YIELD STRESS IN WAXY CRUDE OIL EMULSIONS

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Abstract: *Waxy crude oil is a very complex non-Newtonian material, which exhibits time-dependence related to viscoelasticity and thixotropy. In addition, such material is rather dependent to the temperature history, which turns the measurements of the rheological properties rather difficult. The waxy appears when the oil is subjected to low temperatures, which is typical in oil recovery off shore in deep waters. The flocks of waxy can agglomerate and block pipelines. In fact, such a phenomenon is one of the most dramatic problem in the petroleum industry. Up to now, many works were concerned about dry waxy crude oil, but a very few considered the problem of waxy crude oil emulsion gels and this is the focus of our work. By aid of a rotational rheometer, we conducted a great number of tests to obtain the flow curve, highlighting the static and dynamic yield-stress for a range of concentration of water. We also investigated the effect of the drop size and its distribution in the emulsion.*
Keywords: *Emulsion, Yield-stress, Waxy Cude Oil*

1. INTRODUCTION

The waxy crude oil when submitted to low temperatures gets elasto-visco-plastic thixotropic behaviour. This type of oil is typically found in reservoirs located in ultra-deep water and they are composed by a complex mixture of hydrocarbons. The paraffins are formed mainly due the differences in the temperature at which the oil is subjected. At the time of extraction, the oil leaves the well at a temperature range of $60\,^{\circ}\mathrm{C}$ to $100\,^{\circ}\mathrm{C}$ and when it reaches the well head at the sea bottom, where the temperature achieved is typically $4\,^{\circ}\mathrm{C}$, the wax crude oil is subjected to a cooling process that accelerates the deposition of paraffins at the pipeline well. In fact, such a phenomenon is one of the most dramatic problems in the petroleum industry. A reliable measurement of yield stress is very important and difficult, since this value is highly influenced by shear history, temperature history and the composition of the waxy crude oils as reported by (Kané *et al.* (2004), Moller *et al.* (2006) and Wardhaugh and Boger (1991)).

There are several works that reported the study of this issue, since an appropriate measure of the yield stress is very important to determine the point at which the paraffin structure breaks and flow. For detailed understanding see: Dimitriou *et al.* (2011), Marchesini *et al.* (2012), Dimitriou and McKinley (2014) and Tarcha *et al.* (2015). The authors explained the different parameters that is important to take into account the yield-stress, as: the previous shear flow, the initial cooling temperatures of the oil and the environment, the thermal conductivities of the fluids and the solid materials involved, and the temperature dependence of the parameters that control the kinetics of gelation.

Normally, the oil has a Newtonian behavior from the reservoir until the platform. After a few hours off production, the fluid characteristics is completely modified, because there is a formation of a network of crystal structures composed of solidified paraffin (See Figure 1.). The final structure is directly dependent on the cooling rate experienced. Some typical compounds of the oil, as resins and asphaltenes, also influence the process of formation of the crystalline network, changing the crystallized material, as pointed out by Venkatesan *et al.* (2005) and Soares *et al.* (2013).

Very few papers have been studied the rheology of emulsified paraffinic oil near and / or below the gelation temperature. The gelation temperature is higher in emulsion that contains more water. Moreover, the structure of these oils is modified to decrease the mobility of the material resulting from cooling below the gelation point with the increase of the percentage of water volume. That is, emulsified paraffinic oils with higher water content tend to have higher viscosity, higher yield stress, as reported by Rensing *et al.* (2011), and a high level of elasticity (measured by the storage modulus in oscillatory tests), according to Sun *et al.* (2014). It is worth noting that it is often registered that the material acquires a strongly pseudoplastic character with increasing percentage of water (de Oliveira *et al.* (2010)) and the emulsion rheology in gelled paraffinic oils is more pronounced at high levels of water volume (Visintin *et al.* (2008)). In other words, the differences in the rheology are smaller when it is increased the water percentage of 10% to 20% than when this percentage is increased from 60% to 70%.

Figure 1: **Formation of gelated structure.**

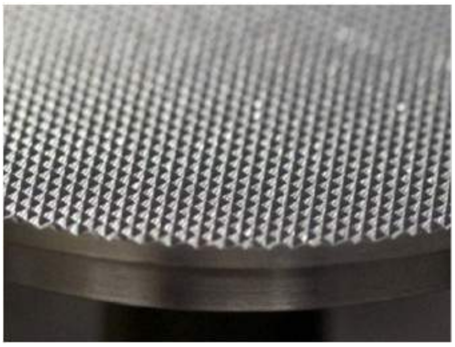

Figure 2: **Details of the serrated parallel plate geometry.**

2. EXPERIMENTAL PROCEDURE

2.1 Emulsion Preparation

The oil used was supplied by PETROBRAS Company. Initially it contained 16% of water. By the gravitational dehydration method, the water was partially removed from the oil. We used the Karl Fischer titration technique to take into account the residual water, which was around 0.3%.

