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# THE INFLUENCE OF COOLING AND SHEAR ON THE GEL STRENGTH OF WAXY CRUDE OIL

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***Abstract****. Precipitation of wax at low temperatures that leads to fluid gelation when the flow is interrupted is a problem of concern in transportation of waxy crude oil. In such cases, the pressure necessary to restart the flow in subsea pipelines can be much larger than usual steady-state pressure. The open literature has shown that the temperature, the shear and cooling history affect the gel strength of waxy crude oils. In spite of the initial cooling temperature being identified as an influential parameter of the gel temperature, its effect on the gel strength has never been investigated. This paper presents a discussion not only about the effects of shear and cooling history but also of the initial cooling temperature on the gel yield stress and on the viscosity of oil. This evaluation is based on rheological tests that were performed in both dynamic and static cooling conditions. It can be anticipated that the effect of initial cooling temperature on the yield stress of the gel structure is quite significant.*

***Keywords****: Waxy crude oils, Rheological tests, Initial cooling temperature, Gel strength.*

## 1. INTRODUCTION

Gelation is one of the main problems found in the production and transportation of waxy crude oils. These materials behave as Newtonian fluid at high temperatures and as non-Newtonian fluid at low temperature because of precipitation of wax (Wardhaugh and Borger, 1987). As subsea oil pipelines are usually in contact with the ocean floor which temperature is approximately 4ºC (COPPE, 2009), waxy crude oil can gelifies when the flow is interrupted for pipeline maintenance, for instance. Under such circumstances, significant pump pressure may be required to break up the gelled material and therefore, to restart the flow.

The properties of waxy crude oils at low temperatures are directly related to the means the material is cooled (Lin *et al.*, 2011). Davenport e Somper (1971), for example, showed that the reduction of temperature increases significantly the material yield stress. The increase of yield stress, storage modulus, *G'*, viscous modulus, *G"*, and viscosity with the reduction of temperature was also observed by several authors (Wardhaugh and Boger, 1987; El-Gamal and Gad, 1998; El-Gamal, 1998; Remizov *et al.*, 2000; Webber, 2001; Venkatesan *et al.*, 2003; Kané *et al.*, 2004; Visintin *et al.*, 2005; Chen *et al.*, 2006; Hou and Zhang, 2007; Lopes and Coutinho, 2007; Lee *et al.*, 2008; Li *et al.*, 2009; Oh *et al.*, 2009; Hasan *et al.*, 2010; Hou and Zhang, 2010; Dimitriou *et al.*, 2011; Ghannam *et al.*, 2012). The growth of such properties was assigned to the appearance of wax crystals when the temperature is decreased (Lin *et al.*, 2011).

The effect of shearing on the gel strength as the material is cooled was also evaluated in several works (Davenport and Somper, 1971; Rønningsen *et al.*, 1991; Wardhaugh and Boger, 1991a; El-Gamal, 1998; Singh *et al.*, 1999; Webber, 1999; Kané *et al.*, 2003; Venkatesan *et al.*, 2005; Lin *et al.*, 2011). By using rheometry results, some authors showed that the increase of cooling rate in dynamic tests contributes to the appearance of wax crystals rising not only the gel temperature[#], $T_g$ (Singh *et al.*, 1999), but also the viscosity at the end of cooling (Webber, 1999). On the contrary, Rønningsen *et al.*, (1991) observed that the rise of cooling rate reduces the viscosity at the end of cooling. Similarly to Singh *et al.* (1999) and Webber (1999), Lin *et al.* (2011) noted that the gel yield stress increases with the reduction of cooling time. For a constant cooling rate, they verified that material strength depended on the final test temperature. They depicted that yield stress of the waxy crude oil of Qinghai evaluated at 26ºC reduced as the shear rate is increased during cooling. In the final temperature of 30ºC, they noted a similar material behavior at low shear rate and an opposite behavior at high shear rates, so that the yield stress increased with the shear rate. Venkatesan *et al.* (2005) verified that the yield stress increases with the shear stress applied to the sample during cooling for low values of shear stress and increases with the shear stress for high values of shear stress. This conflicting behavior can be explained by two competing effects that takes place during dynamic cooling: the enhancement of material mobility that favors wax crystal aggregation and the destruction of formed crystals by shearing. According to Venkatesan *et al.* (2005), "The maximum yield stress occurs when the gelation stress is just enough to achieve maximum size of crystals, without being high enough to break down the structure".

[#] Temperature threshold for the formation of a thermo reversible gel.

