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Rheological Investigation on the Effect of Shear and Time Dependent Behavior of Waxy Crude Oil

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Abstract—Rheological measurements are essential in transporting crude oil, especially for waxy crude oil. Several rheological measurements have been conducted to determine various rheological properties of waxy crude oil including the viscosity, yield strength, wax appearance temperature (WAT), wax disappearance temperature (WDT), storage modulus and loss modulus, amongst others, by using controlled stress rheometers. However, a procedure to determine the correct parameters for rheological measurements is still unavailable in the literature. The paper aims to investigate the effect of shear and time dependent behaviours of waxy crude oil during rheological measurements. It is expected that the preliminary work could lead toward a proper rheological measurement guideline for reliable rheological measurement of waxy crude oil.

1. Introduction

In the oil and gas fields, about 20% of petroleum reserves produced and pipelines are waxy crude oils [1]. Waxy crude oils are aliphatic hydrocarbon having high molecular weight paraffin consisting of both straight and branched chains with carbon number ranging from C_{18} to C_{65} [2]. The solubility of paraffin waxes is dependent on the temperature, i.e. it decreases with decreasing temperature. At reservoir conditions where the temperature ranges around 70 to 150°C with pressure ranges of 50 to 100MPa, the solubility of the paraffins in the crude oil is adequately high. The wax molecules are fully dissolved in the crude oil mixture resulting in a single-phase crude oil, in the absence of other components and contaminants and the crude oil behaves predominantly Newtonian with low viscosity [3]. Once the crude oil leaves the reservoir at a high temperature and flows through cold pipelines placed on the seabed with temperature ranging normally from 20°C down to 5°C, the crude oil temperature begins to drop dramatically due to the heat loss to the surroundings.

When the temperature of crude oil is decreased below the Wax Appearance Temperature (WAT), the solubility of the high molecular weight paraffins in the crude oil is decreased. The saturation limit will be reached causing instability and precipitation of the wax molecules out of the liquid solution. A paraffin deposit will form as the molecules precipitated in the form of solid crystals. These solid crystals will adhere to the cold surface of the pipeline walls, which is normally at the lowest temperature compared to the core of the pipeline. This radial temperature gradient results in the wax mass flux towards the wall of the pipelines [4]. If no mitigation strategies are taken to increase the pipeline temperature, the paraffin deposits will further thicken over time reducing the diameter of the

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operation at platform mainly for maintenance or emergency reasons, the crude is static and under such conditions, the temperature within the pipeline is subjected to the external factors and drops significantly especially in the case for subsea installations and in the arctic regions. Significant temperature decrease beyond the WAT will result in a gel-like structure of which the yield stress and thixotropic behavior are highly significant. Predicting the restart pressure for this gelled waxy crude has always been a challenge due to the high yield strength and the thixotropic nature of the crude.

To overcome the challenges related to flow assurance, specifically for waxy crude oil, a great understanding of the rheological characteristics, amongst others, is required. Based on existing literature available, various rheological measurements have been conducted to assess similar rheological parameter i.e. the elastic modulus, G' and the loss modulus, G", viscoelastic region, yield stress, viscosity and thixotropy, amongst others. In describing the gelation and yielding behavior for gelled waxy crude oil for example, many literatures and findings are available. [5-8] studied the effect of cooling rate on the strength of the waxy crude oil gels formed under static cooling. Contradicting observations were also documented. [5] observed that a larger cooling rate produced stronger gels while [6-8] observed otherwise. The strength of the gelled waxy crude oil described in the literature cited above can be obtained utilizing various geometries on the rheometer; the cone and plate, the parallel plate and the vane geometry; and protocols; the creep-recovery test, the oscillatory test, the stress ramp test and many more which may possibly contribute to the variation of findings.

Reliable rheological measurements and methods are then critical without which findings would tend to contradict. The contradictory findings may arise due various understanding of a phenomena, for example, several definitions on yield stress exists resulting in different experimental protocols developed, and also due to errors. [9] highlighted errors associated with rheology measurements include thermal and shear history, aging, composition (including the loss of light ends during pretreatment and measurements), gap dependency, geometry utilized and also wall slip artefact.

To minimize the errors, proper setting parameters for the rheological measurements are required. This paper aims to first investigate the effect of shear and time dependent behavior of waxy crude oil on the determination of setting parameters for reliable rheological measurement.

