

CRYSTALLISATION AND GELATION OF WAXY CRUDE OILS UNDER FLOWING CONDITIONS

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INTRODUCTION

The crystallisation of wax in crude oils and petroleum products (gelation) causes major difficulties in the transport and the storage of these fluids. Accurate measurements of the flow properties are necessary to provide data for designing the pipelines and predicting the conditions for restarting the line when the oil gelled. These measurements are rather complex as the flow characteristics of waxy crude oils are strongly influenced by the cooling and shearing conditions [1, 2, 3, 4, 5]. They are time and history dependent. In this paper we present an investigation of the effects of the shearing on the building up of the structure of a crude oil, below the wax crystallisation temperature. By comparison, the visco-elastic properties of the gel made at rest are given. The non-Newtonian characteristics of the oil are interpreted by analogy with colloidal suspensions, which allows to understand qualitatively the effect of shearing on the structure of these fluids.

1 MATERIALS AND METHODS

A Carrimed TA Instrument CSL²100 has been used for this study. The cone-plate geometry with a diameter of 4 cm and a cone angle of 2° was adopted for measuring the flow rheograms. The dynamic G' and G'' moduli were measured in a plate-plate geometry, the upper plate has a roughened

surface. The temperature was accurately controlled by a Peltier device ($\pm 0.1^\circ\text{C}$) and the geometrical gap was automatically compensated for temperature vibrations. The sample investigated in a crude oil form an offshore platform in Indonesia. It contains about 23 wt% of n-paraffins $> C_{10}$ and has a pour point of 33°C. Previous to the rheological measurements, the samples were heated during 30 min at 60°C to allow evaporation of volatile components. In these conditions, the results were reproducible with a good accuracy by repeating experiments on the same sample. Small variations of the thermal behaviour appeared from one sample to another.

2 THE WAXY GEL

It is important to realise that in normal operating conditions the waxy crude oils are produced in a fluid state, as they circulate due to the well pressure or due to the pumping. When the oil is allowed to gel in quiescent conditions, like for instance after a shut down, a totally different state is reached. In order to illustrate this property, we have measured the visco-elastic properties of the crude oil sample cooled at rest. The experiment was performed at a cooling rate of $-0.5^\circ\text{C}/\text{min}$ between 40 and 20°C in the rheometer, with a plate-plate geometry. Using this rate of decrease of the temperature, no time dependence of the moduli could be seen for the cooling curve. The amplitude of deformation was 10^{-3} and the frequency was 1 Hz. In Figure 1, one can see a steep increase, around 37°C, of the visco-elastic moduli, G' and G'', which then reach a quasi plateau between 32°C and 20°C, with very high values of $G' = 2 \cdot 10^6 \text{ Pa}$ and $G'' = 10^5 \text{ Pa}$. (These results have been

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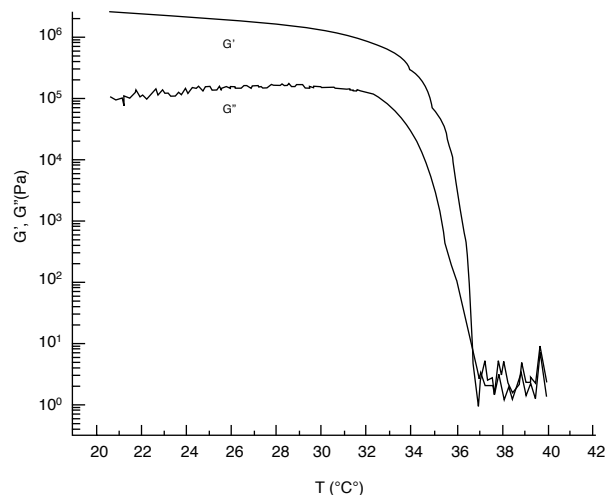


Figure 1

The shear moduli G' and G'' measured during cooling of the crude oil sample between 40 and 20°C. The frequency is 1 Hz and the amplitude of deformation 10^{-3} .

