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ORIGINAL CONTRIBUTION

Influence of the initial cooling temperature on the gelation and yield stress of waxy crude oils

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Abstract One of the major problems in waxy crude oil production and transportation is oil gelation that takes place within pipelines as a result of wax crystallization at low temperatures. In such cases, the pressure needed to restart the oil flow in subsea pipelines can be much larger than the usual steady-state pressure, as the temperature in such environment can be as low as 4 °C. The literature has shown that not only the temperature itself but also the fluid shear and thermal histories have significant influence on the yield stress of waxy crude oils. This paper investigates the effect of the initial cooling temperature on the waxy crude oil viscosity, gelation temperature, and yield stress. In order to accomplish that, rheological tests were carried out under static and dynamic cooling conditions. The results show that there is a critical range for the initial cooling temperature that provides maximum values for viscosity, gelation temperature, and yield stress. In other words, the highest values of those properties are observed when the cooling started within this temperature range. The effect of a thermal pretreatment usually used to remove light ends was also investigated. In spite of not changing the initial temperature critical range, the yield stress was slightly affected by the thermal treatment. It is worth noting that the yield stress varies from approximately zero to hundreds after dynamic cooling or to thousands after static cooling within the tested range of the initial cooling temperatures.

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Introduction

Because of wax precipitation at low temperatures, oil gelation can become one of the major problems in waxy crude oil production and transportation, mainly when pipeline flows are shut off. As subsea oil pipelines usually lay down over the ocean floor at temperature as low as 4 °C, waxy crude oil can gel when production is interrupted for pipeline maintenance (Wardhaugh and Borger 1987). Under such circumstances, significant pump pressures are required to break up the gel structure and, therefore, to restart the fluid flow.

As reported in several works, the properties of waxy crude oils are related not only to the temperature itself but also to the cooling conditions in which the oil is subjected (Davenport and Somper 1971, Smith and Ramsden 1978, Wardhaugh and Boger 1987, 1991a, 1991b, Rønningsen et al. 1991, Chang et al. 1998, 2000, Lin et al. 2011). Davenport and Somper (1971), for example, showed that the reduction of temperature enlarges significantly the material yield stress. The increase of yield stress, the storage modulus, G', the loss modulus, G'', and the viscosity with the temperature reduction was also observed by several authors (Wardhaugh and Boger 1987; El-Gamal and Gad 1998; El-Gamal 1998; Remizov et al. 2000; Chang 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, 2010; Lopes-da-Silva and Coutinho 2007; Lee et al. 2008; Li et al. 2009; Oh et al. 2009; Hasan et al. 2010; Dimitriou et al. 2011; Ghannam et al. 2012; Rønningsen 2012). The rise of such properties was attributed to wax solubility reduction in oil as the temperature decreases (Venkatesan et al. 2003).

The effect of cooling under shearing over the gel properties 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). Some authors showed that raising the cooling rate applied during dynamic tests increases not only the gelation temperature, T_g, (Singh et al. 1999) but also the viscosity at the end of the cooling period (Webber 1999). The authors advocated that the increase of cooling rate reduces the shearing time and, consequently, the influence of shearing on wax aggregation. On the contrary, Rønningsen et al. (1991) observed that the rise of cooling rate reduces the viscosity at the final cooling temperature. Similarly to Singh et al. (1999) and Webber (1999), Lin et al. (2011) noted that the gel yield stress increases with the rise of the cooling rate. For a constant cooling rate, they verified that the material yield stress depended on the final cooling temperature. They showed that the yield stress of the waxy crude oil of Qinghai evaluated at 26 °C is reduced as the shear rate is increased during cooling. At the final temperature of 30 °C, however, they noted that the yield stress reduces and increases with the shear rate applied during the cooling at low and high shear rates, respectively. Venkatesan et al. (2005), nevertheless, observed the opposite so that the yield stress increased with the shear stress applied to the oil specimen during cooling for low values of shear stress and decreased with the shear stress for high values of shear stress. They stated that this conflicting behavior can be explained by two competing effects that take place during dynamic cooling: the enhancement of material mobility that favors wax crystal aggregation and the destruction of formed crystals by shearing. According to them "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."