The emulsions were prepared rigorously following the procedure described below: Initially the oil and the formation water were heated to $80\,^{\circ}\mathrm{C}$ in closed bottles for 1 hour. Then, the samples were cooled down spontaneously at the room temperature. When the samples reached the ambient temperature, they were mixed manually, and next, with a blender, keeping its velocity in 10.000 rpm to obtain the final emulsion. Finally, the sample was shaken manually for 3 minutes and deposited in the plate geometry to start the test.

2.2 Equipment and methodology

We used a commercial rheometer with stress control, model Haake Mars III. The temperature was controlled by a Peltier thermostatic bath, in which a precise temperature control is possible. In fact, any change in temperature can be obtained in few seconds. All the tests were performed using a 35-mm-diameter parallel-plate geometry with a gap of 0.5 mm and serrated surface (see Fig. 2) to avoid wall slip (Dimitriou et al.2011). The gap used for this work was 0.5 mm (the same used in Tarcha *et al.* (2015)) and the sample was thermally insulated during the tests, by aiding of a cover.

The necessary volume of oil for each test was 0.5 ml. As recommended by Tarcha *et al.* (2015), we carefully followed three steps at the beginning of each experiment to certify the sample homogenization. 1) the agitation of the bottle for three minutes; 2) the immediate sample collection; 3) the insertion of the sample in the rheometer.

In all tests, the sample was heated from $25\,^{\circ}\mathrm{C}$ until $80\,^{\circ}\mathrm{C}$, temperature in which is not expected to have more crystals of paraffin. As the dissolution process is not instantaneous, the sample was kept for 20 min at $80\,^{\circ}\mathrm{C}$ before starting the cooling process.The cooling rate was $0.6\,^{\circ}\mathrm{C}$/min, the same used by Tarcha *et al.* (2015). After reaching $4\,^{\circ}\mathrm{C}$, the sample was kept at that temperature sufficient time to precipitate the wax crystals in the oil and forming the gelled structure.

3. RESULTS AND DISCUSSION

A large number of tests was conducted to obtain reliable results. Figure3 shows the deposition time of the paraffin crystals. The test was conducted at a constant strain rate ($\dot{\gamma} = 500\mathrm{s}^{-1}$), for a emulsion with 10% of w/o and the temperature ranging between $60\,^{\circ}\mathrm{C}$ and $4\,^{\circ}\mathrm{C}$. It can be seen a clear change in the tendency when the temperature is around $20\,^{\circ}\mathrm{C}$, which suggests of the presence of paraffin crystals.

Figure 4 shows the flow curve for the dried oil. Due to the deposition of paraffin crystals, the flow curve is highly dependent of the cooling rate and the time in which the sample remains at rest at $4\,^{\circ}\mathrm{C}$. To obtain a flow curve in a steady state as described by Soares *et al.* (2013), many tests were conducted, between 1 and 3 hours for crystallization times at $4\,^{\circ}\mathrm{C}$. In principle, one hour is a sufficient time for total precipitation of the paraffin. Paraffin oil is highly thixotropic. Therefore, the tests were conducted for 2 hours to guarantee the steady state regime. After a large number of tests, we obtained the yield stress for the dried oil of 3.5 Pa at $4\,^{\circ}\mathrm{C}$.

Since the duration of the tests is approximately 5 hours, and the sample between the plates is in contact with the atmosphere, some components of the oil can evaporate. In fact, there is evaporation, but at $4\,^{\circ}\mathrm{C}$ this phenomenon seems to be not very relevant, as shown in Figure 5. After 7 hours of testing, the increase of the viscosity was around 25 %, suggesting that there is indeed evaporation but it is not dramatic.

