Experimental determination of time dependent yield properties

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ABSTRACT

A rheological method that can be used with modern type rheometers is presented. The method creates data points of yield stress versus elapsed time, and a curve fitting procedure gives values of the three important model parameters; initial yield stress, yield stress after infinite time and the time constant.

Examples from different fluids are presented.

INTRODUCTION

The rheological behaviour of real crude oils and water in crude oil emulsions has been investigated by several authors[1, 2]. The yield of crude oils is important when the required start-up pressure for a gelled oil pipeline shall be determined[3]. In this case there is often a significant wax content in the oil giving rise to the formation of solid plugs.

The yield stress of fluids is often time dependant, where a reduction in yield stress is observed over time if a stress is applied to the fluid. From some initial value at time equal to zero the yield stress reduces gradually to a lower value reached after infinite time. In order to use models describing this complex fluid behaviour it is important to have an experimental method that can determine the yield stress values and the time constant of the yield stress reduction.

It is assumed that the yield stress of a gelled oil plug is a function of time according to the following equation[3-5]:

$$\tau_y(t) = \frac{\tau_0 - \tau_\infty}{1 + kt} + \tau_\infty \qquad (1)$$

This reflects that the yield stress decreases with time from an initial value, τ_0, at time equal to zero to a lower value, τ_∞, at infinite time. The time constant is k.

This type of fluid behaviour has previously been reported[4, 5], and it is therefore of interest to be able to determine the rheological constants from laboratory tests.

METHOD

The yield stress versus time method generates data that give the three constants in Eq. 1. The first part of the method generates rheological data that in the second part are analyzed for determination of the constants.

Part 1: Rheological data

Experimental methods have been established for both atmospheric systems and high pressure systems.

The measuring system should be chosen based on knowledge of sample behaviour obtained from initial rheological tests. A Paar Physica MCR301 rheometer was used in this work.

Testing at atmospheric pressure

Measuring system: DG26.7 (double gap)

1. The samples were conditioned at 50 °C for six hours before the samples were transferred to the rheometer.
2. Heat to 80 °C and keep sample at 80 °C for 15 minutes.
3. Cool to 50 °C in 15 minutes with a shear rate of 100 s^{-1}.
4. Hold temperature for 5 minutes at 50 °C to stabilize at a shear rate of 100 s^{-1}.
5. Cooling at -0.5 °C/minute during oscillation to reach the test temperature (here 5 °C) while performing controlled stress oscillation (1 Hz, 0.1 Pa). If the resulting strain is less than 0.01 %, then the system is programmed to switch to direct strain oscillation (DSO) at 0.01% strain. System is kept at temperature level (here 5 °C) for 30 minutes.
6. Shear stress is set to 1 Pa in rotation mode, and it increases linearly at 0.5 Pa/s to the specified shear stress test level (Fig. 2). Temperature is controlled.
7. Yield occurs when the shear rate exceeds 0.003 s^{-1} (Fig. 3).
8. The above procedure must then be repeated for different values of shear stress level to generate a sufficient number of data points for determination of the constants in Eq. 1.

Testing at elevated pressure

Measuring system: CC23Pr/Q0 (bob)

1. The samples were conditioned at 50 °C for six hours before the samples were transferred to the rheometer.
2. The high pressure cell is pressurized to 50 bars with natural gas, and the sample is saturated at 80 °C for minimum 15 minutes.
3. Cool to 50 °C in 15 minutes with a shear rate of 500 s^{-1}.
4. Hold temperature for 5 minutes at 50 °C to stabilize at a shear rate of 500 s^{-1}.
5. Cooling at -0.5 °C/minute during oscillation (1 Hz, 0.6 Pa) to reach the test temperature (here 28 °C) while performing controlled stress oscillation. If the resulting strain is less than 1 %, then the system is programmed to switch to direct strain oscillation (DSO) at 1% strain. System is kept at temperature level (here 28 °C) for 30 minutes.
6. Shear stress is set to 1 Pa in rotation mode, and it increases linearly at 0.5 Pa/s to the specified shear stress test level (Fig. 2). Temperature is controlled.
7. Yield occurs when the shear rate exceeds 0.003 s^{-1} (Fig. 3).
8. The above procedure must then be repeated for different values of shear stress level to generate a sufficient number of data points for determination of the constants in Eq. 1.

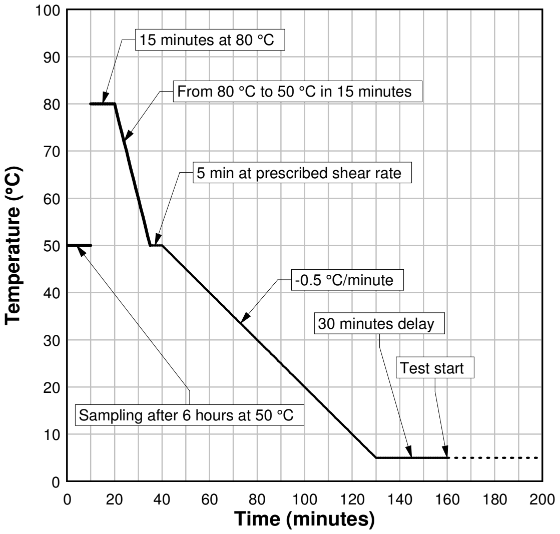

Figure 1. Temperature versus time plot where test temperature is 5 °C.