The effect of the static cooling rate was also investigated 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; Chang et al. 2000, Lin et al. 2011). Most of them concluded that the higher the cooling rate, the lower the material yield stress (Rønningsen, 1992; Venkatesan et al. 2005; Chen et al. 2006; Lin et al. 2011) and the lower the gelation 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 said 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 the 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 after the test temperature being reached can also affect gelation of waxy crude oils. Wardhaugh and Boger (1991b) noted that an aging time of 65 h after a dynamic cooling did not affect either the material yield stress or the equilibrium material viscosity. Chang et al. (2000) also reported that aging time has no influence either on the mechanical behavior of the studied oil or on the dimension and shape of the crystal wax. On the other hand, recent works (Visintin et al. 2005; Lopes-da-Silva and Coutinho 2007; Lin et al. 2011) described an increase on the storage modulus, G', with the aging time.

There is a fifth factor that can act upon the yield stress of waxy crude oils and that was not fully investigated in the open literature: the initial cooling temperature, T_i. All works reported that the oil was firstly heated to an initial high temperature in order to eliminate any thermal history that exists in the material and then cooled down to the test temperature. Smith and Ramsden (1978), for instance, noted a "critical" initial cooling temperature that provided the highest gelation temperature, T_g, when the specimen was subjected to a constant cooling rate under rest. For initial cooling temperatures smaller or larger than this value, T_g was smaller than that observed at the critical value. Along the same line, Rønningsen et al. (1991) analyzed 17 samples of crude oils at two different initial cooling temperatures: 40 and 80 °C. With exception to only one oil sample, in which T_g was not affected by the initial cooling temperature, the increase of the initial cooling temperature reduced the gelation temperature. Marchesini et al. (2012) also showed that there was a critical initial cooling temperature that yielded the largest viscosity and the largest crystallization temperature at the end of cooling of a waxy crude oil. In a recent work, Jemmett et al. (2013), by using formulated model oil in a flow loop, analyzed the influence of the initial cooling temperature on the pressure necessary to break up the gel and resume circulation. The authors concluded that the initial cooling condition affects significantly the yield stress of the model oil at 4 °C. They noted that the restart pressure was doubled when the initial cooling temperature was varied by only 5 °C.

As already reported, many works have been conducted to investigate factors that affect waxy crude oil properties, such as the following: test temperature, shear and cooling history, and aging time. In spite of the initial cooling temperature being identified as a determining factor of the wax crude oil rheology, none of the prior works has evaluated directly the influence of this parameter on the material yield stress, which can be quite important on the start-up of gelled crude oils. In order to accomplish that, this work presents a discussion about the effect of the initial cooling temperature on the rheological properties of wax crude oils, mainly on the yield stress, by analyzing rheometry test results performed under dynamic

and static cooling. Additionally, the influence of the thermal pretreatment to remove light ends on the yield stress and a thermal cycle procedure are also investigated. It can be anticipated that the effect of initial cooling temperature on the yield stress of the gelled crude oil is quite significant.

Experimental tests

Samples of waxy crude oils obtained from two different Brazilian oil fields, nominated from now on oil A and B, were used to conduct the investigation. The analysis is performed for oil A, and then, some results are discussed for oil B.

Firstly, a sample of oil A was submitted to the thermal treatment proposed by Wardhaugh and Boger (1987) and Marchesini et al. (2012). The treatment consisted in heating up 500 ml of oil to 50 °C in an open bottle for 3 h then rising the temperature to 60 °C and maintaining at this temperature for one more hour. Finally, the whole sample was spontaneously cooled down to the ambient temperature (~23 °C) and stored in a closed container. The thermal treatment was used to evaporate light ends and to enhance the composition stability of the specimen during the rheometric tests.