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The effect of static cooling, situation that the material is cooled under rest was also evaluated by several authors (Rønningsen, 1992; Webber, 2001; Kané *et al.*, 2003; Venkatesan *et al.*, 2005; Visintin *et al.*, 2005; Chen *et al.*, 2006; Lee *et al.*, 2008; Lin *et al.*, 2011). Most of them concluded that the higher the cooling rate the lower is the material yield stress (Rønningsen, 1992; Venkatesan *et al.*, 2005; Chen *et al.*, 2006; Lin *et al.*, 2011) and the lower is the gel temperature (Visintin *et al.*, 2005). An opposite behavior was observed by Webber (2001) for mineral lubricant oils that showed an increase of yield stress with cooling rate. Lee *et al.* (2008) proposed an interesting discussion to explain the physical phenomena that take place during start-up of gelled oils. Citing Venkatesan (2004), the authors say that the flow can restart either by the fracture of the gel structure, called cohesive failure, or by the gel slipping at the pipe wall, called adhesive failure. According to the magnitude of shear rate applied, both failures can take place simultaneously affecting the material behavior. From results of rheometric tests, Lee *et al.* (2008) observed that the material yield stress increases with the cooling rate for low values of cooling rates and reduces for larger values.

The aging time imposed at the test final temperature is also a variable that can affect gelation of waxy crude oils. Wardhaugh and Boger (1991b) noted that an aging time of 65h after a dynamic cooling did not affect either the material yield stress or the equilibrium material viscosity. On the other hand, recent works (Visintin *et al.*, 2005; Lopes and Coutinho, 2007; Lin *et al.*, 2011) depicted an increase of the storage modulus, *G'*, and consequently, of gel strength, with the rise of aging time.

There is a fifth factor that can act upon the gel strength and that was not fully investigated in the open literature: the initial cooling temperature, $T_i$. In most works, the cooling starts at a temperature that is higher than the wax appearance temperature (WAT). Smith and Ramsden (1978) noted a "critical" initial cooling temperature that provides the highest gel temperature, $T_g$, when the sample is subjected to static cooling and constant cooling rate. For initial cooling temperatures smaller or larger than this value, $T_g$ was smaller than that observed at the critical value. Rønningsen *et al.* (1991) analyzed 19 samples of oils at two different initial cooling temperatures: 40°C and 80°C. With the exception of a specific oil in which $T_g$ was not affect by the initial cooling temperature, the increase of $T_i$ reduced the gel temperature. In a recent work, Marchesini *et al.* (2012) showed that there is a "critical" initial cooling temperature that yields the largest viscosity at the end of cooling and the largest WAT.

Many works have been developed to verify which factors affect the structure of waxy crude oils and some cooling effects have received greater emphasis, such as: test temperature, shear and cooling history and aging time. In spite of the effect of the initial cooling temperature on some rheological properties of wax crude oils being studied by some authors, none of the works evaluated the influence of this parameter on the material yield stress, which is quite important on the start-up of gelled crude oils.

This work presents a discussion about the influence of cooling rate on the yield stress of waxy crude oils, by analyzing rheometry test results performed under dynamic and static cooling. Afterwards, the effect of initial cooling temperature on the rheological properties of wax crude oils, mainly on the yield stress, is examined. It can be anticipated that this temperature has a great influence not only on the gelation but also on the gel strength at low temperatures.

## 2. MATERIALS AND METHODS

The waxy crude oil was firstly submitted to a thermal treatment for evaporation of light ends, as proposed by Wardhaugh and Boger (1987) and Marchesini *et al.*, (2012). A sample of 500ml was heated to 50°C in an open bottom and kept at this temperature for 3 hours. After that, the sample temperature was raised to 60°C and maintained at this temperature for one more hour. Finally, the whole sample was stored at the ambient temperature (~23°C) in a closed recipient. It is worth saying that the maximum initial temperature of the rheometric tests was 60°C. According to Marchesini *et al*. (2012), this thermal treatment promotes the evaporation of the light ends assuring the composition stability of the sample during the tests.

