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# ARE THE COOLING RATE, THE CRYSTALS MORPHOLOGY AND THE YIELD STRESS DIRECTLY RELATED IN WAXY OILS?

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**Abstract.** Crude oil gelation is a huge problem faced by the petroleum industry. At temperatures below the crystallization one, the precipitated crystals may entrap the oil into a gel-like structure. It is known that the thermal history influences on the rheological behaviour of waxy oils at low temperatures. In recent work it was showed that the cooling rate affects the supercooling presented in the precipitation of the first crystal in solution. The metastable zone width is directly related to the nucleation rate and, consequently, to the final crystals morphology. In the current work, by means of rheometric and microscopic experiments, it is analyzed the influence of the cooling rate on the crystals morphology and on the gel strength of a model waxy oil. It can be anticipated that it was observed a non-monotonic influence of the cooling rate on the critical stress of the tested waxy oil.

**Keywords:** waxy oils, rheometric experiments, cooling rate, crystal morphology, rheological properties

## 1. INTRODUCTION

The recent waxy oil reserves found in deep waters of the Brazilian coast have brought about significant challenges for oil production. One example is the precipitation of wax crystals in the oil (Venkatesan et al. 2003) when the temperature is reduced from high temperatures (70 – 150 °C) at reservoir to 4 °C at the seabed. The crystallization not only increases the oil viscosity but also may gel the material when the flow is interrupted (Wardhaugh and Boger 1987). The gel break-up, and consequently the flow start-up, demands pressures much higher than the usual steady-state operational pressure. Therefore, an adequate prediction of start-up pressures is essential for designing appropriately pipelines so as to avoid damage to the system and/or overestimation of design costs (Oliveira and Negrão 2015).

Mendes (2015) states that is not possible to determine the rheological characteristics of waxy oils only with the information of the solution composition. It is well known that the rheological properties of waxy oils at low temperature depend on the quantity, dimensions and morphology of the wax crystals precipitated in the solution (Smith and Ramsden 1978; Geri et al. 2017). And, as mentioned by Marchesini (2012), the morphology of the wax crystals are directly related to the thermal history of the sample.

The properties of waxy crude oils and the temperature are directly related. Mendes et al. (2016), for example, showed that the reduction of temperature increases significantly the critical stress to restart the flow. The increase of yield stress, storage modulus,  $G'$ , loss modulus,  $G''$ , and viscosity with the reduction of temperature was also observed by several authors (Wardhaugh and Boger 1987; El-Gamal 1998; El-Gamal and Gad 1998; Remizov 2000; Webber 2001; Kané et al. 2003; Venkatesan et al. 2003; da Silva and Coutinho 2004; Visintin et al. 2005; Lee et al. 2008; Ghannam et al. 2012; Geri et al. 2017). The growth of such properties was assigned to the growth of wax crystals when the temperature is decreased, i.e., the lower the temperature the larger the crystals (Lin et al. 2011).

The initial cooling temperature,  $T_i$ , also affects the rheological characteristics of the waxy oil at low temperatures. In other words, the temperature in which the oil is heated in the beginning of the experiments influences the mechanical behavior of the material at the end of the cooling. Smith and Ramsden (1978) and Rønningsen et al. (1991), for instance, observed that the initial cooling temperature affects the pour point of waxy crude oils. Marchesini (2012) noted that the crude oil viscosity at low temperatures is influenced by the heating temperature. Jemmett et al. (2013), by using a waxy model oil in a flow loop, observed that the pressure necessary to start-up the flow is dependent on the initial cooling temperature. Finally, Andrade et al. (2015) showed that the  $T_i$  affects the yield stress of waxy crude oils.