The rheometric tests were carried out by employing the Haake Mars III rotational rheometer (Haake Co., Germany) that can measure a minimum torque of 5.10^{-8} Nm. All tests were performed by using a 35-mm-diameter parallel-plate geometry with a gap of 1 mm and serrated surface to avoid wall slip (Dimitriou et al. 2011). The temperature in the rheometer was controlled by a Peltier thermostatic bath system. Before any test, the pretreated sample was completely mixed and a small amount of material was collected and placed in the rheometer plate at 25 °C by using a syringe. The rotor was then lowered to its measuring position, and the oil specimen was heated to the initial test temperature, T_i. The temperature was then kept at T_i for 30 min to assure thermal homogenization of the specimen. In all rheometric tests, a sample hood was used to minimize evaporation of light ends. This procedure was based on the work of Marchesini et al. (2012) which suggested that heating up the specimen at the rheometer provides good test repeatability. After holding the temperature at T_i for 30 min, the specimen was cooled from T_i to 4 °C and then maintained quiescently for ten more minutes. Finally, the yield stress experiments were conducted. The experimental procedure applied to the oil sample A is depicted in Table 1. With exception to initial cooling temperature, all test parameters were maintained constant.

Table 1 Experimental procedure for the analysis of oil A

Rotor type	Serrated parallel plates, 35-mm diameter, gap of 1 mm
Initial cooling temperature (°C)	35, 40, 45, 50, 55, 60
Test temperature	4 °C
Cooling rate	1.0 K/min
Dynamic cooling	Shear rate=2 s^{-1}
Static cooling	Small amplitude oscillatory test, ω=0.5 Hz, strain amplitude=10^{-3}
Aging time at 4 °C	10 min
Test for evaluation of yield stress	Oscillatory stress amplitude sweep, ω=0.5 Hz, τ_i=10^{-1} Pa, τ_f=10^4 Pa (100 points per decade)

Results and discussion

The influence of the initial cooling temperature on different properties of the waxy crude oil is now analyzed. The oil sample was submitted to two types of cooling: dynamic and static. In the first, a fixed shear rate was imposed and the viscosity was measured as the temperature was varied. In the latter, the oil specimen was cooled down quiescently. As shown in Table 1, a small amplitude oscillatory strain was imposed during the static cooling in order to determine the gelation point. After being cooled, the specimen was maintained aging for 10 min, and then, the yield stress was measured.

Effect of initial cooling temperature

Viscosity

All dynamic tests described in the current section were performed under a constant shear rate of 2 s^{-1} (Marchesini et al. 2012) and a cooling rate of 1.0 K/min. Figure 1 shows the viscosity as a function of temperature for three different initial cooling temperatures. As shown, the viscosity curves are quite similar to each other from the beginning of the test to approximately 27 °C when the viscosity starts to increase differently.

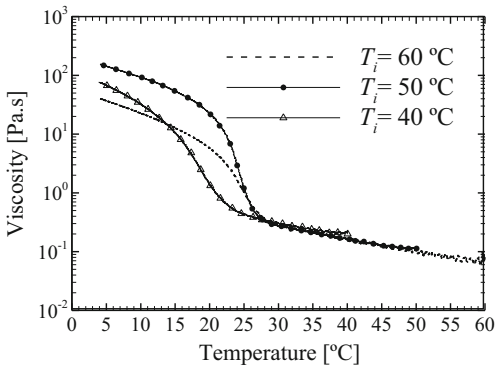

Fig. 1 Viscosity of oil A as a function of temperature during dynamic cooling for three different initial cooling temperatures

The temperature at which the first paraffin molecules begin to precipitate out of the oil is known as cloud point or wax appearance temperature (WAT). As the WAT is a thermodynamic property, its value does not depend on the cooling process (Venkatesan et al. 2003). Below the WAT, new wax crystals precipitate, and then, at some point, the oil mechanical properties begin to be more affected by the temperature reduction. The temperature at which the wax crystals starts to change the oil behavior, characterized by the variation of the curve slopes in Fig. 1, is called crystallization temperature (Marchesini et al. 2012). Below 27 °C, the viscosity in Fig. 1 varies at higher rates for T_i=50 and 60 °C in comparison with the curve of T_i=40 °C. It is worth noting that the slope of the viscosity curve for T_i=40 °C changes at 24 °C.