2. Methodology

A waxy crude oil from Malaysia basin is utilized in this study. Controlled stress rheometer AR-G2 was used for all rheological measurements using a 40 mm cross hatched parallel plate geometry to minimize apparent wall slip phenomena. It is worth noting that this method of minimizing wall slip is still being researched and discussed as highlighted by [9]. Parallel plate geometry was utilized (instead of cone and plate geometry) to anticipate the availability of wax crystals during measurement which cannot be accommodated by small truncation gap in case of cone and plate geometry. As consequence, non-uniform shear rate produced by parallel plate was compensated by calculating the relevant shear rate Fiona, (2009),

$$\dot{\gamma}_r = R\frac{d\omega}{dR} \tag{1}$$

where, R is radius of the geometry (m) and ω is the angular velocity (rad/s). A solvent trap was also used to minimize evaporation of the light end components from the sample for all the rheological measurements and subsequently the stability of the sample composition is maintained.

2.1 Shear dependent behavior

Thermal cycle tests were first conducted to determine the gelled temperature, Newtonian and Non-Newtonian regions of the sample as well as the wax appearance temperature (WAT) and the wax disappearance temperature (WDT) as proposed by [9,10]. In this work, the sample was sheared at a constant rate ($\dot{\gamma}_h$) of 10, 50, 100, and 200 s^{-1} to investigate shear dependent behavior of the sample. The measurement was started from an initial temperature (T_i) of 45°C, a temperature well above the anticipated WAT, to a low temperature (T_o) of 15°C, at constant cooling rate ($\dot{T}_h$) of 1°C/min. Once it reached T_o, the sample was heated back to T_i at same rate.

2.2 Thixotropy effect

Thixotropy effect is time dependent behavior of the sample under which the sample tries to regain stability under the given conditions (response time). If the equilibrium time allowed is shorter than the response time of the sample, the measurement results would be highly influenced by the shear and thermal history of the sample.

To achieve the purpose, a time sweep test was conducted on the sample to determine the response time. The test is conducted at a frequency of 10 rad/s and a constant strain of 0.5%, i.e. within the LVE region, at two measurement temperatures of 45°C (Newtonian region) and 15°C (Non-Newtonian region) for 15 minutes. The response time is assumed to be lesser than the specified time of 15 minutes. Another set of stress sweep measurements were done afterwards to investigate the thixotropy effect under different equilibrium steps.

3. Results and discussions

3.1 Shear dependent behavior

A thermal cycle tests at 10, 50, 100, and 200 s^{-1} were conducted to determine the Newtonian and Non-Newtonian regions as well as WAT and WDT and shear dependent behaviours. The results are presented in Figure 1.

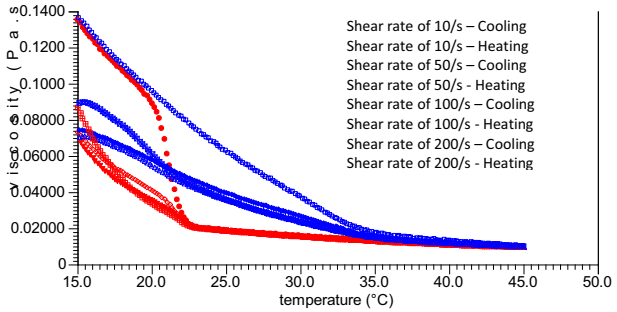

Figure 1. Thermal cycle test at various shear rates

From the experiments, it was clear that the measurement temperature range covers both Newtonian and non-Newtonian regions of the sample. Similar trend was observed for the entire applied shear rate. Typical Arrhenius temperature dependent trend of Newtonian fluid is observed at temperatures above 22°C and 34°C for the cooling and heating curves, respectively while non-Newtonian regions were found to be predominant below the respective temperatures. [10] refer the two temperatures as WAT (from the cooling curve) and WDT (from the heating curve). The WAT and WDT are also independent of the shear rate imposed during cooling and heating of the samples.

It is also evident from the data that, though the WAT and WDT are independent of the shear rates, the viscosity of the sample below WAT and WDT at the lowest shear rate ($10s^{-1}$) is significantly higher compared to that at higher shear rates of 50, 100, and $200s^{-1}$. The experiment was repeated and similar trend is observed indicating shear rate dependent viscosity typical of a non-Newtonian material. Hence, the shear rate should be set according to the actual conditions (production rate) to ensure the applicability of the rheological measurement.

It is important to highlight that the viscosity difference (irreversible process) on Newtonian region (Arrhenius sector) were very small and negligible compare to the work done by [9] indicating that there was no irreversible thermal and shear effects and rheological measurements can be conducted on the same sample in series. It will significantly reduce the measurement time and sample required.