The rheometric testes were performed by employing a rotational rheometer, Haake Mars III (Haake Co., Germany), a cone-and-plate geometry with a 35mm diameter and 2° cone angle. The cone-and-plate geometry was used to assure uniform shear rate throughout the whole sample, as proposed by several works (Wardhaugh e Boger, 1991b; Rønningsen *et al.*, 1992; Chang *et al.*, 1998; Singh *et al.*, 1999; Kané *et al.*, 2003; Venkatesan *et al.*, 2003; Kané *et al.*, 2004; Venkatesan *et al.*, 2005; Oh *et al.*, 2009; Magda *et al.*, 2009; Hasan *et al.* 2010; Dimitrou *et al.*, 2011). The temperature is controlled by a Peltier-thermostatic bath system. $5.10^{-8}$ Nm is the minimum torque that can be measured by the rheometer.

Before starting any test, the pre-treated sample of oil is mixed and, by using a syringe, a small amount of material is placed in the rheometer plate at 25°C. The cone is then lowered to its measuring position and the sample is slowly heated to the initial test temperature, $T_i$. The temperature is then kept at $T_i$ for 30 minutes for dissolution of any wax crystal that have formed at the ambient temperature. The procedure was based on Marchesini´s *et al.* (2012) work which suggested that the sample heating at the rheometer can provide good test repeatability.

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## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Cooling rate

Solubility of wax in oils reduces significantly as the material temperature decreases (Venkatesan *et al.*, 2003). At cristalization, precipitation of wax crystals starts to affect the fluid viscosity (Marchesini *et al.*, 2012). As the temperature is reduced, the amount of precipitated wax crystals increases (Webber, 2001) and the oil behavior changes from viscous to visco-elastic. This transition is characterized as gelation.

In gel state, the material shows a yield stress, $\tau_0$, that is significantly affected by shear and thermal histories. The effect of cooling rate, $\dot{T}$, on the oil yield stress was then evaluated in static and dynamic tests. For this evaluation, the initial and final cooling temperatures were 60ºC and 0ºC, respectively. During the static cooling, the sample was kept within the cone-and-plate sensor at rest and subjected to three different cooling rates: 0.1ºC/min, 0.5ºC/min and 1.0ºC/min. After being cooled, the sample was maintained aging at the final cooling temperature for 30 minutes. Finally, a shear stress rate of 4 Pa/min was imposed to the sample and the yield stress was measured at the final temperature.

At the test start-up, the material viscosity and strain increase continuously and then undergo a sharp change when the gel structure is broken. The shear stress reached at the sudden change of strain is assumed to be the material yield stress (Venkatesan *et al*., 2005). Visintin *et* al. (2005) observed approximately the same strain ($\gamma$=1~2) when the wax crude oil is yielded. In the current work, the yield stress value is determined when the strain reaches 1.0. Fig. 1(a) shows the change of $\tau_0$ as a function of the cooling rate for the static cooling. As can be seen, the higher the cooling rate the smaller is the yield stress. For static cooling, the increase of cooling rate reduces the time available for growth of wax crystals providing a gel structure of small crystals that diminishes the gel strength (Lin *et al.*, 2011).

The same procedure was applied for dynamic cooling with shear rate of 2 $s^{-1}$ applied to the sample. For instance, the yield stress was so small that could not be measured after 30 minutes of aging when a cooling rate of 0.1ºC/min or less was applied. The procedure was then performed with the cooling rates of 2ºC/min and 4ºC/min. As can be seen in Fig. 1(b), the yield stress decreased one order of magnitude in the dynamic cooling, as shear inhibits formation of wax crystals. In contrast with the static cooling, the yield stress now increases with the cooling rate. According to Venkatesan *et al.* (2002), the cooling time is reduced as the cooling rate is increased which diminishes the time in which the sample is under shear.