Besides the initial and the final cooling temperature, the properties of waxy oils are also related to the means the material is cooled (Lin et al. 2011). It is well known that the thermal history influences on the rheological behavior of waxy oil, i.e., the magnitude of the rate of change of temperature during the cooling affects the crystal morphology and the rheological characteristics of the material. The effect of the static cooling rate was investigated by several authors (Rønningsen 1992; Webber 2001; Kané et al. 2003; Venkatesan et al. 2005; Lee et al. 2008; Lin et al. 2011). The majority of them concluded that the higher the rate of change of temperature not only the lower the material yield stress but also the lower the gelation temperature.

In a recent work, Andrade et al. (2017) showed that is necessary a supercooling for the precipitation of the first crystal in solution. The higher the rate of change of temperature the higher the supercooling. As theoretically the magnitude of supercooling affects the nucleation and the growth of the crystals, in the current work, by means of rheometric and microscopic experiments, it is discussed if there is a relation between the cooling rate, the crystals morphology and the rheological properties of waxy oils.

## 2. EXPERIMENTAL PROCEDURE

The analyses were conducted with a model waxy oil composed by a mineral oil (Sigma Aldrich 330779) and 5 wt% of paraffin wax (Sigma Aldrich 327212). The Haake Mars III rotational rheometer was used to perform the experiments. A microscope system was coupled in the rheometer to get images of the crystals. Polished surface geometries were used to facilitate the microscope visualization and in the yielding experiments it was employed serrated surface plates to avoid wall slip. Before any test a specimen is placed in the rheometer and after holding the temperature for 80 °C for 30 min, the specimen was cooled from 80 °C to 4 °C at different rates of change of temperatures and then maintained quiescently for one hour. All analyses were performed after this aging time. The experimental procedures and the experiments parameters are depicted in Table 1. It is important to point out that the higher cooling rate was limited by the equipment.

Table 1. Experimental procedure for the analysis of crystals morphology and the rheological characteristics of the waxy oil

Variable	Visualization	Critical Stress Experiment
Rheometer	Haake Mars III	
Geometry	Polished Parallel Plate 35 mm diameter; 0.3 mm gap	Serrated Parallel Plate 35 mm diameter; 0.3 mm gap
Initial temperature [°C]	80	
Final temperature [°C]	4	
Rates of change of temperature, $\dot{T}$ , [K/min]	6.4, 5.0, 1.0, 0.5, 0.1 and 0.05	8.5, 5.0, 1.0, 0.5, 0.1 and 0.05
Aging time [min]	60	
Analysis at the end of aging time	Images with a 20x lens, camera <i>Black-and-white 'progressive' scan</i> CCD, and 1 $\mu\text{m}$ resolution.	Oscillatory stress amplitude sweep to determine the critical stress necessary to break-up de gel $\omega=1.0$ Hz; $\tau_i=10$ Pa; $\tau_f=2.10^4$ Pa; (20 points per decade)

## 3. RESULTS AND DISCUSSION

Figure 1(a) to (f) show the crystal morphology at 4 °C after six different rates of change of temperature. It is important to point out that, by means of rheometric and calorimetric experiments, Andrade et al. (2017) showed that the higher the cooling rate the larger the metastable zone width. It is known that crystallization rate increases, consequently the crystals length decreases, with the supercooling. It can be noted in Figure 1 that the higher the cooling rate the smaller the crystals, as proposed by Mullin (2001). One can observe that in all the cases the crystals show a needle like morphology. Figure 2 presents the crystal length,  $L_c$ , as function of the rate of change of temperature. The points shown are average values obtained from measures of ten crystals and the error bars represent the standard deviation in each condition. It's worth noting that the crystals present  $L_c=110$   $\mu\text{m}$  when the cooling rate is 0.05 K/min and  $L_c=30$   $\mu\text{m}$  when the rate of change of temperature is 6.4 K/min.

An oscillatory stress sweep was performed to determine the dynamic moduli in the linear viscoelastic range and the  $G'-G''$  crossover stress. Figure 3(a) shows the  $G'-G''$  crossover stresses at 4 °C after one hour of aging time and different cooling rates. As can be seen a non-monotonic behavior is observed. At low cooling rates the higher the rate of change of temperature the lower the critical stress and the inverse is observed for high cooling rates.

