMENTS

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