As also noted in Fig. 1, the highest viscosity for all curves takes place at the final cooling temperature and the maximum final viscosity is obtained for the initial cooling temperature of 50 °C, hereafter called the critical initial temperature for oil A. For instance, the maximum viscosity measured for T_i=50 °C (~160 Pa s) is four times larger than the final viscosity obtained for T_i=60 °C (~40 Pa s). Marchesini et al. (2012) have already noted that the initial cooling temperature affects the final viscosity of waxy crude oils.

Figure 2 presents the final viscosity of oil A as a function of the initial cooling temperature, measured after the dynamic cooling. The points shown are average values obtained from test results measured three times, and the error bars represent the maximum and minimum values in each test condition. As shown, the final viscosity observed at T_i=50 °C is within the error bar for T_i=45 °C. Although the error bars can be as large as 30 Pa s, the variation of the final viscosity is significantly larger than that, when the initial cooling temperature was varied.

Gelation temperature

The temperature in which the amount of precipitated wax crystals changes the oil behavior from viscous to viscoelastic during a static cooling is called gelation temperature (Li et al. 2009). In the current section, gelation was determined by using oscillatory tests as proposed by others (Webber 2001; Venkatesan et al. 2003; Lopes-da-Silva and Coutinho 2004, 2007; Kané et al. 2004; Visintin et al. 2005; Magda et al. 2009; Tinsley et al. 2009; Phillips et al. 2011). Low-amplitude and low-frequency oscillating shear strain was applied to the oil specimen within the linear viscoelastic region. The storage, G′, and loss, G″, moduli were evaluated from the stress response as the temperature was reduced. For a material with dominant viscous behavior, G″ is larger than G′, and the opposite is also true when the elastic behavior prevails, such as the case of a gel.

The storage and loss moduli obtained for oil A in three different initial cooling temperatures (40, 50, and 60 °C) are shown in Fig. 3. At high temperatures, the material response is more viscous than elastic as G″ is larger than G′. Both G′ and G″ increase with the temperature reduction 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. Although these moduli cannot be used to define a material property as they both depend on the test frequency (Winter 2002), the temperature in which the G′-G″ crossover takes place will be named as gelation temperature, T_g. The results will only be used to evaluate the influence of the initial cooling temperature on T_g. It is worth mentioning that all the other parameters of the tests were kept constants, and only the initial cooling temperature was changed from one test to another. As noted, G′ and G″ values are almost independent of the initial cooling temperature in the predominantly viscous region. However, the gelation temperature is significantly modified by the initial temperature value, as also observed by Smith and Ramsden (1978). In addition, Fig. 3 shows that the values of the storage and loss moduli at the lowest temperature are also very much affected by the initial cooling condition.

Figure 4 depicts the gelation temperature as a function of the initial cooling temperature. As shown, there is a critical

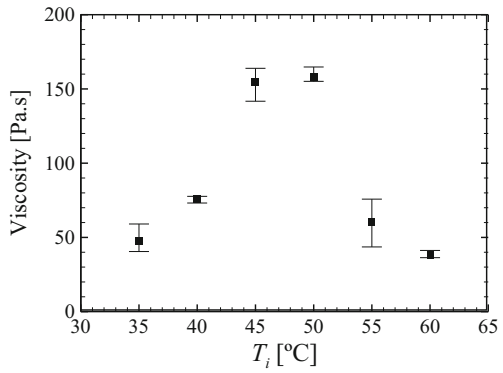

Fig. 2 Maximum viscosity as a function initial cooling temperature for oil A

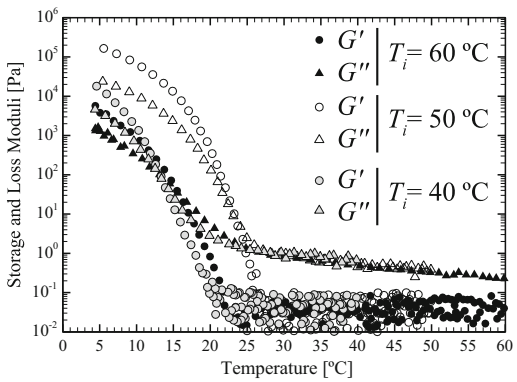

Fig. 3 G' and G'' for oil A as a function of temperature for three initial cooling temperatures

range for the initial cooling temperature, between 45 and 55 °C, in which the gelation temperature reaches the maximum value. Within this range, T_g is larger than 20 °C, whereas for T_i equal to 60 °C, the gelation takes place at 15 °C and lower than 15 °C for T_i=40 and 35 °C.

