



## MEASURING THE YIELD STRESS OF WAXY CRUDE OILS CONSIDERING ITS TIME-DEPENDENCY AND APPARENT-YIELD-STRESS NATURE

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**Abstract.** *Production in reservoirs located in deep and ultra-deep water that contain waxy crude oils faces a huge obstacle imposed by the low temperatures of the environment. When the waxy crude oil is subjected to a temperature below the Gelation Temperature, as in the case investigated in the present work, it exhibits a variety of non-Newtonian features: elasticity, plasticity, viscous effects, and time-dependency, which renders to this material a highly complex behavior. A crucial feature that is frequently ignored when the determination of the yield stress is being carried out, is the time-dependency nature of these materials. We demonstrate how significantly different values of yield stress can be obtained if this character of the material is neglected. We use the asphaltene properties as inhibitors of wax formation and propose a protocol to capture yield-stress parameters. One important conclusion is that wax crude oils can be classified as apparent-yield-stress fluids, and not (true-) yield-stress materials, with the presence of a dynamic and a static yield-stresses.*

**Keywords:** *Waxy crude oils; re-start problem; yield stress measurement; time-dependent material; wax formation inhibitors*

## 1. INTRODUCTION

After a long tradition of oil production on shore and a period of off-shore exploration, reservoirs located in deep and ultra-deep water are an attractive source for the increasing demands of oil. Typically, waxy crude oils are the type of oil found in these deep water reservoirs. Waxy crude oils are paraffinic systems which are composed by a complex mixture of hydrocarbons containing saturates, aromatics, naphthenes, asphaltenes, and resins. When these materials are cooled and achieve the so-called *Wax Appearance Temperature* (WAT), also called *Cloud Point* (CP), there is a formation of wax crystallites. Theoretically, the WAT is defined in a purely thermodynamic basis, being independent of operational conditions Venkatesan-et-al- (2003). Below the WAT, another important characteristic temperature of the problem is the so-called *Gelation Temperature* (GT), where the oil presents a gel character. At these low temperatures, these paraffin waxes precipitate out of the crude oil mixture and form a gel-like structure consisting of a solid paraffin crystal network and entrapped liquid oil (Venkatesan-et-al-, 2003). The GT is dependent on the flow conditions. The structuring evolution of the oil takes place by a growth of these crystallites and the formation of crystals of larger sizes that continue to interact to each other in this flocculating process. At an even lower temperature, the so-called *Pour Point* (PP) is achieved. The PP is defined as the lowest temperature at which the oil flows freely under condition specified by the American Society for Testing and Materials (ASTM). Below the GT the oil loses its Newtonian character and assumes a viscoplastic character, with an associated yield stress. Besides that, the yield stress of the gelled oil is strongly dependent on temperature, being a decreasing function of this variable (Visitin-et-al , 2005). The extent of increase in the yield stress values with the decreasing temperature is greater when the percentage of wax is higher (Oh-Deo , 2009).

Typically, the oil leaves the reservoirs and enters the pipeline at a temperature ranging 60°C to 100°C. The temperature in very deep water environment can achieve 4°C. This temperature difference generates a heat flux from the oil to the environment. During normal operational conditions, the main problem faced by the oil industry is related to the paraffin precipitation and deposition in the pipe. Hence, the waxy crude oil is subjected to a cooling process that accelerates the deposition of paraffin at the pipeline wall. The production losses and the necessary investments to remediate such kind of

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problem are responsible for significant costs in the petroleum industry and the understanding of this complex process is a challenging task which is worthy to follow (Azevedo-Teixeira, 2003). An important correlated problem is the so-called *re-start problem*. It occurs when there is a shutdown of the pumping process, that is caused for operational reasons. In this case, when there is no flow, the oil is cooled and its temperature surpasses the GT and so the gel structure is inevitably formed. These different crystallization processes, in quiescent and under shearing conditions were analyzed by Kane et al. Kane-et-al (2004) on trying to establish a correlation between structure and rheology. After hydrate precipitates, wax precipitates are the most common cause for blockage in oil pipes (Dimitriou-et-al , 2011).

In order to re-start production, the pumping pressure at the pipe inlet must be high enough so that it can rupture the internal gel structure and sustain a steady-state flow. In other words, the pumping pressure must overcome the resistance imposed by the yield stress of the material. This re-start pressure can be significantly different from the pressure necessary to operate in normal conditions, i.e. when the steady-state is achieved. The pump that can handle both situations has to operate in a wider pressure range. In this sense, a good estimative of the yield stress of the oil when it is in the complete gelled state would be useful for the hydraulic plant project.

From the discussion above, we can conclude that gel formation and gel breakage processes are extremely relevant for the logistic of transportation of waxy crude oils in ultra deep water (Zhao-et-al , 2012). These two processes are highly influenced by shear history, temperature history and the composition of the waxy crude oils. Hence, the previous shear flow conditions before shutdown, the initial temperatures of the oil and the environment, the thermal conductivities of fluids and solid materials involved, and the temperature dependence of the parameters that control the kinetics of gelation are important factors to determine the final state of the gel formation. The gelation process is responsible for a structuring in the material that can be quantified by the mechanical property *yield stress*. Understanding the yielding of the gel structures is crucial for the strategies of gel breakage and re-start. Singh et al. Singh-et-al (1999) reported that slower cooling rates lead to greater reduction on the yield stress. However, determining the re-start pressure from a simple measure of the yield stress is not a simple task. In fact, there is a significant discrepancy between what is measured for a waxy crude oil in the rheology laboratory and what is obtained in pipeline tests (Magda-et-al , 2009). There are strong evidences that laboratory rheological measurements overestimates the upstream pressure needed for re-starting the flow.

