

Shear thinning behavior of heavy oil samples: laboratory measurements and modeling.

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Summary

Viscoelastic measurements of four heavy and extra-heavy oil samples were carried out to analyze the dependence of complex viscosity, loss and storage modulus with temperature and frequency. The dynamic rheological tests showed a shear thinning phenomenon typical of non-Newtonian fluids, highly pronounced for seismic and sonic frequencies and for temperatures below 50°C. The Power-Law method that explains the shear thinning behavior was modified to incorporate the liquid crystal theory and the viscosity dependence on temperature based on the concept of activation energy. An expression was derived to predict complex viscosity based on frequency and temperature changes.

Introduction

The need to characterize fluid flow properties of unconventional reservoirs, such as heavy and extra-heavy oils, has increased significantly in the last few years. Heavy oil properties are particularly dependent on frequency and temperature changes. According to its rheological properties, it can be considered a Non-Newtonian viscoelastic fluid, which means shear stress and shear strain rate are not linearly correlated. Since such materials have an elastic component, they are able to support shearing.

Previous ultrasonic measurements have shown that shear wave velocity dispersion might be significant for heavy oils at in-situ conditions. Velocity dispersion (for P- and S-waves) seems to be negligible for heavy oils in the liquid and glass (elastic) phases (Han et al., 2007).

There have been numerous studies in the past on crude oils concerning the shear-thinning (complex viscosity decrease as shear strain rate increases) behavior obeying the Power-Law model at reservoir temperatures (Wang et al., 2006). Above a certain temperature, sometimes called the liquid point temperature (Han et al., 2006), heavy oil becomes Newtonian and viscosity becomes independent of the shear strain rate (or frequency).

This paper aims to model the shear thinning behavior of heavy oil at a given temperature as frequency increases by using the concept of activation energy of the Arrhenius equation and liquid crystal theory. Laboratory measurements of the viscoelastic properties of four heavy and extra-heavy oil samples are used to improve the model.

Theory and experiment procedure

For non-Newtonian viscoelastic materials, the complex shear modulus (G^*) is given by the in-phase elastic component or storage modulus (G') and the out of phase viscous component or loss modulus (G''). G' and G'' represent the ability for a material to store energy elastically and to dissipate energy respectively, according to the following equation:

$$G^*(\omega) = G'(\omega) + G''(\omega) \quad (1)$$

where G^* represents the overall resistance to deformation.

The complex viscosity (η^*) or resistance to flow is simply the ratio of the complex shear modulus and frequency.

$$\eta^*(\omega) = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \quad (2)$$

In the case of a Newtonian fluid, the elastic component is zero or negligible and phase lag (δ) is also zero. However, for viscoelastic fluids, δ varies between 0 and 90 degrees.

$$\tan \delta = \frac{G''}{G'} \quad (3)$$

For a detailed explanation of these relationships, the reader is referred to the book by Ferry (1980).

The dynamical rheological measurements consist of subjecting the oil sample to a continuously oscillating (sinusoidal) strain (γ) over a range of frequencies and measuring the peak value of the stress (σ) and the corresponding phase lag. This is usually referred as Dynamic Frequency Sweep testing. It is fundamental to verify that measurements are done within the region where the Boltzmann superposition principle is valid (linear viscoelastic regime). Initial and final frequencies selected are 0.01 to 100 rad/s with a temperature range from 15 to 75 °C.

A total of four heavy and extra-heavy oil samples were used for this experiment. Table 1 summarizes their densities and API gravities.

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Sample	API gravity	Density (g/cc)
1	9.38	1.004
2	14.27	0.971
3	10.97	0.993
4	8.6	1.009

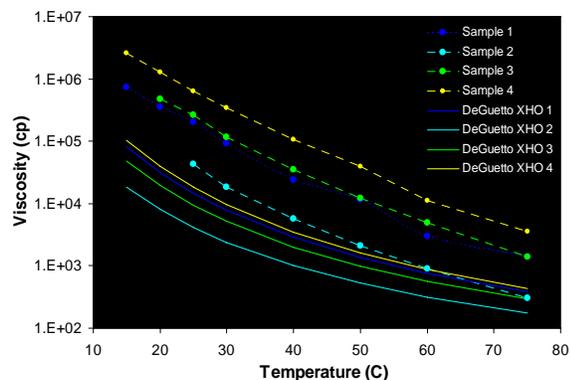
Table 1. Densities were measured at standard conditions.