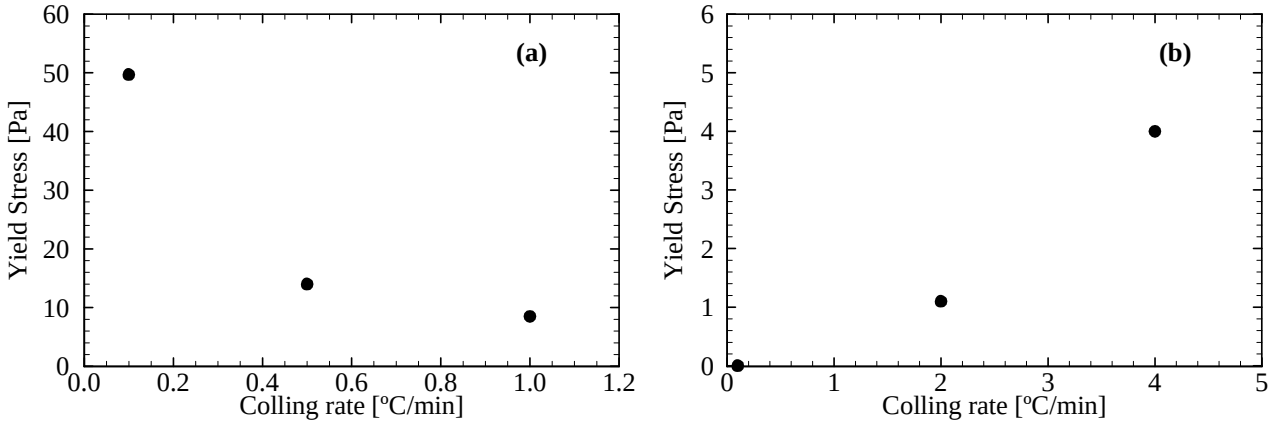


Figure 1. Yield stress as a function of cooling rate for: (a) static and (b) dynamic cooling.

### 3.2. Effect of Initial Cooling Temperature

3.2.1. Gel Temperature

In the current section, gelation is defined by using oscillatory tests as proposed by others authors (Winter, 1987; Webber, 2001; Venkatesan *et al.*, 2003; Lopes-da-Silva and Coutinho, 2004; Kané *et al.* 2004; Visintin *et al.*, 2005; Lopes-da-Silva and Coutinho, 2007; Magda *et al.*, 2009; Tinsley *et al.*, 2009; Phillips *et al.*, 2011). Low amplitude and low frequency oscillating shear stress is applied to the oil sample under the viscoelastic region. The storage, $G'$, and loss, $G''$, modules were determined from the strain response as a function of temperature. For a material with dominant viscous behavior, $G''$ is larger than $G'$ and the opposite is also true when the elastic behavior prevails, as the case of a gel.

In order to evaluate the influence of the initial cooling temperature, the oil sample was submitted to a 0.2Pa amplitude and 0.2Hz frequency oscillatory test while was cooled from two starting temperatures, 60ºC and 45ºC, at a

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constant cooling rate of 1.0ºC/min. The storage and loss modules obtained for the two initial temperatures are shown in Fig. 2. After the test start-up at higher temperatures, the material response is more viscous as G´´ is larger than G´. As the temperature is reduced, both G´ and G´´ increase and at a certain temperature G´ starts growing faster than G´´. When G´ exceeds G´´ at a lower temperature the material behavior changes from viscous to predominantly elastic. The crossover of the curves is considered by Venkatesan *et al.* (2002) as the gelation point and the temperature in which this point takes place is called gel temperature, $T_g$. As noted, the predominantly viscous region, G´and G´´ values are almost independent of the initial temperature. However, the gel point is significantly affected by the initial temperature value, as already observed by Smith e Ramsden (1978). For $T_i$ = 60 ºC, the gelation takes place at 3.8ºC whereas for $T_i$ = 45ºC, the gel temperatures rises to 18ºC (red dotted lines in Fig. 2).

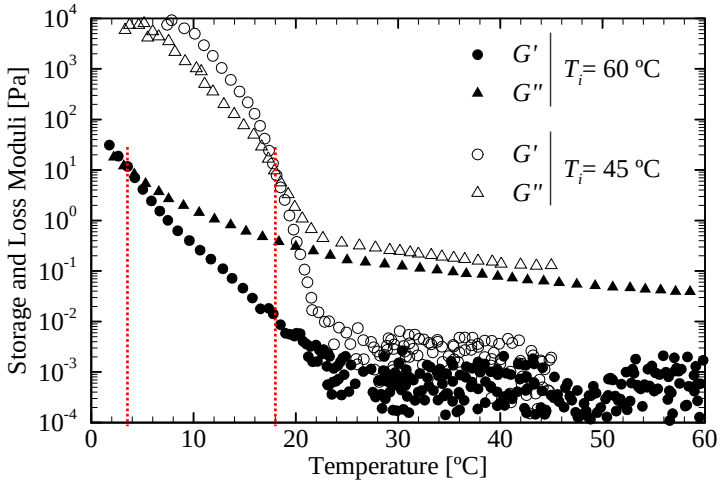


Figure 2. G´ and G´´ as a function of temperature for two initial temperatures. Cooling rate = 1.0 ºC/min.