Yield stress

When a material gels, a certain level of shear stress must be applied in order to yield it. This yield stress for waxy crude oils, τ_0, depends significantly on shear and thermal histories. The influence of the initial cooling temperature on yield stress of wax crude oils is now evaluated.

Despite the different methods employed to evaluate the yield stress (Chang et al. 1998), an oscillatory stress amplitude sweep was used to determine the yield stress of the gelled oil A at 4 °C, as described in Table 1. At the beginning of the test, low stress amplitudes are applied to the material and both G′ and G″ do not change with the amplitude. Within this linear viscoelastic region, G' is much larger than G'' because the material is gelled. As the amplitude is increased, the gel structure starts to break down and the values of G' and G″ begin to drop. Although both moduli reduce with the stress amplitude, G' diminishes faster than G″, and at some point, the elastic modulus becomes smaller than the viscous counterpart when the structure is completely broken. In the current work, the stress amplitude obtained at the G' and G'' crossover was admitted to be the yield stress.

Figure 5a, b shows the effect of the initial cooling temperature on the yield stress of oil A, measured after dynamic and static cooling, respectively. Similarly to what has been shown for the oil viscosity, the largest yield stress is obtained for T_i= 45 °C, independently whether the cooling is static or dynamic. Nevertheless, the yield stresses for both T_i=45 and 50 °C are of the same order of magnitude, and they are much larger than those values observed for initial cooling temperatures out of this temperature range. For instance, the yield stress evaluated after dynamic cooling for T_i=45 °C is 20 times larger than that for T_i=60 °C. The yield stress obtained after static cooling is one order of magnitude larger than that observed after dynamic cooling. For example, the yield stress at the critical initial cooling temperature measured after static cooling is larger than 5000 Pa, whereas after dynamic cooling, it is approximately 500 Pa. Additionally, the yield stress evaluated after static cooling is more affected by the initial cooling temperature than that observed after dynamic cooling. For instance, the yield stress is approximately 5,000 Pa for T_i=45 °C and drops to about 400 Pa for both T_i=35 or 60 °C, after a static cooling.

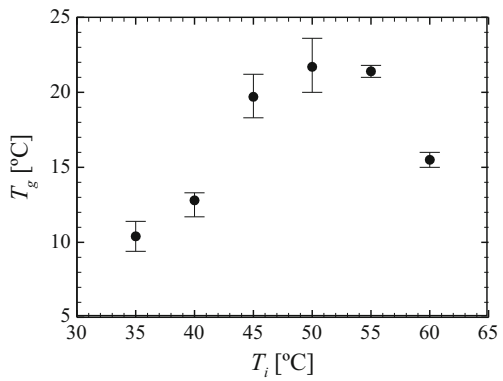

Fig. 4 Gelation temperature of oil A as a function of the initial cooling temperature

Influence of the thermal pretreatment

Waxy crude oils are composed of complex mixture of hydrocarbons (Venkatesan et al. 2003; Chen et al. 2006; Dimitriou et al. 2011, Rønningsen 2012; Soares et al. 2013). As known, many parameters can affect the mechanical properties and the yield stress of these materials. The experimental results shown above were conducted by using a pretreated oil sample. Despite the thermal pretreatment being performed to enhance composition stability of the specimen (Marchesini et al. 2012), the sample composition changes because of light-end evaporation.