A first challenge to face is that the measurement of the yield stress of a material does not have a standard protocol consensually accepted. In fact, this issue is a matter of profound discussion in the literature, where a fundamental point concerns questioning the very existence of the yield stress barnes-walters (1985); barnes (1999); evans (1992); astarita (1990); souzamendes-thompson (2013). Together with the term *yield stress* there are other expressions to designate correlated entities such as *elastic yield stress*, *static yield stress*, *dynamic yield stress* (Chang-et-al , 1998), *apparent yield stress* (barnes, 1999), a terminology that will be discussed later. Besides that, an additional complication comes from the fact that gelled material exhibits time dependent properties due to changes in microstructure in a time scale that needs to be accounted for (barnes , 1997; moller-mewis-bonn , 2006; mewis-wagner , 2009; souzamendes-thompson , 2012). The hindrance is that is not easy to evaluate if the steady state was achieved, and the value of the yield stress becomes a function of the experimental protocol, the accuracy of the rheometer at low shear rates and the patience of the experimentalist. These time dependent materials are sensitive to the time scale over which the gel is subjected to a given shear stress. Therefore, another source of different behavior can be identified if laboratory and pipeline are submitted to different time scales of imposed shear stress (Chang-et-al , 1999).

A second point concerns the gelation process. The temperature potential difference provokes a spatial temperature gradient, which acts together with the diffusion of wax forming molecules rendering a spatial distribution of wax crystals in the gel formation. These different layers of structuring often present different yield stresses associated, turning the gel in the oil pipeline into a inhomogeneous material with respect to its mechanical properties such as viscosity and yield stress. This intricate behavior makes difficult the prediction of the re-start pressure by models that not take this fact into account (Davidson-et-al , 2004; Dimitriou-et-al , 2011). Another difference in gel formation is the possible presence of voids in the pipe due to shrinkage during the gelation process (Vinay-et-al , 2006). Therefore, different protocols followed in the laboratory render different shear and temperature histories to the material, what leads to different final bulk properties.

Wax inhibiting strategies are often adopted in order to minimize transport problems, like adding chemical substances that act as wax crystals modifiers or as surface active agents (Ibrahim-Iden , 2004). However, some substances frequently present in waxy crude oil composition can act as *natural* inhibitors of paraffin deposition and wax crystallization. Polar compounds such as asphaltenes and resins are known to have this property. Hence, even being part of the oil distillation residues and not being desirable components of oil production from the refine perspective, the presence of asphaltenes can be extremely helpful in the case of the necessity of stopping the production, when the oil is subjected to a gelation process. Asphaltenes are generically defined as compounds of petroleum that are insoluble in alkanes. They are not a unique substance, but a mixture of poly-disperse and chemically heterogeneous species (Roux Broseta, 2001). The asphaltene fraction is formed by many series of relatively large molecules containing aromatic rings, several heteroaromatic and naphthenic ring plus relatively short paraffinic branches. They also constitute the most polar and heaviest species of oil distillation residues compound. They usually form aggregates or flocculates and this character is used to explain their

effect as inhibitors of wax crystals formation in a oil pipeline. These aggregates form obstacles for waxy crystals to grow and to merge with other crystals. In the flow of oil in a pipeline, the pressure drop in a pipe is the main cause of the solvent degradation with respect to the solute asphaltene. In other words, a pressure decrease to the bubble point is responsible for the precipitation of the asphaltenes in the solution and hence they could loose their capacity of inhibiting the formation of the gel structure. Hence, the final effect due to pressure drop is quite similar to that encountered after a flocculant such as n-pentane or n-heptane is added after the mixture is cooled.

The great majority of the models intended to represent the flow curve of waxy crude oils have a yield stress as a parameter. However, due to the difficulties on defining and measuring the yield stress of the material and the time dependent character of the gelled oil, a discussion on the measurement of the yield stress and on the available viscoplastic models is pertinent in the present context. The intrinsic problem that is in the very concept of the yield stress was clearly stated by Evans (1992). He observe that the definition of yield stress excludes the possibility of experimental proof of its existence. In the context of time dependent materials, this observation is even more critical. If we apply a certain stress, and apparently there is no flow associated, how can we guarantee that this state of affairs will remain? This fact was observed by Moller et al. (2006), who proposed an alternative definition that the experimentalists need to employ: "the highest stress at which no flow is detectable within the duration of the experiment." However, the strain rate can be so low in this case that, although no *detectable* flow is occurring, one cannot prove that after a long time, the material will stay in the same undeformed state.

In fact, Barnes and Walters (1985) show that some materials that were thought to be yield-stress materials do flow when the applied stress was below the value of the previously measured yield stress. Even though, the yield stress concept was useful for these materials, since it was invoked with the creation of the expression *apparent yield stress*. Although there was a flow for stresses below a certain value, the rate of strain associated was very small. When the apparent yield stress was achieved, a major collapse of microstructure took place with a pronounced decrease of the viscosity.

Wardhaugh and Boger (1991) identified three yield stress quantities in order to fully characterize the yielding of a gelled waxy crude oil. The first one is the *elastic yield stress*. It is the value of stress below which the material is in the elastic (recoverable) regime. The *static yield stress* is more associated to the classical definition of yield stress, and is defined as the stress value where the gel material starts to fracture and the breaking process. The *dynamic yield stress* can be viewed as the value of stress towards to the material is attracted, when the shear rate is decreased departing from the unstructured state. As discussed in Wardhaugh-Boger (1991) these whole plethora of "yield stresses" are features of solid-like behavior that are uncommon in general viscoplastic materials, and are signals of a very complicated yielding process. It is worth noticing that this complicated behavior is present in other systems besides waxy crude oils (Paumier-Pantet-Monnet-Touze-Foltz, 2009; Galindo-Rosales-Rubio-Hernandez, 2010). The identification of an elastic yield stress in waxy crude oils in the gelled state adds another degree of complexity to the problem. This puts this kind of material into the category of elasto-viscoplastic time dependent materials. In general, there are not many examples of models that can handle this kind of material. A very important subcategory of materials with such behavior is when the time dependency has a thixotropic character, i.e. when the flow curve of the material is unique and not a function of the previous history undergone by the material.

As discussed by de Souza Mendes and Thompson (2012) there are two classes of models that were conceived to model elasto-viscoplastic-thixotropic models. The first type, called Type I, takes a Bingham-like viscoplastic constitutive equation and includes elasticity and thixotropy. The second kind, called Type II, takes a Maxwell-like constitutive equation and adds yield and thixotropic features. The line of arguments they developed resulted in the conclusion that there are some advantages in adopting Type II models. Among these advantages are: i) the capacity of the model to tend smoothly to particular cases such as viscoplastic-thixotropic systems and elasto-viscoplastic systems, ii) the constitutive equation does not need an extra-evolution equation for the elastic strain, iii) there is no necessity to relax the definition of the yield stress, by making this quantity a function of the structuring level. Additional features that would be interesting for both types were also stressed, such as the inclusion of the flow curve as an input of the model and the attribution to the stress level (and not the strain rate level) the responsibility for the breakage of the material structure.