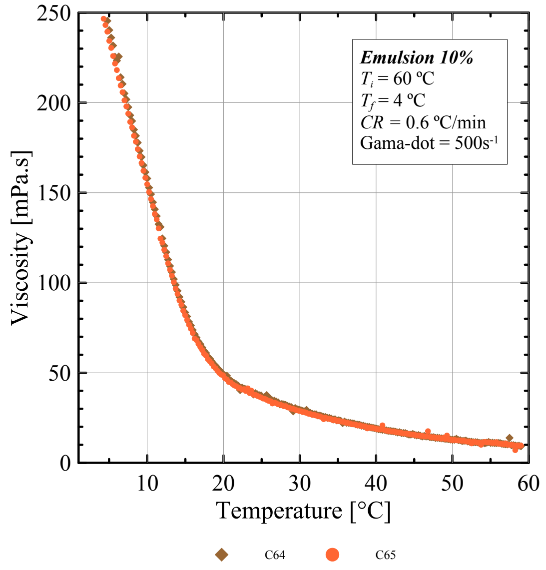

Figure 3: **Waxing temperature indication.**

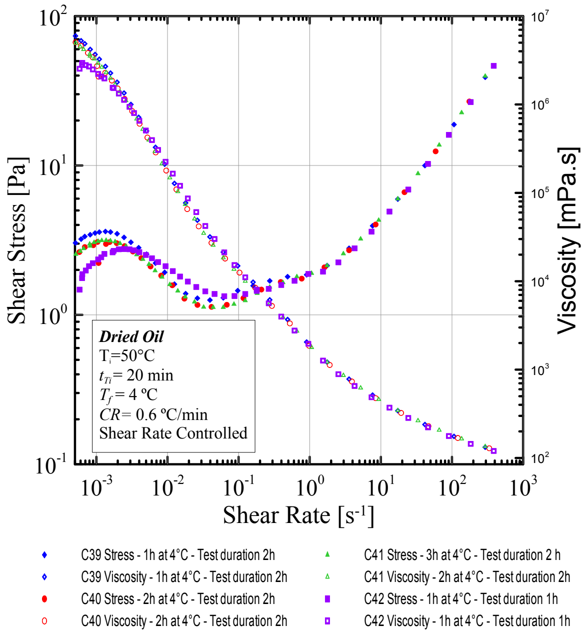

Figure 4: **The experimental appropriate time.**

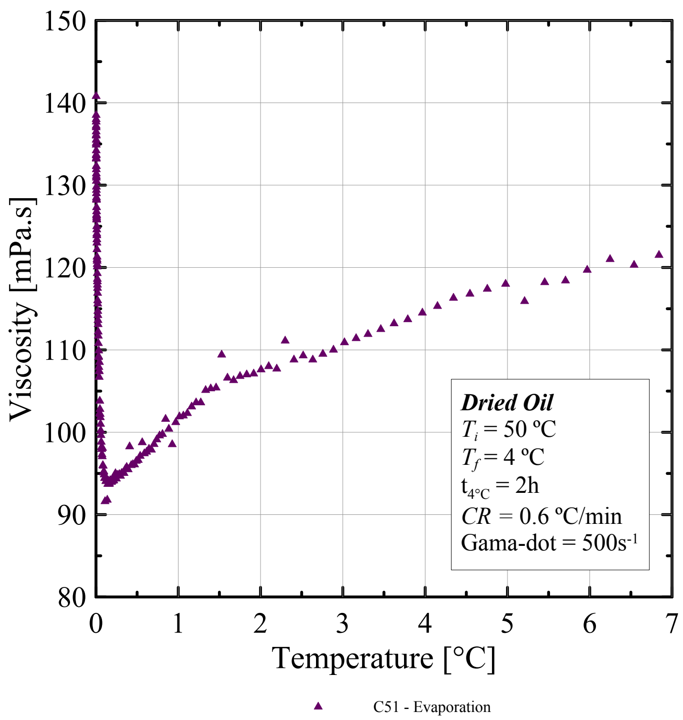

Figure 5: **Analysis of loss of volatile in terms of changing the viscosity.**

In Table 1 there are two different samples, with the same quantity of oil, at differents times. The first sample is at the ambient temperature of 25 °C, and the other, heated in a kiln with temperature at 80 °C. It was verified that the difference is less than 1 %, which does not affect the precision of the tests.

Table 1: **percentual variation of loss of volatiles.**

Exposition time	1h	2h	3h	4h
T(25 °C)	0,559%	0,698%	1,035%	1,194%
T(80 °C)	0,68%	1,091%	1,587%	1,814%
difference	0,121%	0,393%	0,553%	0,62%

Figure 6 and Figure 7 show the drop distribution for an emulsion of 2 %. The repeatability of the preparation of emulsified sample is quite good. We can see that the equivalent diameter of the droplets remained is between 5μm and 10μm.The asphaltenes are responsible for the formation of stable emulsions. Fingas *et al.* (2000) describes that emulsions containing asphaltenes content less than 3% did not form stable emulsions. Our oil have small quantities of asphaltenes, therefore, it is rather difficult or impossible to produce stable emulsions with concentration w/o larger than 5%.