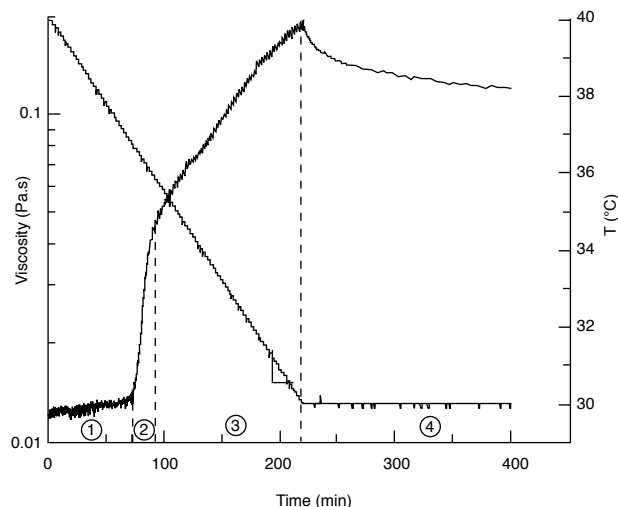


Figure 2

Changes of the apparent viscosity during cooling between 40 and 30°C under shear at 100 s^{-1} . The cooling rate is $0.045^\circ\text{C}/\text{min}$. See text for explanations about the different parts of the curve.

confirmed using a Couette geometry in a different instrument, which proved that these reported values are reliable). During a subsequent temperature increase, we also measured G' and G'' (data not shown): the measurements showed marked, hysterical effects compared with the cooling curve which depended on the final value to which the sample was cooled. The melting curves brought some interesting information on the mechanical stability of the system and the presence of built-in defects.

3 GELATION UNDER SHEAR

In many scenarios of oil production, the crude oils are transported in flow lines where they undergo temperature drop due to the environmental conditions. In this case, a non-Newtonian fluid state is reached when temperature drops below the wax crystallisation temperature. We investigated the changes of the viscosity η of the oil during cooling below 40°C, while a flow was imposed at fixed shear rate. In Figure 2, viscosity in a logarithmic scale and temperature are plotted versus time. The viscosity is defined as the ratio between the shear stress and the shear rate (apparent viscosity). The temperature was lowered by $0.045^\circ\text{C}/\text{min}$ between 40 and 30°C, the shear rate $\dot{\gamma}$ was constant during all the experiment, equal to 100 s^{-1} . This slow rate of cooling is necessary in order to clearly reveal the different stages of the crystallisation process. The curve $\log \eta$ (time) can be composed in four parts: in the 1st part ($0 < t < 80 \text{ min}$), when temperature varies between 40 and 37°C, the viscosity is low (0.01 Pa.s) and changes little with temperature. Starting around 37°C, in the 2nd part of the curve ($80 < t < 100 \text{ min}$), a

steep increase of the viscosity occurs, which corresponds to the beginning of the crystallisation for the longest paraffins. A large increase of the viscosity, is observed within one °C, at 36°C (end of the 2nd part), up to 0.05 Pa.s. In the 3rd part ($100 < t < 220 \text{ min}$), between 36 and 30°C, the rate of increase of the viscosity changes again, an increase of the viscosity with temperature lowering is still observed, but, due to the shearing, the viscosity increases more gently and reaches at the end of the cooling stage only 0.32 Pa.s (at $T = 30^\circ\text{C}$, end of part 3). This is the maximum value reached during cooling. In the 4th part of the curve ($t > 220 \text{ min}$), temperature is constant, equal to 30°C and the changes in viscosity are recorded versus time during 180 min. In this part, in contrast with the beginning of the curve, viscosity decreases with time: the shearing destroys the existing microstructure and the viscosity reaches a time independent, lower value, after a few hours.