In the present work we perform yield stress measurements of a Brazilian crude oil with different concentrations of asphaltenes. In this connection, we use the yielding nature of the material to quantify the ability of the asphaltenes as natural inhibitors of wax formation. We show that not taking into account the time-dependent nature of waxy crude oils, turns the yield stress measurement dependent on the protocol. However, a more carefully approach gives a single result.

## 2. Viscoplastic models

A non-Newtonian viscosity proposed by Pedersen and Ronningsen (2000) is a function of the volume fraction of wax particles in the combined oil plus wax phase,  $\Phi_{wax}$ . It is given by

$$\eta = \eta_{liq} \exp(D\Phi_{wax}) \left[ 1 + \frac{E\Phi_{wax}}{\sqrt{\dot{\gamma}}} + \frac{F\Phi_{wax}^4}{\dot{\gamma}} \right] \quad (1)$$

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where  $\dot{\gamma}$  is the shear rate and  $D$ ,  $E$ , and  $F$  are parameters used to fit the viscosity function. This function has a yielding-like character, since viscosity diverges in the limit  $\dot{\gamma} \rightarrow 0$ . Pedersen and Ronningsen Pedersen-Rifnningesen (2003) tested a number of waxy crude oils obtaining a good fitting using Eq. (1).

The works of Dimitriou-et-al (2011) and Marchesini-et-al (2012) explores the viscosity dependency on temperature. Both works highlight the non-Arrhenius character of this dependency, below the Gelation Temperature. An Arrhenius dependency is characterized by an equation of the following type

$$\eta = \eta_{ref} \exp \left[ \alpha \left( \theta^{-1} - \theta_{ref}^{-1} \right) \right] \quad (2)$$

where  $\eta_{ref}$  is the viscosity at a reference temperature  $\theta_{ref}$  and  $\alpha$  is a quantity with dimension of temperature which rules the intensity of the temperature dependency. As shown by Marchesini et al. Marchesini-et-al (2012), when the oil is being cooled from a liquid unstructured state, the material begins with an Arrhenius-like dependency, but, at a certain point it starts a different kind of behavior. This point can be a good estimate for the GT. Dimitriou et al. Dimitriou-et-al (2011) argues that, since the pure waxy state is well capture by a VFT (Vogel–Fulcher–Tammann) model, given by  $\eta = \eta_v \exp \left[ \beta \left( \theta - \theta_\infty \right)^{-1} \right]$ , the combined behavior must be something in between these two extremes. In order to fit the constant temperature data of a model waxy crude oil Dimitriou-et-al (2011) uses the Cross model

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty) \left[ 1 + \left( \frac{\dot{\gamma}}{\dot{\gamma}^*} \right)^m \right]^{-1}, \quad (3)$$

where  $\eta_0$  and  $\eta_\infty$  are limiting values at low and high shear rates, respectively,  $\dot{\gamma}^*$  is a characteristic shear rate and  $m$  is a parameter that controls the shear-thinning intensity. They also used the Herschel-Bulkley model. They found that, while the Cross model was successful on fitting the viscosity data in the whole range of shear rates, the Herschel-Bulkley model was capable to provide a good fitting only in the high limit range. This result, together with others present in the literature, e.g. Rifnningesen (1992), give evidence to affirm that waxy crude oils are apparent-yield-stress fluids and not yield-stress materials.

In order to consider the time dependent nature of waxy crude oils, Zhao et al. Zhao-et-al (2012,?) use as starting point, an equation for the evolution of a structure parameter proposed in DeKee-et-al (1983) given by

$$\frac{d\lambda}{dt} = -a\dot{\gamma}^b (\lambda - \lambda_e)^n, \quad (4)$$

and developed a model that is based on a time dependent yield stress of the form

$$\tau_y = \tau_A + \frac{\tau_B - \tau_A}{1 + \dot{\lambda}_c (t - t_y)}, \quad (5)$$

where  $\tau_A$  and  $\tau_B$  are the residual and original yield stresses,  $t - t_y$  is the local duration of shearing and  $\dot{\lambda}_c$  is the gel degradation rate.

As discussed previously a different perspective of understanding yielding can be employed from the framework of Type II models (souzamedes-thompson, 2012). In this case, another philosophy is adopted where the time dependency nature of the material is handled without making the yield stress a function of time (or equivalently, structure). The yield stress is interpret as the stress value for starting the major break-down process. In this case the flow curve, which is determined experimentally, is considered the locus of the attractor points which are in a non-equilibrium state, i.e. when the microstructure is changing. A quite general function for the viscosity at the equilibrium state that is conceived to model apparent-yield-stress fluids was proposed in (souzamedes-dutra, 2004; souzamedes, 2009) and is given by

$$\eta_{eq}(\dot{\gamma}) = \left[ 1 - \exp \left( -\frac{\eta_o \dot{\gamma}}{\tau_y} \right) \right] \left\{ \frac{\tau_y - \tau_{yd}}{\dot{\gamma}} e^{-\dot{\gamma}/\dot{\gamma}_{yd}} + \frac{\tau_{yd}}{\dot{\gamma}} + K \dot{\gamma}^{n-1} \right\} + \eta_\infty \quad (6)$$

where  $\eta_o$  and  $\eta_\infty$  are the viscosities values associated to  $\dot{\gamma} \rightarrow 0$  and  $\dot{\gamma} \rightarrow \infty$ , respectively,  $\tau_y$  is the static yield stress,  $\tau_{yd}$  is the dynamic yield stress and  $K$  and  $n$  are the power-law parameters (consistency and exponent, respectively). Besides that,  $\dot{\gamma}_{yd}$  is the characteristic dynamic shear rate, which marks the transition between static and dynamic yield stresses. In order to complete the thixotropic model proposed in souzamedes-thompson (2013) there is a evolution equation for the structure parameter,