Results

Viscosity versus Temperature

The complex viscosity trend with temperature for Newtonian and viscoelastic fluids indicates that η^* decreases significantly as temperature increases at low temperatures, while for high temperatures η^* decreases slowly with temperature at high temperatures. This is clearly shown by the DeGuetto empirical model (Figure 1), which predicts similar η^*-T trend but with considerably lower viscosities.

Measured data reflects three stages. In the first stage viscosity decreases rapidly by 2 orders of magnitude for temperatures below 30 °C. For temperatures between 40 and 50°C, the viscosities decrease more slowly. At higher temperatures, η^* decreases faster than stage 2 but lower than stage 1 (Figure 1). Results for Sample 1 were repeated using two different rheometers giving similar response.

Figure 1. η^* versus temperature for a frequency of 10 Hz. Lab data and DeGuetto empirical model are compared.

Phase transition theory for liquid crystal polymers (LCP) can be used to explain our observations. A liquid crystal state is a distinct phase observed between crystalline (solid) and isotropic (liquid) phases. In this state, the nematic phase is characterized by no positional order but molecules tending to align in the shear direction (Figure 2). The solid-nematic transition corresponds to stage 1 to 2, while the nematic-isotropic transition corresponds to stage 2 to 3. These transitions are very subtle for these oil samples since no actual crystallization occurs among other reasons.

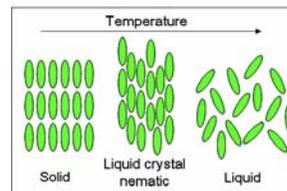
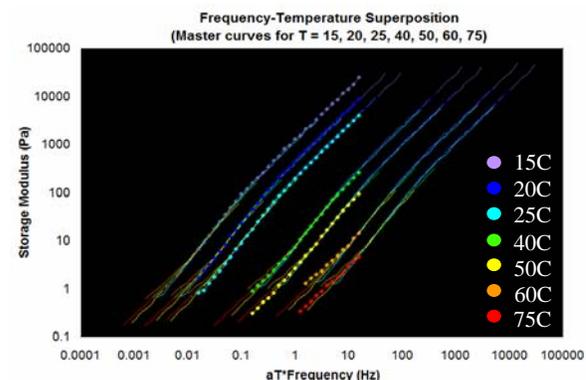


Figure 2. Liquid crystal polymers and their 3 states.

Frequency – Temperature Superposition

The frequency – temperature superposition principle is a very well-known method in rheology to increase the frequency range covered by the original data. This principle is based on the fact that changes measured by the sample at low temperatures are similar to those caused at high frequency and vice versa (Menard, 1999).

For heavy and extra-heavy oils, this principle can be applied; however, for crystalline or multiphase polymers, the presence of multiple relaxation times for each temperature invalidates this approach. This principle can only be used for the liquid crystal phase bounded by the glass transition temperature (T_G) and the isotropic state.

Figure 3. Master curve G' versus frequency for Sample 1. The dot points corresponds to the actual data measured and the lines is the result of the superposition principle.

Master curves are computed by collapsing all the curves to a single reference temperature. This requires a shift factor aT (x axis) accounting for the change in the time scale (Aklonis and MacKnight, 1983). The same shift factor (aT) was applied to G' , G'' and, η^* for each of the samples (Figures 3 and 4).

The trend of the storage modulus (G') with frequency for different temperatures shows a Power-Law region with similar relaxation time although the theoretical plateau zones (Figure 5) corresponding to very low frequency (viscous region) and very high frequency (glassy or elastic region) are absent. This behavior was found for all samples.

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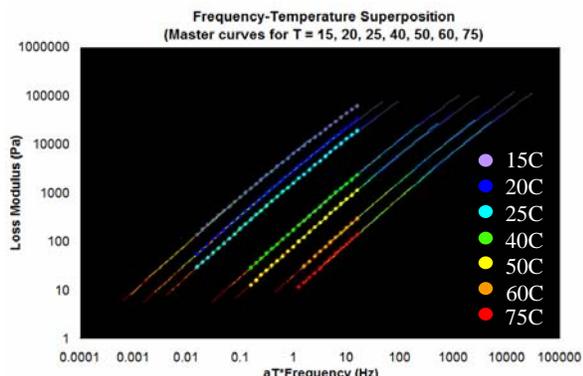


Figure 4. Master curve G'' versus frequency for Sample 1.