Smith and Ramsden (1978) reported that resins and asphaltenes in wax crude oils make the material strength, in this case identified by the gel temperature, also to be dependent on the initial cooling temperature. Resins and asphaltenes are called natural point depressants (PPD) (Rønningsen *et al*., 1991). The presence of such substances changes the interaction between the wax crystals delaying the gelation process (Rønningsen *et al*., 1991; Venkatesan *et al*., 2005). If the oil sample is heated to a sufficiently high temperature, all wax crystals are dissolved and the PPDs that were linked to these crystals is freed again to join new wax crystals that will be formed in a next cooling. On the other hand, if the sample is heated to an intermediate temperature, only a portion of crystals is dissolved and the PPDs mobility is refrained by the remaining wax crystals. In this case, wax crystallization will take place without PPDs interference as the sample is cooled, resulting in higher gel temperatures (Rønningsen *et al*., 1991). According to Rønningsen *et al*. (1991), the maximum gel temperature is obtained when the final heating temperature is high enough to dissolve all wax crystals but not so high to dissolve or dissociate the resins joined to the wax crystals. Although the PPDs are recognized as gel strength depressants there is no consensus about how they interact with wax crystals. For instance, Rønningsen *et al*. (1991) showed by using microscopy that the presence of resins and asphaltenes enlarges the wax crystal sizes. On the other hand, Venkatesan *et al*. (2005) by using the same experimental technique depicted that the PPDs reduce the crystal sizes.

### 3.2.1. Viscosity

As discussed by Marchesini *et al*. (2012), the initial cooling temperature has also a great influence on the oil properties in a dynamic cooling. In the current section, dynamic tests were performed with shear and cooling rates fixed at 2 $s^{-1}$ and 4ºC/min, respectively. Tests were conducted with four different initial temperatures, 40ºC, 45ºC, 50ºC and 60ºC and the final temperature was fixed at 0ºC for all tests. Fig. 3 shows the change of viscosity with temperature for the four different tests. As can be seen, the viscosity curves are quite similar from the start-up to approximately 23ºC. Below 23ºC, the viscosity changes with higher rates for $T_i$= 50ºC and 60ºC in comparison with the other two curves. For initial temperatures of 45ºC e 40ºC, the slope of the viscosity curves changes at 22ºC and 20ºC, respectively. The temperature where the curve slope changes in dynamic cooling is called crystallization temperature.

As also noted in Fig. 3, the maximum viscosity takes place at the final cooling temperature and the highest final viscosity was obtained for the initial cooling temperature of 45ºC, considered the critical initial temperature for the analyzed oil. The samples subjected to initial cooling temperatures higher or lower than the critical initial temperature depicted final viscosity values lower than that obtained for 45 ºC. For instance, the maximum viscosity measured for $T_i$= 45ºC is eight times larger than the final viscosity for $T_i$= 60ºC. As explained by Marchesini *et al*. (2012), that obtained similar results, wax crystals are not completely dissolved at the beginning of cooling for initial cooling

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temperature below the critical value, but they are not large enough to modify the oil viscosity above the crystallization temperature. However, the new precipitated crystals form weaker crystal chains because of the few amount of dissolved wax at the end of cooling, reducing the gel strength and consequently, the maximum viscosity.

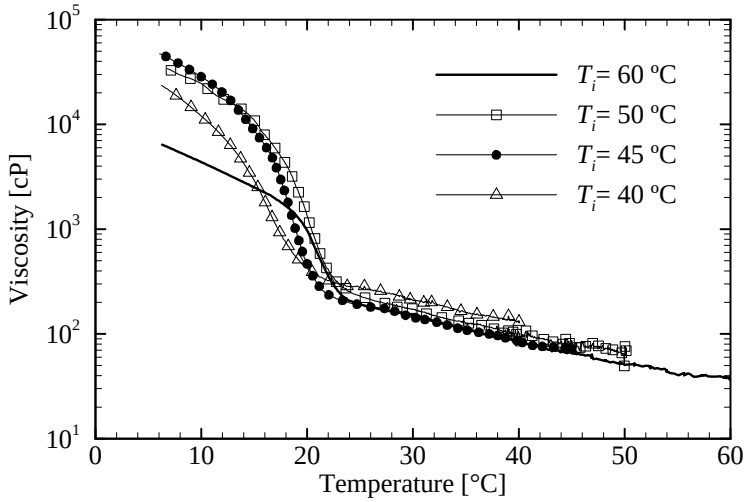


Figure 3. Variation of viscosity during dynamic cooling for different initial cooling temperatures. Shear and cooling rates fixed at 2 $s^{-1}$ and 4 ºC/min, respectively.