$$\frac{d\lambda}{dt} = \frac{1}{t_{eq}} \left[ \left( \frac{1}{\lambda} - \frac{1}{\lambda_o} \right)^a - \left( \frac{\lambda}{\lambda_{eq}(\tau)} \right)^b \left( \frac{1}{\lambda_{eq}(\tau)} - \frac{1}{\lambda_o} \right)^a \right] \quad (7)$$

where  $\lambda_o$  is the maximum value of the structure parameter  $\lambda$  and the subscript  $eq$  is associated to equilibrium quantities. The parameters  $a$ ,  $b$  are for fitting the structure evolution of the material; and an evolution equation for the relation stress-strain rate given by

$$\dot{\gamma} + \theta_2 \ddot{\gamma} = \frac{\theta_2}{\eta_\infty} \left( \frac{\tau}{\theta_1} + \dot{\tau} \right) \quad (8)$$

where the general parameters  $\theta_1$ ,  $\theta_2$  are functions of the structure level  $\lambda$ .

There are several methods for determining the yield stress (Rifningsen, 1992). The methods depend on being indirect or direct methods (indirect would correspond to extrapolation or determination with respect to a curve fitting of a model), on the geometrical device (cone-plate, plate-plate, vane, couette), on imposing controlled stress or controlled strain. A challenge that the characterization of waxy crude oil imposes is associated to its time dependency character. The yield stress can only be achieved if the waiting time for reading the stress value is long enough so that the stress value is changing anymore. Concerning oscillatory tests we can observe two criteria for determining the yield stress: one is point where there is a more pronounced drop on the value of  $G'$ , representing that the material is losing its elastic character, and the other is when the  $G'$  and  $G''$  values are the same, representing the point after which viscous effects are dominant over elastic ones.

### 3. Experimental procedure

The measurements were carried out with a commercial rheometer, model HAAKE MARS II, manufactured by Thermo Scientific, Germany, by using a standard cone-plate geometry, in which a sample of 0.2 ml is required for each test. Our samples of waxy crude oil was supplied by the Brazilian Oil Company (Petrobras). The oil, light and free of both salt and water, contained, at least, 3% of both together, asphaltene and resin. In order to study the effect of such kind of hydrocarbons as natural paraffin inhibitors, we used two different flocculants, n-heptane and n-pentane, to remove asphaltene and resin from the original oil.

As the rheological parameters of waxy crude oil are highly dependent on temperature history, all the samples were previously submitted to a rigorous step-by-step procedure. First of all, each sample was heated up to 60°C. This level of temperature was kept for 20 minutes. After that, by a precise thermal control equipment, the oil temperature was decreased at a constant rate of 0.62°C/min until the test temperature of 4°C was achieved. The sample rested for 1 hour and 20 minutes at this temperature before the beginning of the test. At this level of temperature the paraffin crystals formation was quite intense.

### 4. Results and discussion

A very important conclusion, from the discussion conducted in Sec. 1, is that the complex time-dependent character of waxy crude oils at low temperatures, requires yield stress measurements to follow a protocol that takes this time-dependency into consideration. We show this fact by quantifying the effect of the asphaltenes present in the waxy crude oil composition as natural inhibitors of waxy formation.

Fig. 1 shows the relative amount of asphaltene plus resin removed from the original oil as a function of solvent volume used. It was observed different levels of precipitated hydrocarbons by using n-heptane (black symbols) or n-pentane (red symbols). With 0.5 ml of the former solvent, 2.3% of hydrocarbons were removed from the oil. Using 2 ml of n-pentane, 3% of hydrocarbons were removed from the oil. The amount of asphaltenes in oil is usually defined operationally by using the n-heptane. If we assume that no resin is precipitated with aid of such a solvent, we could infer that the difference on the amount of precipitated hydrocarbons obtained with the two solvents is because the n-pentane causes also the precipitation of resin. Hence, we could assume that, from the total amount of precipitated hydrocarbons occurred by the action of the n-pentane, around 2.3% is asphaltene and 0.7% is resin. However, such discrimination is not precise and we are, actually, taking into account the combined effect. For both flocculants, n-heptane and n-pentane, we can assume that the amount of solvent used to remove the maximum quantity of asphaltene and resin does not change significantly the rheological behavior of the original oil. This hypothesis is supported by the data showed in Fig. 2, in which  $\eta(\dot{\gamma})$  is displayed for three different values of solvent volume. The difference between the original oil viscosity and that with 0.5 ml of n-heptane (Sample 1) and 2 ml of n-pentane (Sample 2) diluted is hardly perceived. Thus, we assume that any other rheological parameter is unchanged at all.

The crystals start to precipitate at a very high temperature, as can be inferred from Fig. 3, where the shear-viscosity is displayed as a function of the shear-rate for a range of temperatures. We can see that the shear-viscosity exhibits Newtonian-like behavior at temperature values higher than  $T = 20^\circ\text{C}$ . As temperature decreases, the non-Newtonian character of the viscosity is clearly noticeable. Our tests were performed at  $T = 4^\circ\text{C}$ , in which the waxy crude oil was highly structured.

We adopt the classical concept of yield-stress i.e. that its measurement must be performed in a steady state regime. Since the waxy crude oils are highly thixotropic, we must, first of all, certify ourselves that our measurements are time independent. With a virgin oil, i.e. without any flocculant addition that could act to provoke asphaltene precipitation, we conducted the test displayed in Fig. 4, where the shear-stress is shown as function of the shear rate. The different flow curves reflect different time intervals for the software of the rheometer to provide the output values. When the rheometer does a shear rate sweep, we must input the range of imposed shear rates and the total time the experiment will take. Hence, when the shear rate is changed to the next one, the rheometer takes a time interval to consider that the new steady state is achieved and to compute the stress value associated to the new shear rate. We are calling this interval