The effect of the shear rate was systematically investigated by applying temperature sweeps of $-0.5^\circ\text{C}/\text{min}$ with a final temperature of 30°C, and imposing shear rates of 1000, 500, 100 and 50 s^{-1} . The results are shown in Figure 3, equivalent to steps 1 to 3 of Figure 2. Viscosity is plotted versus temperature. One can notice on these curves that the beginning of the crystallisation (end of part 1 and beginning of part 2) coincides on all the different runs at $T = 38^\circ\text{C}$ for this particular sample (instead of 37°C of the previous example). We may call this limit the maximum crystallisation temperature. The flow curves distinctly separate below some limiting temperatures, which indicate the end of part 2. These temperatures appear quite precisely on the diagrams: they range between 36.5 and 37.5°C when the shear rate varies from 1000 to 50 s^{-1} . In part 3 the curves

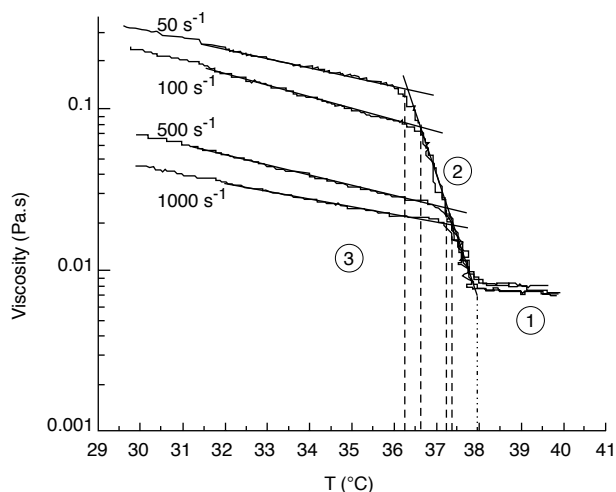


Figure 3

Effect of the shear rate on the viscosity of samples cooled and continuously sheared. The shear rates are indicated on the curves. See text for explanations about the different parts of the curves.

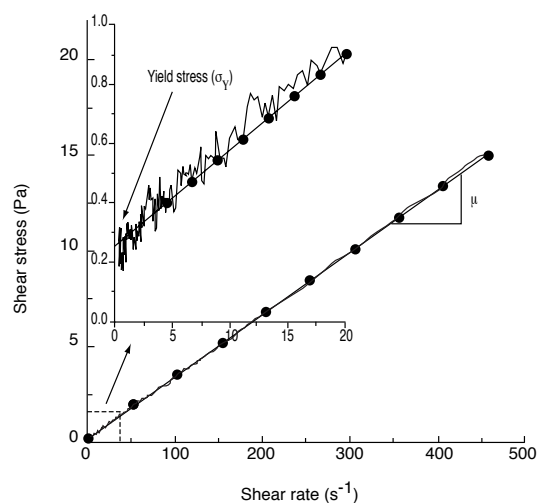


Figure 4

Rheogram of the sheared samples. This particular sample has been sheared under a shear stress of 500 s^{-1} during 5 hours at 30°C . The cooling rate, from 40 to 30°C , was $0.5^\circ\text{C}/\text{min}$. The rheogram is realised by increasing shear rates. The dots indicate the calculated values using a Bingham equation, $\sigma_Y = 0.25 \text{ Pa}$ and $\mu = 0.032 \text{ Pa.s}$.

are parallel, the larger viscosities correspond to the lower shear rates. Viscosity increases slightly when temperature is decreased in this range. The values obtained at 30°C scale between 0.3 and 0.04 Pa.s depending on the shear rate.