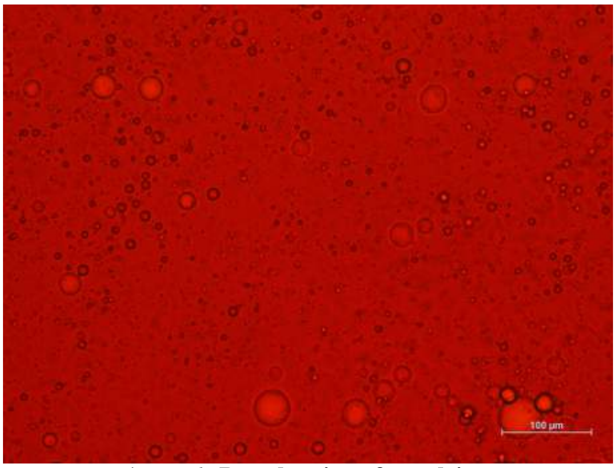

Figure 6: **Droplet size of emulsions**

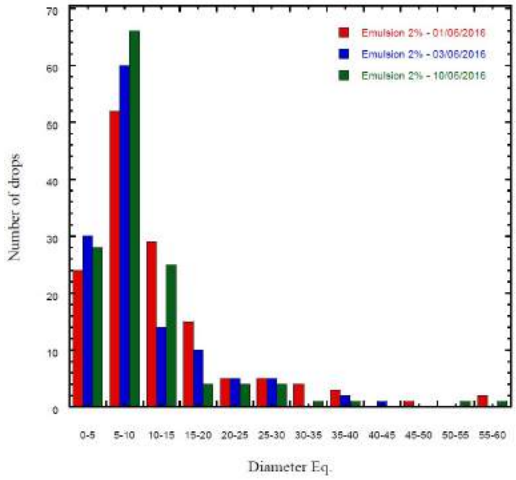

Figure 7: **Droplet size distribution**

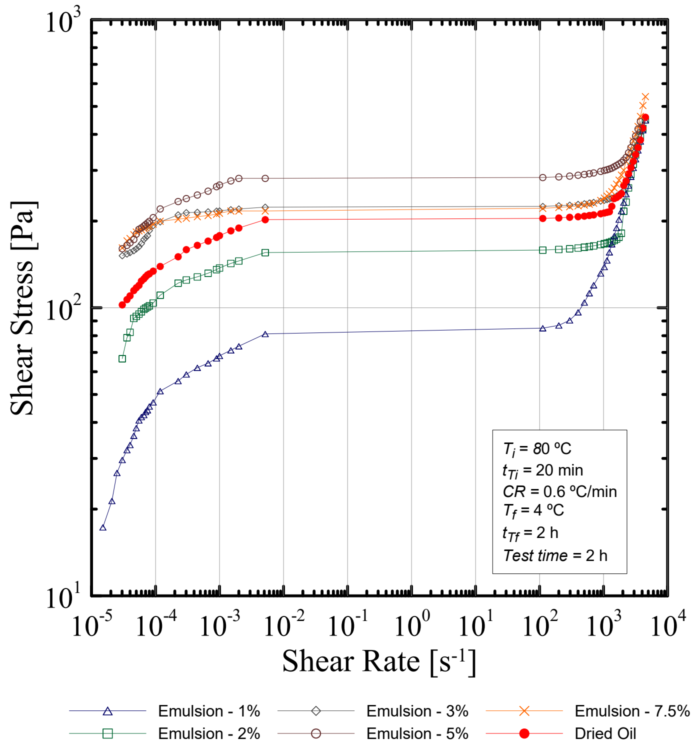

Figure 8: **Flow curve for different emulsions**

Figure 8 displays $\tau \times \dot{\gamma}$ for five values of BSW: 1, 2, 3, 5 and 7.5%. It is observed that a small variation of BSW in the emulsions can dramatically change the value of the yield stress. However, the literature reports that the yield stress tends to raise with increasing BSW (Visintin *et al.* (2008), de Oliveira *et al.* (2010), Rensing *et al.* (2011) and Sun *et al.* (2014)).

We observed that 1% and 2% of water in the emulsion work to reduce the yield stress when compared with the dried oil. Differently, 3% and 5% of water work to increase the yield-stress. The emulsion of 7.5%, which is not stable, showed yield stress below that observed for 3% and 5% and closer to the dry oil. Such a complex dependency of the yield-stress with water concentration deserved more attention.

4. FINAL REMARKS

This paper presents an investigation of the rheological behavior of emulsified paraffinic oils. The analyzes were conducted in a commercial rheometer Haake Mars III using the serrated plate-plate geometry. The results show a complex dependency of the yield-stress with the water concentration. In emulsions with very small water quantities (1% and 2%), the yield stress is lower than that of the dried oil.

5. ACKNOWLEDGEMENTS

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