To investigate the influence of the thermal pretreatment on the results shown in the previous section, some experimental tests were repeated with the waxy crude oil A without pretreatment. A sample hood with solvent trap was used to enhance repeatability. The tests were performed twice in each temperature, and the repeatability was better than what has been observed in the prior section.

Figure 6 depicts the yield stress of the oil A without thermal pretreatment after dynamic (Fig. 6a) and after static (Fig. 6b) cooling as a function of T_i. These new tests were conducted at the initial temperatures of 35, 45, and 60 °C. All figures shown are average values carried out at the same initial cooling temperature. Similarly to the pretreated sample tests, the highest yield stress still takes place at T_i=45 °C for both static and dynamic cases. For the dynamic cooling, the thermal pretreatment does not affect significantly the yield stress of the oil at 4 °C. On the contrary, the value of the yield stress obtained after the static cooling at the critical initial temperature for the untreated sample was smaller than that measured for the pretreated sample (see Fig. 5b). Therefore, the thermal pretreatment seems to enhance the oil yield stress in the critical condition despite not affecting the dependence of the yield stress on the initial cooling temperature. On the other hand, the untreated sample presented a higher yield stress value at T_i=60 °C when compared to the treated sample under both static and dynamic cooling conditions. One possible explanation for this opposite result is that significant evaporation of light ends may have happened during the 30 min that

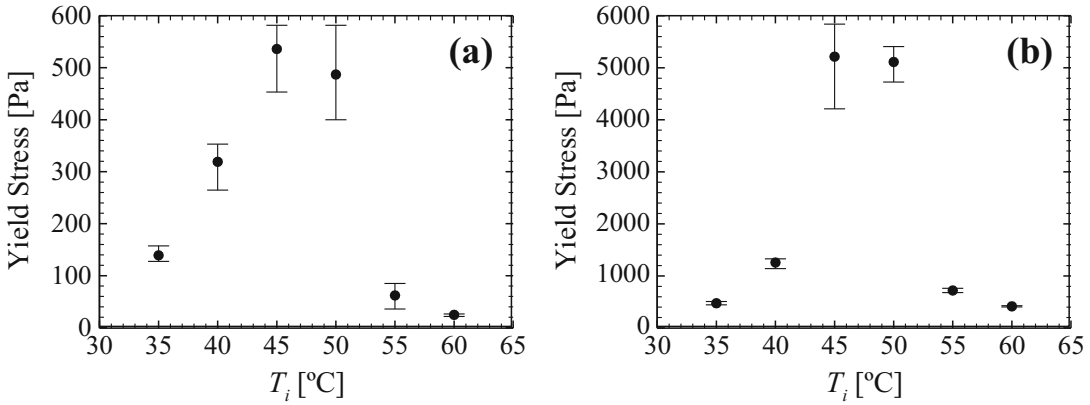

Fig. 5 Yield stress of oil A at 4 °C as a function of the initial cooling temperature after **a** dynamic and **b** static cooling

the untreated sample was kept in the rheometer at T_i=60 °C. It is worth noting that the result obtained without pretreatment provides better repeatability in comparison with that acquired with the pretreated samples.

Some efforts have been made in the literature to understand the influence of some treatments on the yield stress of the waxy crude oils, such as Rønningsen (2012) that studied the effect of adding a low-pour point oil to a high-pour point wax oil. Analyzing the results of the current work, one can see that the influence of the thermal pretreatment on the evaporation of light ends also needs further investigation.

Thermal cycle test

As the initial cooling temperature interferes directly on the yield stress of the waxy crude oil, a thermal cycle procedure was proposed to verify if the results are reproduced after heating the specimen to the T_i once again. This procedure was conducted by using the untreated oil sample. After the evaluation of the yield stress following the procedure of Table 1, the specimen was reheated to the original initial cooling temperature. The specimen was then maintained for 30 more minutes at T_i, and the cooling procedure was repeated identically to the first one. After aging the oil specimen, the yield stress was measured once again at 4 °C.