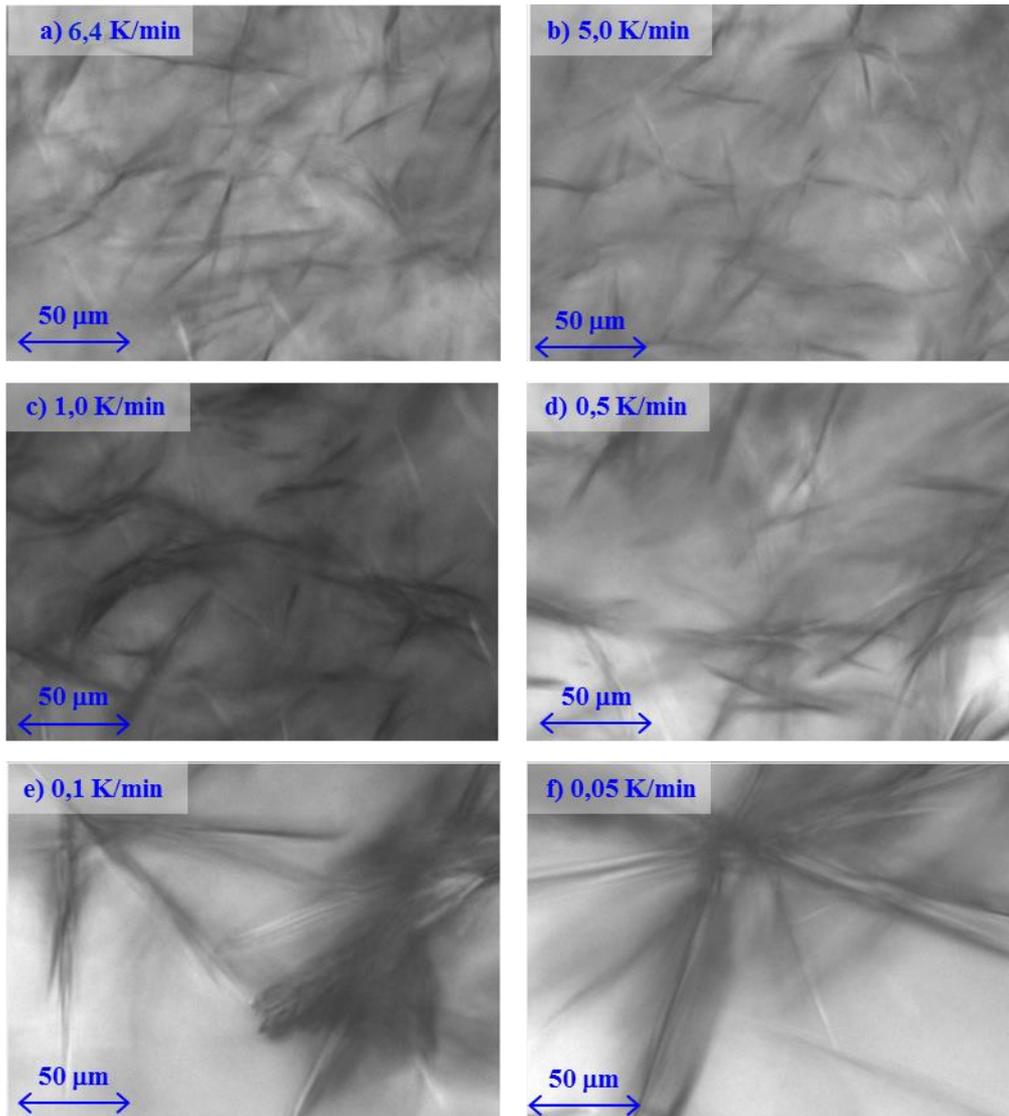


Figure 1. Crystal morphology at 4 °C after different cooling rate: (a) 6.4, (b) 5.0, (c) 1.0, (d) 0.5, (e) 0.1 e (f) 0.05 K/min.