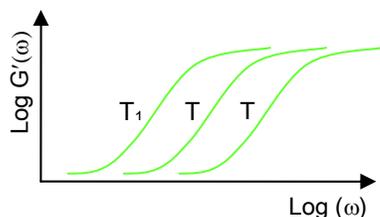


Figure 5. Temperature dependence of G' as a function of frequency (Modified from Christensen, 1971).

Using equation (1) and (2), complex viscosity was calculated based on the results obtained in Figure 3 and 4.

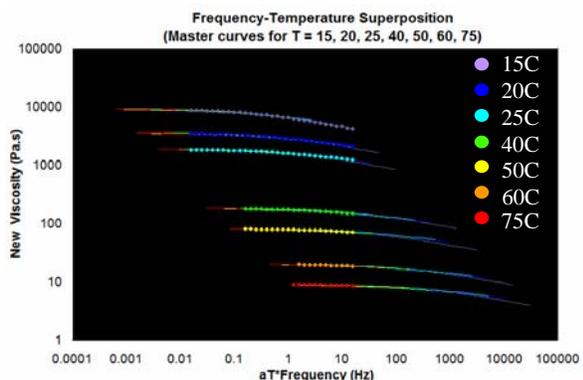


Figure 6. Master curve for complex viscosity as a function of reduced frequency. Note the shear thinning behavior as viscosity decreases with increasing frequency.

Most of the empirical relationships and techniques used for hydrocarbon exploration assume a Newtonian fluid. However, for seismic and sonic frequencies the effect of the elastic component is comparable to the viscous component for temperatures below 50 °C. It is in this range where frequency dispersion and attenuation become

remarkably important. Above that temperature, G'' increases significantly in comparison to G' (one order of magnitude approximately) and for seismic frequencies the Newtonian assumption might be valid.

Viscosity versus frequency

Figure 6 shows complex viscosity decreases as frequency increases. This is called the *shear thinning* phenomenon and it is a typical non-Newtonian behavior that occurs when spherical particles elongate to cigar shapes as shear rate increases. Since they maintain the same volume but cross-section reduces; viscosity decreases. This was evident on all samples and to a lesser degree for sample 2.

Solving the constitutive equations for viscoelastic fluids can be challenging since mechanical and transfer equations need to be solved simultaneously. However, there are several models that can be used to correlate complex viscosity and frequency. One of those is called the Power-Law model and it is strictly used for materials showing shear thinning. The expression for complex viscosity is given by:

$$\eta^* = K\dot{\gamma}^{n-1} \quad (4)$$

where K is a constant, $\dot{\gamma}$ is the strain rate, and n is the Power-Law index.

The activation energy controls the rate of molecular motion and therefore the flow of the liquids (Fan et al., 2003); consequently, viscosity can be considered as a thermally activated process whose temperature dependence is given by:

$$\eta^* = \eta_\infty \exp\left(\frac{E}{RT}\right) \quad (5)$$

where E is the activation energy, R is the ideal gas constant and T is the absolute temperature. If E is independent of temperature, our data should give a straight line when plotted in Arrhenius coordinates, that is $\log \eta$ vs. $1/T$.

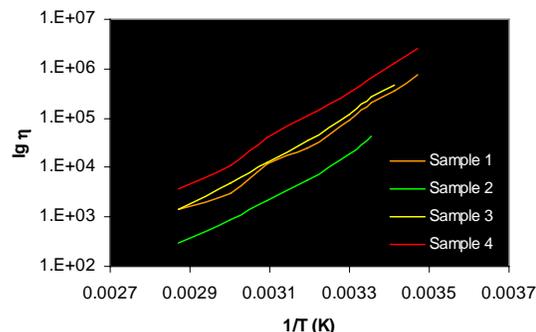


Figure 7. E is independent of temperature.

Combining equations 4 and 5 and, using the liquid crystal theory that bounds the shear thinning region through T_G

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(glass transition temperature) and T_C (temperature at which we “jump” into the isotropic state), we derive the following expression to relate complex viscosity, frequency and temperature:

$$\eta^* = K\omega^n \exp\left(\frac{E}{R}\left(\frac{1}{T_G - T} + \frac{1}{T_C - T}\right)\right) \quad (6)$$

Using the least squares method, we proceed to calculate E , K , T_G and T_C for each of the samples. The Power-Law index is fairly constant with temperature and varies between 0.6 and 0.9 for all the samples. For temperatures above 60-75 °C (333.15-348.15 K), this equation fails to properly predict viscosity since the shear thinning phenomenon is very subtle. T_G estimated through the inversion agrees with the results measured in the lab using differential scanning calorimetry for a heating rate of 10 °C/min. Both T_G and T_C are very similar for all the samples.