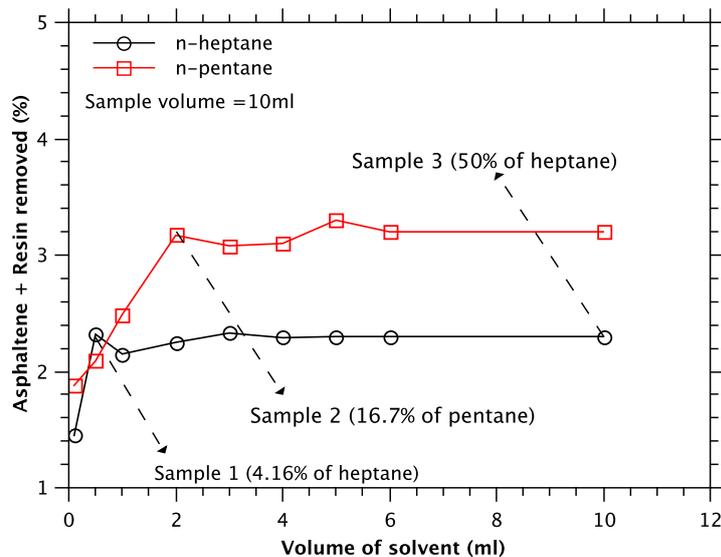


Figure 1. Fraction of Asphaltene and Resin removed from the original oil as a function of the solvent volume introduced.

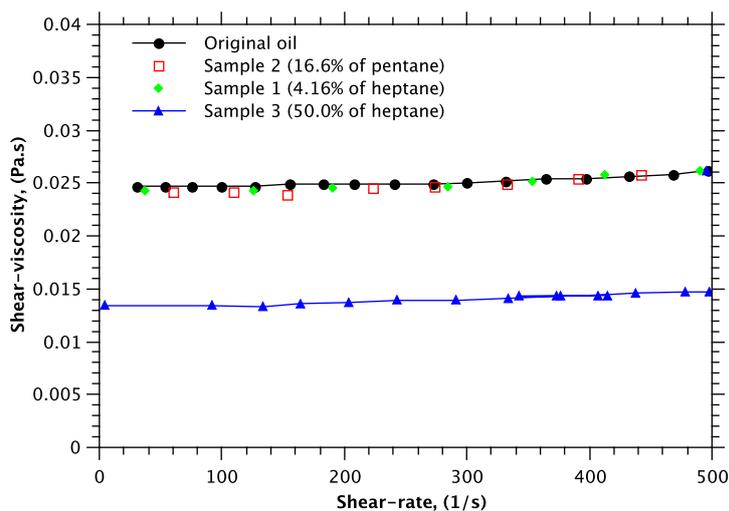


Figure 2. Shear-viscosity,  $\eta$ , of the original oil as a function of shear-rate,  $\dot{\gamma}$ , at different solvent concentrations for temperature fixed at 40°C.

*elapsed measurement time. Hence, for a strain-controlled test, we define the elapsed measurement time as the time the rheometer waits from the instant that the new shear rate value is imposed until the new stress value is computed. Figure 4 shows that very different flow curves can be obtained from different choices of the elapsed measurement time. The curve  $\tau(\dot{\gamma})$  shift down when the time of getting a point is increased from 10 to 30 seconds, which indicates a great stress time dependence. A further increase on time from 30 to 40 seconds shows no difference on  $\tau(\dot{\gamma})$ . Thus, we assume that 30 seconds is a long enough time to ensure that the steady state measure is achieved. From what was discussed, we conclude that the 30 seconds elapsed measurement time corresponds to the flow curve. It is worth noting here that a value of yield-stress computed before the steady state be achieved can be dramatically different and induces to misunderstandings. In order to check and eliminate any doubt if the flow curve was achieved or not, we choose samples of shear-rate values to displace  $\tau$  over the time. The stress starts with a high value, decreases, and achieves the steady state values of the shear-stress corresponding to ones obtained by the 30 seconds elapsed time experiment. This result gives sufficient evidence that our procedure to obtain the steady state stress curve is good enough. However, an important difference from the previous experiment was the longer time interval necessary for the achievement of the steady state values, showing that, an optimized elapsed measurement time depends on the other settings of the experiment.*

Figure 5 shows the flow curve for the original waxy crude oil, a sample that contains, at least, 3% of asphaltene and resin. The shear-stress is measured for a wide range of shear-rate from a very small value,  $\dot{\gamma} = 1 \times 10^{-6} \text{ s}^{-1}$ , to  $\dot{\gamma} = 100 \text{ s}^{-1}$ . Because we were able to achieve low shear rate values, we could identify that the yield process of this

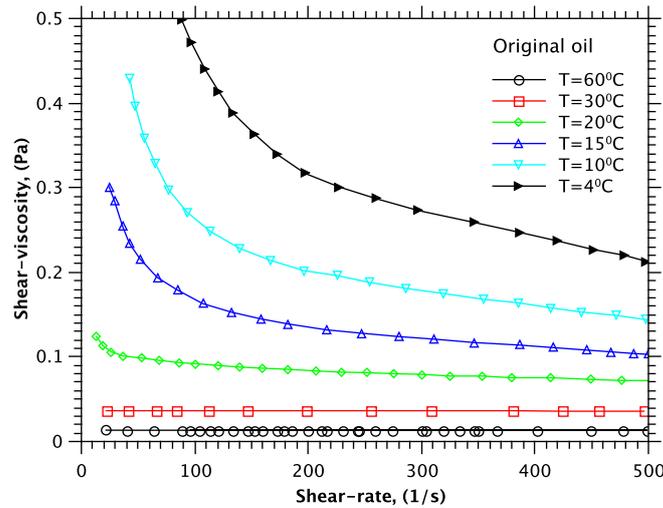


Figure 3. Shear-viscosity,  $\eta$ , of the original oil as a function of shear-rate,  $\dot{\gamma}$ , for a range of temperature.