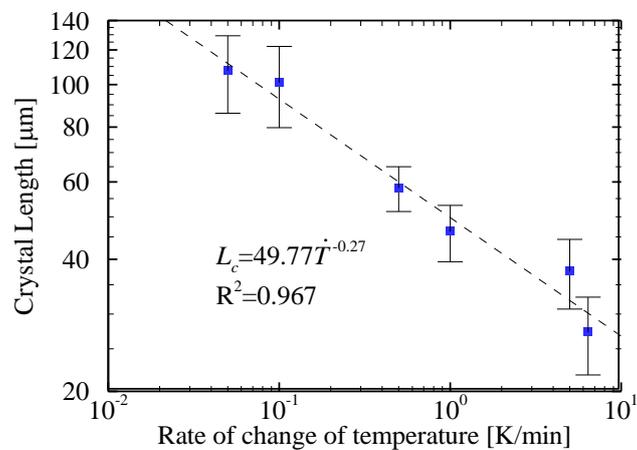


Figure 2. Crystal length as function of the rate of change of temperature.

Lee et al. (2008) observed similar behavior for a model oil and proposed a discussion based on the adhesive versus cohesive failure. The author's theory is that the start-up experiment can promote the breakdown of the gel structure

itself, called as cohesive failure, or it may promotes the breakage of the plate surface and gel interface, called as adhesive failure. As the lower the cooling rate the higher the gel strength, at low cooling rate the start-up occurs due to the adhesive failure.

On the other hand, it is important to remember that in the current start-up experiments it was used a serrated surface to avoid the wall slip, i.e., the adhesive failure. Analyzing the dynamic moduli in the linear viscoelastic range after the different cooling rates (Figure 3.b) it can be concluded that in the present paper the adhesive failure does not explain the results. It is known that when the wall slip is present in an oscillatory experiment the phase angle would be higher in comparison to the case in which the wall slip is not observed. As can be seen, the lower than rate of change of temperature the lower the phase angle, suggesting that the results represent the rheological behavior of the material, and not an error in the measuring (adhesive failure).

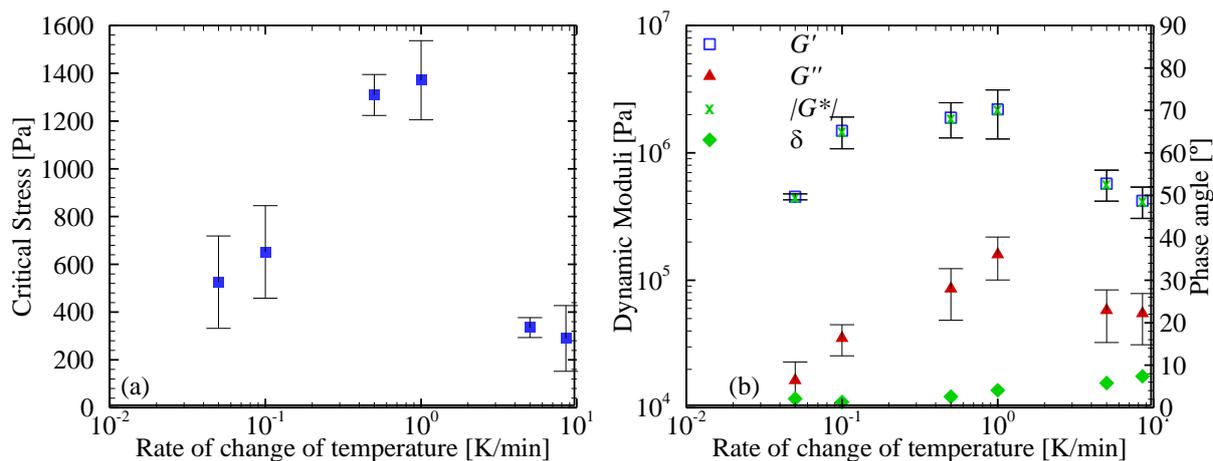


Figure 3. The influence of cooling rate on the (a) critical stress and (b) dynamic moduli.