The inversion results show a very good fit and are summarized in Table 2. The values of E and K are very similar with the exception of sample 2, due to its lower density and the fact that we are missing temperature information for 15 and 20 °C.

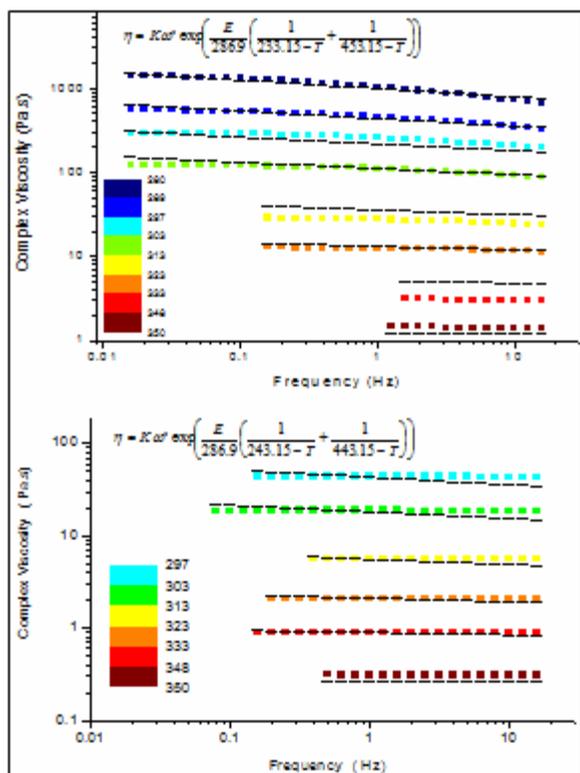


Figure 8. Inversion for sample 1 and 2.

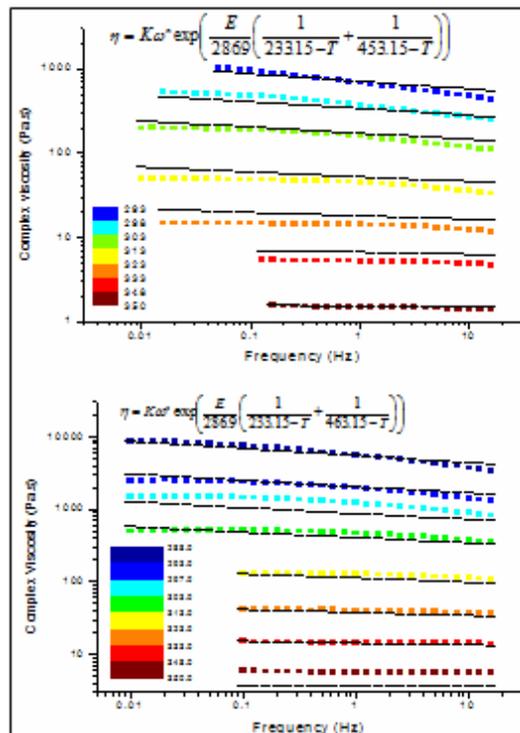


Figure 9. Inversion for sample 3 and 4.

Sample	R^2	K	E
1	0.995	5.146 ± 0.233	133811.25 ± 1211.95
2	0.979	0.408 ± 0.049	118283.35 ± 3115.83
3	0.982	4.141 ± 0.305	183870.99 ± 2810.40
4	0.988	3.661 ± 0.381	168273.68 ± 2490.57

Table 2. Summary of inversion results.

Conclusions

Heavy and extra-heavy oils analyzed in this study display a non-Newtonian behavior due to the presence of an elastic component, which becomes very important for temperatures lower than 50 °C. An expression combining the Power-Law model, Arrhenius equation, and the liquid crystal theory were used to explain not only the shear thinning phenomenon but also to estimate effectively complex viscosity in terms of frequency and temperature.

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EDITED REFERENCES

Note: This reference list is a copy-edited version of the reference list submitted by the author. Reference lists for the 2008 SEG Technical Program Expanded Abstracts have been copy edited so that references provided with the online metadata for each paper will achieve a high degree of linking to cited sources that appear on the Web.

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