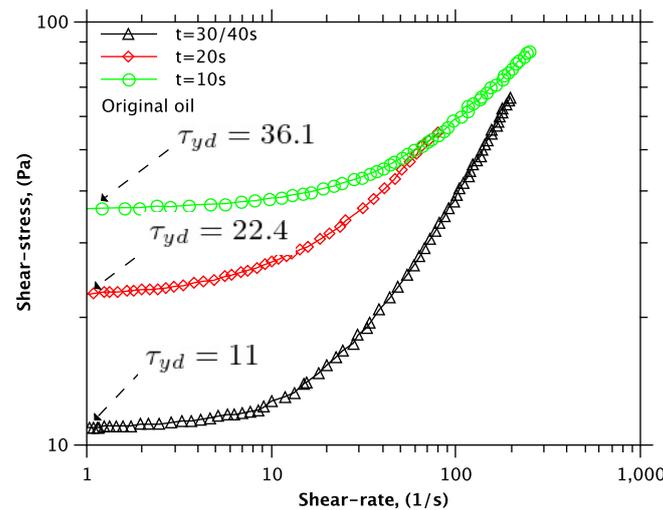


Figure 4. Shear-stress as a function of shear-rate. The test was conducted in an attempt to determine the minimal measuring point time to have a steady state  $\tau(\dot{\gamma})$ , the Flow-Curve (black symbols).

material is classified in the category of apparent-yield-stress fluids. We can see that, for shear rate values below  $10^{-3}\text{s}^{-1}$ , the flow curve falls down some decades in the shear stress measurement. Hence, we identify a creep flow below the “yield stress”. Although it could be argued that this behavior could be caused by slip, this result is in accordance to the findings of Dimitriou-et-al (2011) for another waxy crude oil, where the Hershel-Buckley model could not fit the low shear-rate regime and therefore a Casson model was used. In that work, a cone-plate geometry with roughened surfaces was used to avoid slip. The disadvantage of using the Casson model is that there is no yield stress parameter associated. As discussed in Dimitriou-et-al (2011), the yield-stress value is important even for apparent-yield-stress fluids, because this stress value marks a major break down of microstructure. Besides this apparent-yield-stress nature of the waxy crude oil tested, we can observe a non-monotonic behavior which can be addressed by identifying a static and a dynamic yield stress where the former is greater than the latter. The static and dynamic yield-stress can be directly inferred from the data, as Fig. 5 indicates. The static yield stress,  $\tau_y$ , is the maximum stress value, starting from a very low shear rate and increasing this parameter, in this case,  $\tau_y = 27.8$  Pa. The dynamic yield stress,  $\tau_{yd}$ , can be defined here as the first minimum stress value, starting from a high shear rate and decreasing this parameter, in this case  $\tau_{yd} = 11.4$  Pa. The shear-rate is really small before the static yield-stress is achieved when the visco-plastic structure starts to break and a further increase in  $\dot{\gamma}$  is followed by a decreasing  $\tau$ . The shear-stress falls until the dynamic yield-stress is achieved. This level of stress is characterized by a jump on the shear-rate. In fact,  $\dot{\gamma}$  jumps from around  $0.02\text{s}^{-1}$  to  $10\text{s}^{-1}$  while the shear-stress changes just very slightly. This is caused by a major breakdown on the material structure when  $\tau_y$  is achieved. For the start-up flow problem, where the material is initially at rest, we assume that a stress at least equal the static one is required. Other

wise, as an apparent-yield-stress fluid, the material will undergo a creep flow. Thus, from a practical point of view, the static yield-stress,  $\tau_y$ , is the value of stress that needs to be confronted with the re-start pressure to guarantee a steady state flow. It is worthy noting that the material behavior is quite well predicted by Eq. (6). At shear-rates larger than  $\dot{\gamma} = 0.001 \text{ s}^{-1}$  the data is quite well fitted. Below such shear-rate the material is shear-thickening and, as the referred model consider a constant level of viscosity, the points are not well fitted in the range of  $\dot{\gamma} \leq 0.001 \text{ s}^{-1}$ .

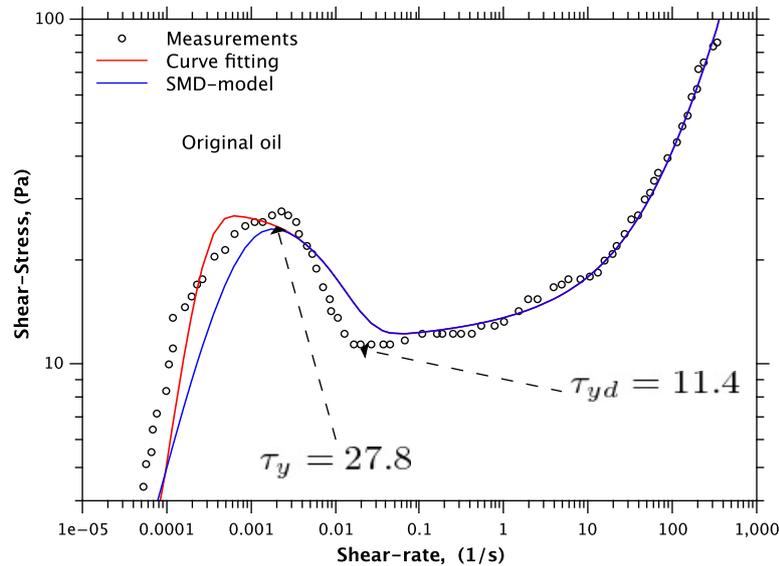


Figure 5. Flow curve of the original oil. The symbols are measurements and the line is a curve fitting provided by a modified SMD model. The rheological curve fitting parameters are:  $\tau_y = 27.8 \text{ Pa}$ ,  $\tau_{yd} = 11.4 \text{ Pa}$ ,  $n = 0.35$ ,  $n_0 = 1.8$ ,  $K = 2 \text{ Pa}\cdot\text{s}^{n+1}$ ,  $K_0 = 90000000 \text{ Pa}\cdot\text{s}^{n+1}$ ,  $\eta_\infty = 0.2 \text{ Pa}\cdot\text{s}$  and  $\dot{\gamma}_{0d} = 0.01 \text{ s}^{-1}$ .