The oil yield stresses measured before and after the thermal cycle are shown in Fig. 7. As depicted in Fig. 7, the yield stress measured after the cycle is larger, smaller, and almost the same as the yield stress measured before the cycle for T_i=35, 45, and 60 °C, respectively. Despite of that, the thermal cycle did not change the influence of the initial cooling temperature on the material yield stress. Marchesini et al. (2012) that evaluated the viscosity of waxy crude oils after a dynamic thermal cycle concluded that the viscosity is slightly increased after the cycle.

Effect of initial cooling temperature on oil B

The same analysis discussed on the prior sections for oil A is now presented for oil B to demonstrate that the initial cooling temperature affects the yield stress of different oil samples. As the repeatability obtained with untreated samples of oil A was better that with pretreated samples, the tests for oil B were conducted only with untreated samples. Specimens of oil B were statically cooled from three different initial cooling temperatures (30, 45, and 60 °C) to 4 °C. In order to also evaluate the effect of the aging time on the yield stress, t_{ag}, the

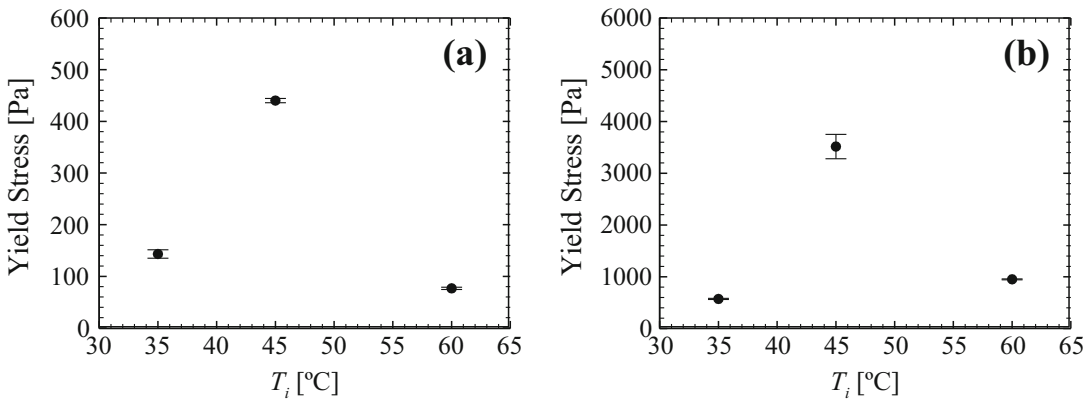

Fig. 6 Yield stress of oil A without pretreatment at 4 °C as a function of the initial cooling temperature after **a** dynamic and **b** static cooling

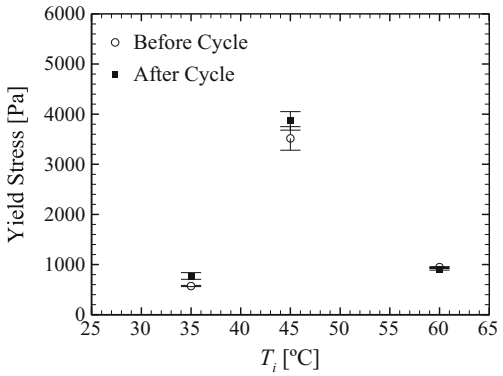

Fig. 7 Yield stress of oil A without pretreatment at 4 °C as a function of the initial cooling temperature before and after a thermal cycling procedure

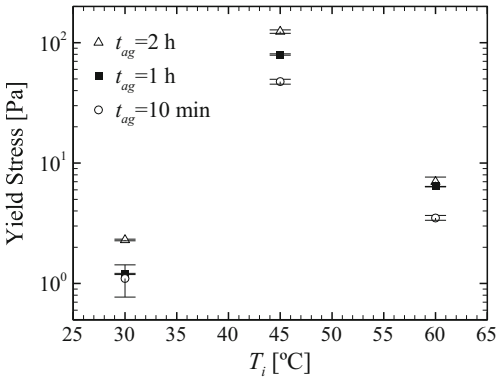

Fig. 8 Yield stress of untreated samples of oil B at 4 °C as a function of the initial cooling temperature after aging for 10 min, 1 h, and 2 h

specimens were aged for 10 min, 1 h, and 2 h after being cooled to 4 °C. After aging, the specimens were submitted to oscillatory stress amplitude sweeps to measure the material yield stress. Table 2 presents the complete experimental procedure applied to specimens of oil B. It is worth mentioning that a sample hood with a solvent trap was used in all tests to reduce evaporation of light ends.