3.2 Thixotropy effect

A time sweep was first applied to the waxy crude sample to determine the response time at which the sample regains its structure. The procedure is crucial in order to determine correct equilibrium time of the sample under the equilibrium step. The result is presented in Figure 2.

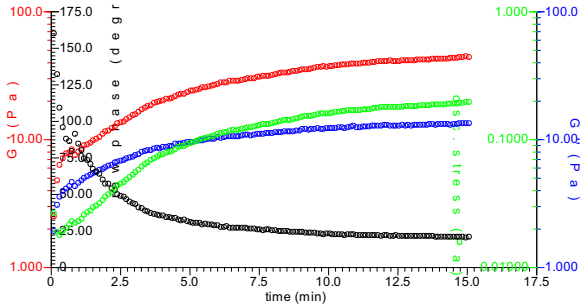

Figure 2 - Response time (thixotropy effect) of the sample under time sweep step

The G', G'',and oscillatory stress are considered as indicators for the stability of the crude sample with an equilibrium plateau indicating that the sample has reached a stable state. It can be observed that at gelled condition (15°C) even with 900s of time duration, the sample was found to still be slightly unstable. For practicality purposes, it is reasonable to consider the response time to be at the point at which the changes in the slopes within the curve are significantly reduced. In this case, 360s can be taken as the equilibrium time for the gelled waxy crude. It should be noted that the sample was subjected to a temperature ramp from 45°C to 15°C under an imposed shear rate of 100s-1 before being subjected to the time sweep measurement. Hence, the equilibrium time under the imposed shear and thermal history is 360s, a time required prior to any other measurements.

Within the Newtonian region at 45°C, the raw phase angle monitored throughout the time sweep were all above 150° indicating that the data is inertially dominated and hence not presented. Another sets of stress sweep measurements were done by using 3 different equilibrium step: time (oscillatory) sweep, peak hold (constant shear), and conditioning step (no shear). The measurements were all carried out for same time duration, 15 minutes. The results are as shown in Figure 3.

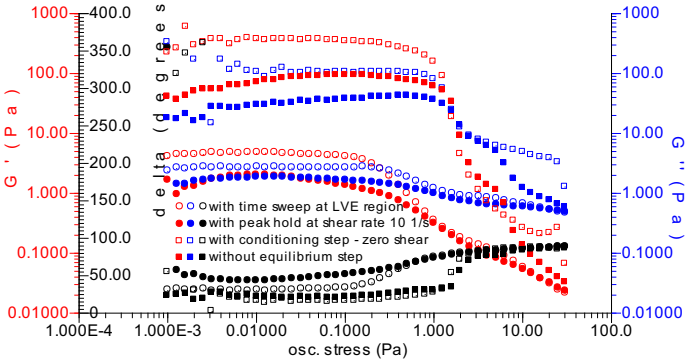

Figure 3 - Thixotropy effect under different equilibrium step

Conditioning step with zero shear obviously showed greatest G'and G" values (strongest structure) while peak hold with constant shear gives lowest G' and G" values (weakest structure). Six minutes constant shear rate under peak hold step destroy the sample since G" > G' value at the beginning of the stress sweep. The sample was then tried rebuilt the structure as the G' increased above G" value. However, the sample did not have ample time to fully recover as the increasing oscillatory stress break the sample again. It is indicated by the second cross point between the G' and G" values.

Under dynamic condition, the time sweep and peak hold step bring equilibrium condition to the sample. However, peak hold step gives lower G' and G" values than the conditioning step. It is due to the continuous shear applied that disturbed the built up structure of the sample. Equilibrium step with no shear gives G' and G" values close to that without equilibrium step. It indicated that no shear equilibrium step bring equilibrium to the sample under static condition as experienced by waxy crude oil under process shut down.

4. Conclusions

It is demonstrated that the WAT and WDT of the crude oil are 22°C and 34°C, respectively and are independent of applied shear rate. The results also showed that the waxy crude oil has no irreversible thermal effect and hence, the sample can be used for several rheological measurements in series. Time sweep measurements confirmed that the crude oil sample needs an equilibrium time as long as 360s in order to regain a stable structure. Zero shear promotes strongest structure and is suitable to represent static condition. Continuous shear break the structure and thus, give the weakest structure. Time sweep with oscillatory stress within LVE region give intermediate strength between zero and continuous shears and is suitable to represent dynamic conditions. The experimental protocol used in this work can be used to determine critical parameter values that are important for reliable rheological measurements. The protocols may be applied to any other crude oil rheological measurements as preliminary measurement.

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