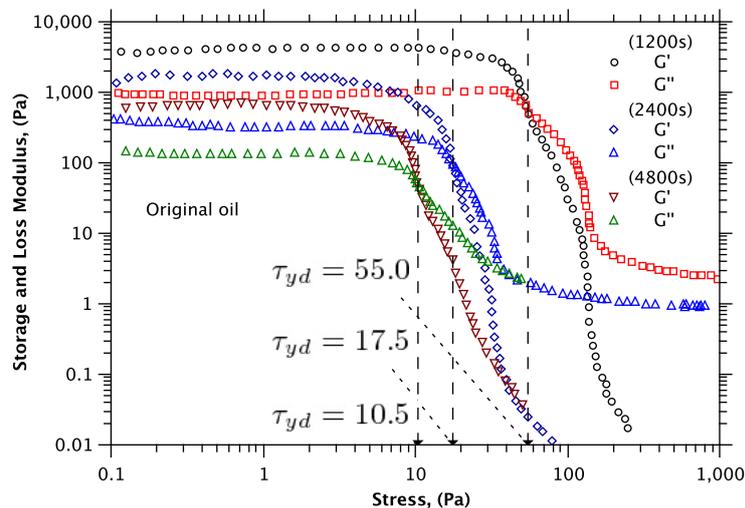


Figure 6. The storage and Loss Modulus,  $G'$  and  $G''$ , respectively, as a function of the Stress intensity,  $\tau$ , at three different test time. The test is conducted by increasing the amplitude of deformation at a fixed frequency  $\omega$ .

As mentioned before, there are many ways to infer about the yield-stress and an oscillatory test that take into account the storage and loss modulus as a function of shear-stress is widely used by the industry, and is worthy of mentioning here. Such kind of test is displayed in Fig. 6. The modulus  $G'$  and  $G''$  is computed by increasing the deformation amplitude with a fixed frequency. As mentioned previously, the dynamic yield-stress can be assumed to be the value of stress where the two curves intercept to each other, i.e. when the loss modulus becomes more important than the storage modulus. As the rheological properties of our oil are time dependent, the same care, when the flow curve was determined, must be taken, i.e. tests must be carried out over a long enough time to certify the steady state was achieved. Keeping in mind such time dependency, we measured  $G'$  and  $G''$  over a range of stress,  $0 \leq \tau_{od} \leq 1000 \text{ Pa}$ , for different periods of time. The value of stress at the intercepting points falls dramatically with an increasing experimental time. In fact, this critical

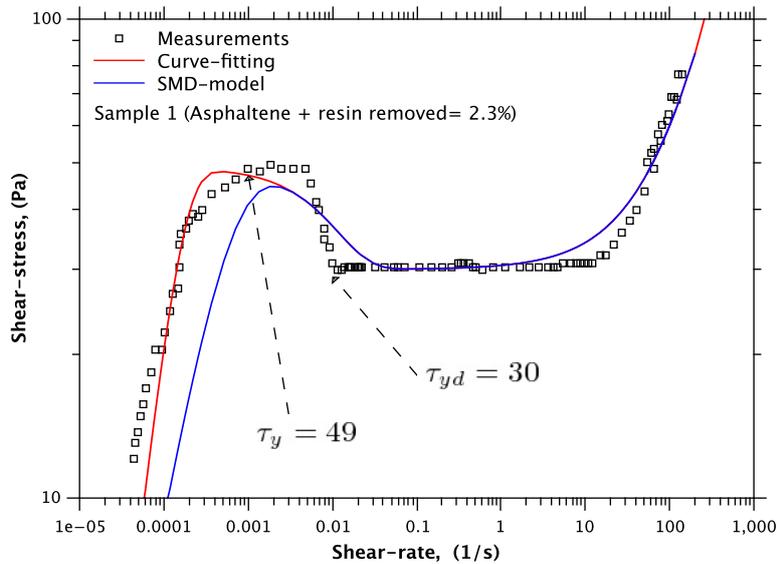


Figure 7. Flow curve with 2.3% of Asphaltene and Resin removed from the original oil. The symbols are measurements and the line is a curve fitting provided by a modified SMD model. The rheological curve fitting parameters are:  $\tau_y = 49$  Pa,  $\tau_{0d} = 30$  Pa,  $n_0 = 1.62$ ,  $n = 0.8$ ,  $K = 0.5$  Pa.s $^{n+1}$ ,  $K_0 = 80000000$  Pa.s $^{n+1}$ ,  $\eta_\infty = 0.1$  Pa.s and  $\dot{\gamma}_{0d} = 0.01$  s $^{-1}$ .

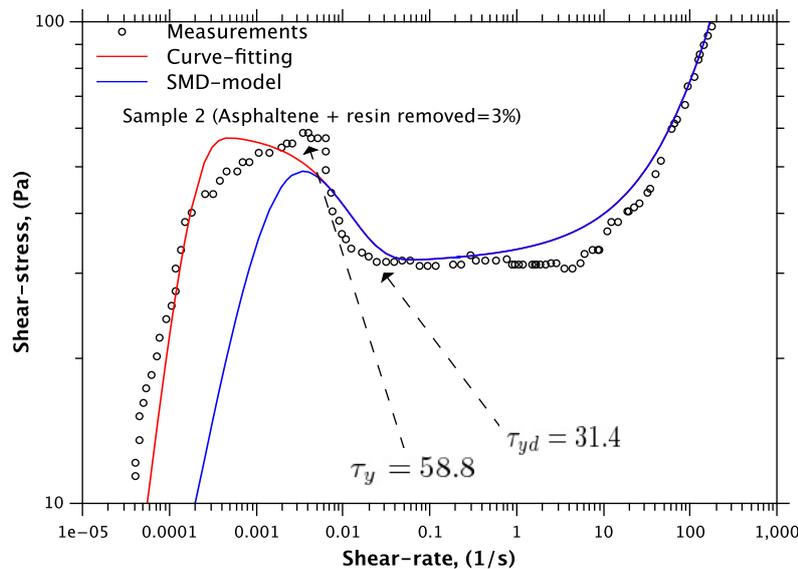


Figure 8. Flow curve with 3% of Asphaltene and Resin removed from the original oil. The symbols are measurements and the line is a curve fitting provided by a modified SMD model. The rheological curve fitting parameters are:  $\tau_y = 58.8$  Pa,  $\tau_{yd} = 31.4$  Pa,  $n = 0.45$ ,  $n_0 = 1.6$ ,  $K = 2$  Pa.s $^{n+1}$ ,  $K_0 = 70000000$  Pa.s $^{n+1}$ ,  $\eta_\infty = 0.28$  Pa.s and  $\dot{\gamma}_{0d} = 0.01$  s $^{-1}$ .