3.2.1. Yield Stress

In spite of yield stress being one of the most important properties for oil flow start-up, the influence of initial cooling temperature on the yield stress has never been evaluated. In this section, the oil yield stress was determined after static and dynamic cooling for four different initial cooling temperatures, 40ºC, 45ºC, 50ºC and 60ºC, a constant cooling rate, 4ºC/min, and the same final cooling temperature, 4ºC. In dynamic cooling, a 2 $s^{-1}$ constant shear rate was imposed. After being cooled, the sample was maintained aging for 10 minutes at 4ºC. Finally, a 4 Pa/min constant shear stress test was applied to the sample in order to determine the yield stress at 4ºC.

The change of yield stress with the initial cooling temperature for dynamic cooling is shown in Fig. 4(a). Similar to what has been noted for the final oil viscosity, the maximum yield stress is observed at 45ºC. As can be seen, the yield stress for the critical temperature is at least twice larger than the yield stress evaluated at 40 and 50ºC, respectively. Fig. 4(b) shows that not only the yield stress magnitude is increased six times after static cooling but also the critical temperature is more influential on enlarging the yield stress. Whereas the yield stress is approximately 900 Pa for $T_i$=45ºC, its value drops to the order of 150 Pa for either $T_i$= 40ºC or 50ºC.

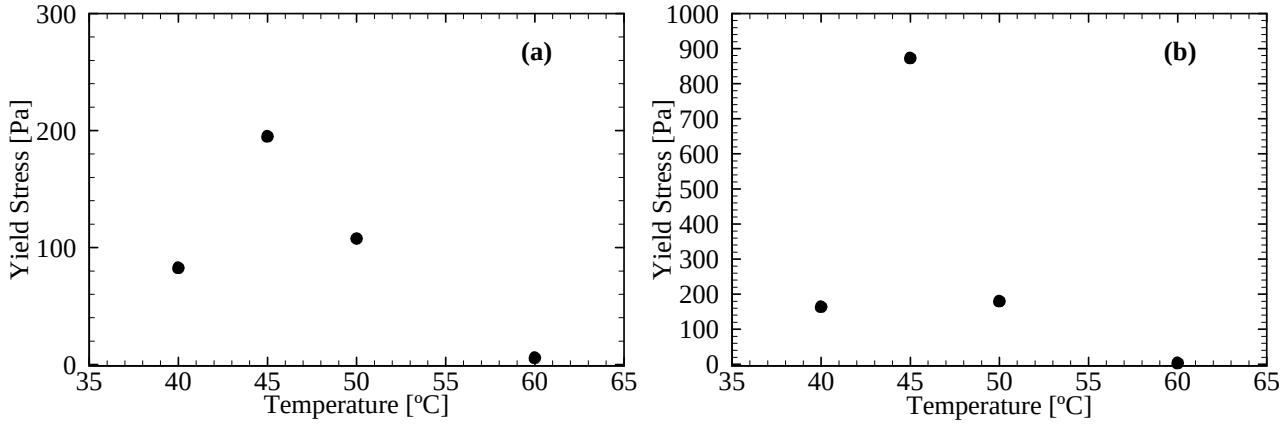


Figure 4. Yield stress as a function of the initial cooling temperature after: (a) dynamic cooling at a 2 $s^{-1}$ shear rate and, (b) static cooling. The cooling rate is fixed at 4 ºC/min.

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## 4. CONCLUSIONS

The behavior of wax crude oils at low temperatures depends on both shear and cooling histories experienced by the material. Rheometry results show that the effect of the cooling rate on yield stress depends on the cooling conditions. Whereas the yield stress is reduced with the increase of cooling rate in static cooling, the opposite is observed in dynamic cooling once the shearing time is reduced for higher cooling rates. It is worth noting that not only the cooling and shear rates, the final test temperature, and the aging time that affect the mechanical properties of wax crude oils but also the initial cooling temperature. The effect of this temperature on the oil viscosity during cooling, on the gel temperature and on the yield stress after dynamic and static cooling was investigated. As observed, there is a critical initial cooling temperature, 45ºC for the current oil that provides maximum values for the oil viscosity and the yield stress. The yield stress evaluated for this critical temperature was at least six times larger than those evaluated for other initial cooling temperatures.

In addition to the parameters already identified by the literature, the effect of initial cooling temperature on gelation still needs further investigation. As discussed above, this parameter can affect significantly the gel strength and can be more important than the others.

## 5. ACKNOLEDGMENTS

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