As the Lee et al.'s theory does not explain the results presented in the current work, it is now proposed an explanation for the non-monotonic influence of the cooling rate on the gel strength of waxy oil. Figure 4 presents three different hypothetical situations. As presented in Figure 2 the higher the rate of change of temperature the lower the crystal length. Then, Figure 4(a) represents the crystals if the rate of change of temperature would tend to infinity. In this case, the paraffin molecules would have no time to move and it would crystalize many very little crystals. As the amount of precipitated wax is only 5 wt%, it can be deduced in this case that it is not possible the gelation occur. In the case in which the cooling rate is reduced, the nucleation rate diminished and then at the end of the cooling the crystals would be larger than the first case. In this case, represented in Figure 4(b), it would increase the possibility of interaction among the crystals; consequently, the gelation would be possible. It is well known that the van der Waals forces are responsible for the attraction among the wax crystals (Abdallah e Weiss 2000; Lopes-da-Silva e Coutinho 2007; Mendes 2015). Then, if there are more links between the crystals the gel strength tends to increase.

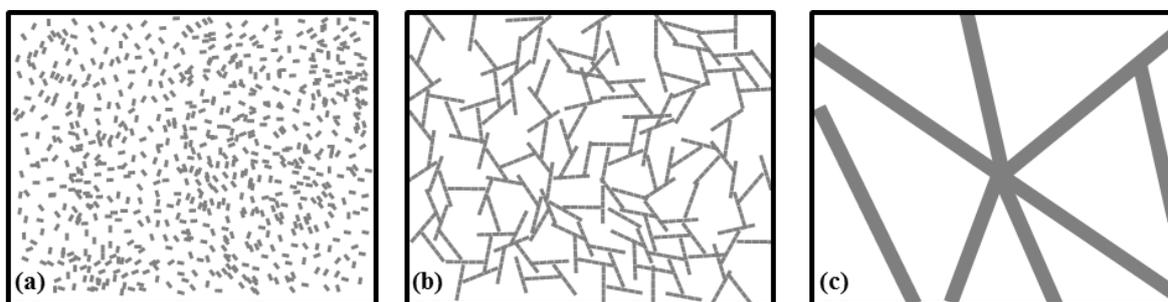


Figure 4. The influence of the rate of change of temperature on the wax crystal length. (a) Rate of change of temperature tending to infinity; (b) Critical rate of change of temperature; (c) Rate of change of temperature tending to zero.

In the last hypothetical case, Figure 4(c), the rate of change of temperature tends to zero. One can concluded that the wax molecules would have enough time to move and, as consequence, the precipitated crystals would be as large as possible. In this specific case, as the number of crystals would decrease, it would have few links among the crystals. Then, the gel strength would decrease. As a conclusion, the critical rate of change of temperature would be the one that yields more links between crystals. Cooling rate higher or lower than this critical one would provide less links among the crystals, and consequently, the gel strength of the material would be lower than the obtained in the critical situation.

#### 4. CONCLUSIONS

By means of rheometric and microscopic experiments it can be concluded that the higher the cooling rate, the higher the supersaturation, the higher the nucleation rate and, as consequence, the smaller the crystals length. The cooling rate and the crystals morphology are not directly related to the measured critical stress and dynamic moduli of the material at low temperatures. The critical stress and the dynamic moduli, in the linear viscoelastic range, increased with the cooling rate for low values of temperature rate and decreased with the cooling rate for high values of temperature rate.

The theory of adhesive and cohesive failure did not explain the results presented. In the current work, it is proposed a hypothesis to explain the non-monotonic influence of the cooling rate on the rheological characteristics of waxy oil at low temperature. The explanation is based on the crystal length and on the number of links between the crystals. The critical rate of change of temperature would be the one that yields more links among the wax crystals.

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