4 RHEOGRAMS OF THE SHEARED OIL

The oil cooled and sheared simultaneously reached a fluid state, with a rather low viscosity. We have fully investigated the rheological state of these fluids (cooled from 40 to 30°C , at a cooling rate of $-0.5^\circ\text{C}/\text{min}$, under different shear rates, then sheared continuously during 5 hours at 30°C). All the rheograms correspond to a yield stress fluid, with a very low yield value. An example is given Figure 4, for a sample sheared at 500 s^{-1} . Rheograms, like the one shown in Figure 4, can be interpreted as Bingham fluids obeying to the relation:

$$\sigma = \sigma_Y + \mu \dot{\gamma} \quad (1)$$

where σ_Y is the yield stress and μ is the Bingham viscosity. In the present example $\sigma_Y = 0.25 \text{ Pa}$. and $\mu = 0.032 \text{ Pa.s}$. The rheograms are reversible as long as the shear rates do not exceed the shear rate imposed during the cooling stage.

The fact that the fluid behaves as a solid material below the yield stress was corroborated by dynamic measurements of G' and G'' for oscillations with an amplitude of 0.03 Pa : the modulus G' was frequency independent and well above G'' ($G' = 250 \text{ Pa}$ and $G'' = 140 \text{ Pa}$, for the example of Figure 4).

The value of G' , G'' measured at 1 Hz , σ_Y and μ for samples sheared at various shear rates, are given in Table 1. The yield stress and the visco-elastic moduli vary little with the shear rates. They reveal the presence of a weak network which builds when the oil is let at rest. The ratio σ_Y/G' is constant for the cases investigated and of the order of 10^{-3} . This ratio is homogeneous to a deformation and is the maximum deformation to which the network can be submitted without flowing. For ideal crystals, without defects, σ_Y and G' are of the same order of magnitude, thus, such low values of the maximum deformation are generally ascribed to the movement of dislocations of the network under shear. Comparable values have been observed in ordered suspensions of monodispersed latexes by Mitaku *et al.* [6].

In Table 1, the Bingham viscosity varies by a factor of 10 for the range of shear rates investigated: the sheared suspensions probably contain various types of crystalline aggregates, the larger the shear rate to which the oil has been submitted, the lower the viscosity.

We introduce in the next section the theoretical framework which can be used to interpret qualitatively the effect of the shearing on the structure of a waxy crude oil cooled below its crystallisation temperature.

5 INTERPRETATION AND DISCUSSION

A waxy crude oil contains, among other, large amount of *n*-paraffins of high molecular weights which crystallise at

TABLE 1

Rheological parameters for samples sheared at different shear rates during 5 hours at 30°C and cooled under shear. For the experiment performed at 5000 s⁻¹ we used a cone-plate geometry with an angle of 0.5°

	10 s ⁻¹	50 s ⁻¹	100 s ⁻¹	500 s ⁻¹	1000 s ⁻¹	5000 s ⁻¹
G'	–	–	210 Pa	250 Pa	270 Pa	–
G''	–	–	165 Pa	140 Pa	140 Pa	–
σ _γ	0.21 Pa	0.2 Pa	0.22 Pa	0.25 Pa	0.25 Pa	0.27 Pa
μ	0.25 Pa.s	0.1 Pa.s	0.888 Pa.s	0.034 Pa.s	0.026 Pa.s	0.01 Pa.s

different temperatures, below the maximum crystallisation temperature (in the present case 37-38°C). Crystallites are assembled into aggregates or clusters suspended into the continuous fluid phase. So, in the present description we distinguish individual particles or crystallites from aggregates or clusters, built of individual particles. Particles tend to aggregate and are held together in clusters by weak interactions of a physical nature (Van der Waals interactions, components limiting the growth of the paraffin crystals, bridging by entangled molecules at the surface of the particles). However, the clusters are rigid and can break when they are submitted to bending forces. According to Wessel and Ball [7], the clusters in suspension evolve under flow towards a maximum stable size, determined by the applied shear rate and the breaking condition. In other words, the hydrodynamic forces due to the shear limit the growth of aggregates and prevent them from building a network. Let *a* be the radius of a particle supposed to be spherical, *R* the radius of gyration of a cluster, η₀ the viscosity of the surrounding fluid or solvent. The suspension is submitted to a flow at a shear rate $\dot{\gamma}$.