The measured yield stresses after a static cooling for the three initial cooling temperatures and three different aging times are presented in Fig. 8. As the orders of magnitude of the yield stresses in Fig. 8 are so different, a logarithm scale was chosen to show the results so as to emphasize the values obtained for T_i=30 and T_i=60 °C. Similarly to what has being shown for oil A, the initial cooling temperature affects significantly the yield stress of the current waxy crude oil and the initial critical temperature is 45 °C. For instance, after aging for 2 h, the yield stress for the initial critical temperature is 50 and 20 times larger than that for T_i=30 and 60 °C, respectively.

It is also clear that the aging time affects the yield stress. Whereas the yield stress for T_i=45 °C increase with the aging time, the yield stresses for T_i=60 °C measured after 1 and 2 h of aging are almost the same and both larger than that obtained after 10 min. On the other hand, the yield stresses for T_i= 30 °C do not change when the aging time increases from 10 min to 1 h but enlarges when it rises to 2 h. In spite of changing the yield stress value, the aging time does not affect the dependency of the initial cooling temperature on the yield stress of the waxy crude oil.

Table 2 Experimental procedure for the analysis of oil B

Rotor type	Serrated parallel plates, 35-mm diameter, gap=1 mm
Initial cooling temperature (°C)	30, 45, 60
Test temperature	4 °C
Cooling rate	T_i→13 °C, 1.5 K/min
	13 °C→4 °C, 1.1 K/min
Static cooling	Shear rate=0 s^{-1}
Aging time at 4 °C	10 min, 1 h, 2 h
Test for evaluation of yield stress	Oscillatory stress amplitude sweep, ω=0.5 Hz, $\tau_i=10^{-1}$ Pa; $\tau_f=10^4$ Pa (100 points per decade)

Conclusions

Properties of wax crude oils are very much influenced by both shear and cooling histories. The current work showed, by using rheometry results, that not only the cooling and shear rates, final test temperature, and aging time affect the mechanical properties of wax crude oils, but also the initial cooling temperature. The effect of the initial cooling temperature on the oil viscosity during cooling, on the gelation temperature, and on the yield stress after dynamic and static cooling was investigated for a Brazilian waxy crude oil. Afterward, the influence of the initial cooling temperature on the yield stress of another Brazilian waxy crude oil was also evaluated. A critical range for the initial cooling temperature that provides maximum values for viscosity, gelation temperature, and yield stress was identified.

Within the tested range of initial cooling temperatures, the main results are summarized as follows:

1. The maximum values for the viscosity, gelation temperature, and yield stress were obtained within a critical range of 45 and 50 °C.
2. The maximum viscosity varied as much as four times, and the gelation temperature changed from 10 to 23 °C.
3. Not only the order of magnitude of the yield stress evaluated after static cooling was much larger than that obtained after dynamic cooling, but also it was more affected by the initial cooling temperature.
4. The yield stress varied from approximately zero to hundreds after dynamic cooling or to thousands after static

cooling within the tested range of the initial cooling temperatures.

An investigation of the effect of the thermal pretreatment used to remove light ends and, therefore, to assure composition stability to the specimen was also carried out. Despite the increase of the oil yield stress in the critical initial cooling condition, the result repeatability and the influence of the initial cooling temperature on the yield stress of the waxy crude oil did not change after the extraction of light ends. Unexpectedly, the repeatability was even better for the untreated samples. A thermal cycle was also proposed to verify whether the influence of the initial cooling temperature is affected or not by a second heating. In spite of raising slightly the material yield stress, the thermal cycle did not alter the influence of the initial cooling temperature.

Considering that nowadays the initial cooling temperature is not taking into account on the design of new oil pipelines, the authors believe that these findings can help significantly the petroleum industry.

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