value fell from 55.0 Pa, at a test of 1200 s, to 10.5 Pa, at a test of 4800 s. Such time dependency is very pronounced and a difference of 423% between the two extreme values is really worth of attention. The dynamic yield-stress inferred by the test of 4800 s ( $\tau_{yd} = 10.5$  Pa) is quite close that one obtained by the flow curve, Fig. 5, in which  $\tau_{yd} = 11.5$  Pa. Hence, we can assume that such kind of test could, eventually, be a good alternative to accomplish the value of the dynamic yield-stress close enough to the standard one, obtained by the flow curve. One possible way to infer the static yield stress that is sometimes used is to assign to this entity the stress value where the  $G'$  deviates from the low-shear-stress plateau. However, this procedure is not unequivocally correlated to the concept the static yield-stress,  $\tau_y$ . If we assume that  $\tau_y$  is the main quantity that needs to be calculated for the re-start problem, the analysis of flow curve seems to be more appropriate for practical applications and this is, in fact, the kind of test we conducted here to investigate the role of asphaltene and resin on the paraffin crystal formation.

By adding 0.5 ml of n-heptane, an amount of 2.3% of asphaltene and resin was removed from the original oil. A new

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flow curve was obtained and displayed in Fig. 7. The values of the static and dynamic yield-stress increased dramatically. The former has risen 76.3% while the latter, 163.2%. With addition of 2 ml of n-pentane a larger amount of asphaltene and resin was taken away from the oil and, again, the flow curve was measured and shown in Fig. 8. With respect to the previous results, the dynamic yield stress slightly changed, but the static one increased around 18%. Related to the original waxy crude oil,  $\tau_y$  and  $\tau_{yd}$  increased, respectively, 175.4% and 111.5%. Such an increase is quite impressive and call for attention.

Figures 5, 7, and 8 were fitted by Eq. (6), the blue curve. We found a good agreement between this curve and the experimental data, specially in the shear rate region above the static yield stress. However, for very low values of the shear rate this curve detaches from the experimental one. It is observed a shear-thickening behavior below the static yield stress. A different expression is proposed here that can account for this behavior. It is a slight modification of the one proposed by Eq. (6) and is given by

$$\eta_{eq}(\dot{\gamma}) = \left[ 1 - \exp\left(-\frac{K_o \dot{\gamma}^{n_o}}{\tau_o}\right) \right] \left\{ \frac{\tau_o - \tau_{od}}{\dot{\gamma}} e^{-\dot{\gamma}/\dot{\gamma}_{od}} + \frac{\tau_{od}}{\dot{\gamma}} + K \dot{\gamma}^{n-1} \right\} + \eta_{\infty}. \quad (9)$$

Figures 5, 7, and 8 show that Eq. (9) has a better agreement with the experimental results, allowing a good description at low shear rates values. A decrease in the consistency index,  $K_o$  and the thickening power-law exponent,  $n_o$  is obtained for oil with less quantities of asphaltenes and resins. The viscosity in the minimum structure level differs from the maximum one by a factor of  $10^5$  or  $10^6$ . Hence, when the stress value is above the dynamic yield stress, the waxy crude oil achieves a more mobile state. By comparing these results, we notice that with less asphaltenes in the oil, changes in viscosity occur at a lower range of stress intensity, assuming a more vertical line in the graph. Another important result is that not only the yield stress level increases with the removal of asphaltenes, but the maximum viscosity level also increases.

As the literature also reports, our results strongly suggest that asphaltene and resin play a significant role on the paraffin crystal formation. However, the real effect of asphaltenes on the yield stress needs to be measured considering the time dependency nature of the waxy crude oil. A protocol that does not take this time dependency into account can lead to very different values for the yield stress and, consequently the measured quantity will not represent the real influence of the asphaltenes as wax inhibitors from the rheological perspective. Since the yield stress is a crucial parameter on the determination of the re-start pressure and, consequently, on the pumping project, the accuracy of its measurement is something that the oil industry must pursue.

## 5. Final Remarks

We analyzed the rheology of a waxy crude oil at the temperature of 4°C in a process of constant cooling rate that started from 60°C, and null shear rate, simulating the shut down conditions obtained in ultra-deep oil reservoirs, where a re-start of the production is necessary. The main conclusion of the present analysis concerns the necessity of taking into account the time-dependency nature of the material at these low temperatures. In particular we found that for the Brazilian oil tested, the differences in the dynamic yield stress can achieve more than 300%. These differences can make an enormous impact on the prediction of the re-start pressure and can be a reason for the known fact that laboratory characterization overestimates the yield stress and consequently the re-start pressure.

We used the known property of the asphaltenes as inhibitors of wax formation to quantify its effects from the rheology perspective. To this end we added different amounts of two types of flocculants: n-pentane and n-heptane in order to precipitate asphaltenes and resins. When the virgin oil was characterized, its corresponding static yield stress was  $\tau_y = 11\text{Pa}$ . For a precipitation of  $\approx 2.3\%$  of asphaltenes and resins and a further rheological test made this value rise to  $\tau_y = 49\text{Pa}$ ; while the associated static yield stress value for a precipitation of  $\approx 3\%$  of asphaltenes and resins was  $\tau_y = 58.8\text{Pa}$ .

We also found that the brazilian waxy crude oil tested is an apparent-yield stress fluid and, therefore, it flows at very low shear rates below the static yield stress. This feature, combined with the presence of a dynamic and a static yield stress renders to the flow curve a non-monotonic behavior with a very particular character. In fact, a new flow curve fitting is proposed, adapted from a previous one proposed by souzamedes (2009). This new curve fitting reveals a shear-thickening behavior for very low stress values, in the pre-yielding regime. The whole non-monotonic flow curve can only be obtained in a constant shear rate input, because a constant shear stress input leads to more than one value as a corresponding shear rate. Because of this fact, there is a part of the flow curve that is considered not stable Maki-Renardy (2010) and leads to the possibility of shear banding effects Bautista-et-al (2012).

## 6. ACKNOWLEDGEMENTS

This research was partially funded by grants from CNPq (Conselho Nacional de Pesquisa e Desenvolvimento), ANP (Agência Nacional de Petróleo) and PETROBRAS.

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