During flow, a cluster experiences at its surface a shear stress σ which is given by $\sigma \sim \dot{\gamma} R$ and corresponds to the force:

$$F \sim R^2 \sigma \quad (2)$$

This force exerts a bending moment $\Gamma = R F$, thus:

$$\Gamma \sim R^3 \sigma \quad (3)$$

Due to their microstructure, one can assume that above a critical value of the torque, Γ_c , the clusters break into smaller units. The critical value Γ_c depends on the physical interactions inside the cluster. The breaking condition relates the maximum stable cluster radius or critical radius R_c to the solvent viscosity and to the shear rate $\dot{\gamma}$:

$$\Gamma_c \sim R_c^3 \eta_0 \dot{\gamma} \quad (4)$$

or

$$R \sim (\Gamma_c)^{1/3} (\eta_0 \dot{\gamma})^{-1/3} \quad (5)$$

This very simple presentation allows to predict the effects of the shear rate on the growth the crystalline clusters under shear. The largest clusters are formed at the lower shear rates.

According to this model, a power law dependence is expected for the critical radius versus the shear rate with an exponent $-1/3$.

The relation between viscosity and the size of the clusters can be derived by assuming that the clusters behave like compact spheres screening the fluid in the interior from outside. The viscosity of the suspension then is related to the cluster volume fraction Φ .

Let *n* be the number of particles per unit volume, *N* the number of clusters per unit volume. Thus the volume fraction of particle is:

$$\psi \sim n a^3 \quad (6)$$

and the volume fraction of clusters with a radius *R* is:

$$\Phi \sim N R^3 \quad (7)$$

The number of particles per cluster is *n/N*. If we assume that the clusters have a fractal structure with a fractal dimension *D*, then,

$$\frac{n}{N} \sim \left(\frac{R}{a}\right)^D \quad (8)$$

In the limit of a dilute regime, Einstein's equation applies and the relative increment of viscosity η of the suspension is proportional to the volume fraction of clusters. Thus one can establish a simple relation between the viscosity η of the suspension and the shear rate $\dot{\gamma}$:

$$\frac{\eta - \eta_0}{\eta_0} \sim \Phi \sim \psi \left(\frac{R}{a}\right)^{3-D} \quad (9)$$

or

$$\frac{\eta - \eta_0}{\eta_0} \sim \psi \left[\frac{\eta_0 \dot{\gamma} a^3}{\Gamma_c} \right]^{-\frac{3-D}{3}} \quad (10)$$

For fractal clusters, the viscosity of the suspension is thus proportional to the volume fraction of individual particles ψ and it varies with the shear rate with an exponent $D/3-1$ where $1 < D < 3$. The viscosity decreases with the shear rate.

This simple analysis is rigorously valid for very dilute suspensions, but it allows to qualitatively predict the consequences of shearing on a suspension to high shear rates, when individual non interacting clusters are present.

The conclusions which one can draw from the present investigation are the following:

when temperature is lowered, crystals of paraffin begin to form progressively, building clusters. When the clusters are small, the suspension is Newtonian, not shear depending. The clusters grow until they reach the maximum size allowed by the shear rate and the internal cohesion forces. These features appear clearly in Figure 3: the change from part 2 to part 3 occurs when the maximum size of the clusters was reached. Further cooling the crude oils brings only a small increase of the viscosity which can be ascribed to new crystallites nucleated in the surrounding fluid (part 3 of the viscosity

versus temperature curves). This increase of viscosity depends very little on the shear rates: one can interpret this behaviour by assuming that in this range of temperatures the new clusters are smaller than the critical size and the shear does not control their growth. When the shearing is stopped, a solid like behaviour is observed which is a very weak solid (compared with the gel made at rest, a factor of 10^4 !). This physical soft network is made of individual clusters hold together by weak interactions.

Investigations of the structural parameters of the sheared suspensions and of the gels made at rest are necessary in order to understand more quantitatively the well marked changes that appear in the rheology of these fluids.

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