Yield stress is defined as the required stress to initiate motion. The chosen value of 0.003 s^{-1} is small, but much larger than the instrument measuring accuracy.

Steps 1 - 5 above prepare the samples for the yield stress testing that is performed in steps 6 - 7. A temperature versus time diagram is showed in Fig. 1.

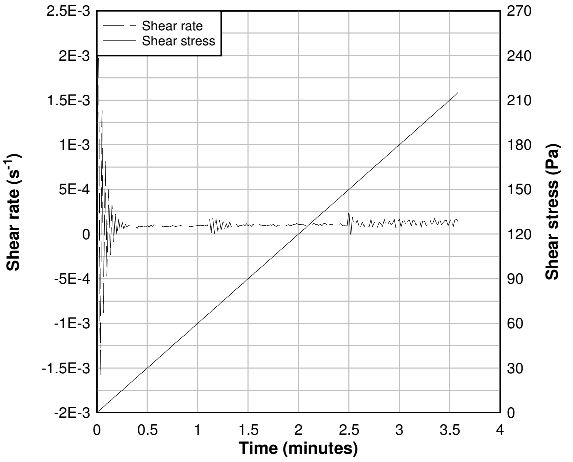

Figure 2. Test start-up; 0.5 Pa/s until stress level has been reached.

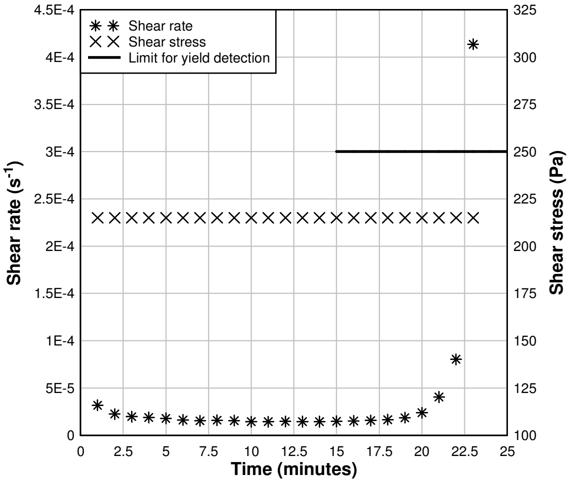

Figure 3. Detection of yield stress when shear rate exceeds 0.0003 s^{-1}.

Part 2: Determination of constants

A curve fitting procedure has been used to determine the yield stress at zero time, the yield stress at infinite time and the time constant.

It is not possible to linearize Eq. 1 and afterward use linear regression techniques to determine the best values of the three constants in the equation. A script was therefore written in MATLAB using the function *fminsearch* to minimize the value of the function *J* given by:

$$J = \frac{1}{N} \sum \left(y - \hat{y} \right)^2 \tag{2}$$

where *N* is the number of data points *(x, y)*, and the predicted value, $\hat{y}$, is given by the equation:

$$\hat{y} = \frac{A-B}{1+Cx} + B \tag{3}$$

Here *x* is experimental time, and *y* is experimental yield stress.

The MATLAB function *fminsearch* searches for the best combination of values of the constants *A*, *B* and *C* for the given data set that minimizes the prediction error function *J*. By comparison with Equation 1 it is seen that $A = \tau_0$, $B = \tau_\infty$ and $C = k$.

SAMPLE DATA

The method has been tested on two oils from the North Sea and on an oil from Africa.

An example plot for test start-up for the African oil is shown in Fig. 2, and detection of yield is shown in Fig. 3. The shear stress level is kept constant at 215 Pa, and the sample yields approaching 22 minutes. The criterion for yield is a shear rate larger than 0.003 s^{-1}.

The African oil was tested at 50 bar and 28 °C. The North Sea oils were tested at 1 bar and 5 °C.

The yield stresses versus time data are shown in Fig. 4 for North Sea oil A, in Fig. 5 for North Sea oil B and in Fig. 6 for the African oil.

The quality of the curve fit is clearly different for the three data sets. The value of *J* for North Sea oil A, North Sea oil B and the African oil are 94.9 Pa^2, 22.0 Pa^2 and 34.7 Pa^2, respectively. *J* becomes large if the data poorly fit Eq. 1. We therefore see that the data from North Sea oil B exhibit the best agreement with Eq. 1.

A summary of the fluid data for the three oils is shown in Table 1 and a comparison between the fluids is shown in Fig. 7.

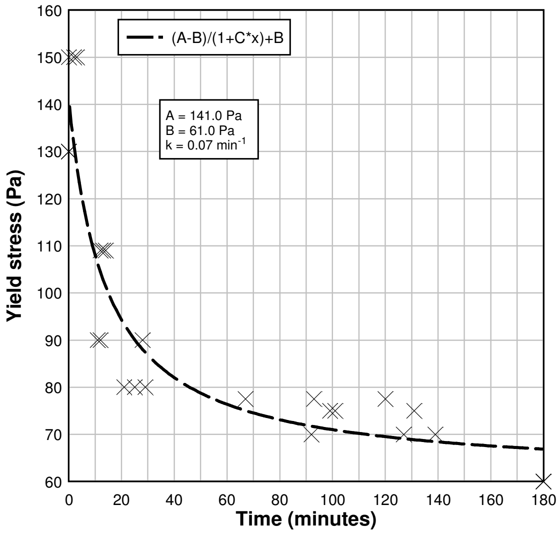

Figure 4. Results North Sea oil A at 1 bar and 5 °C.

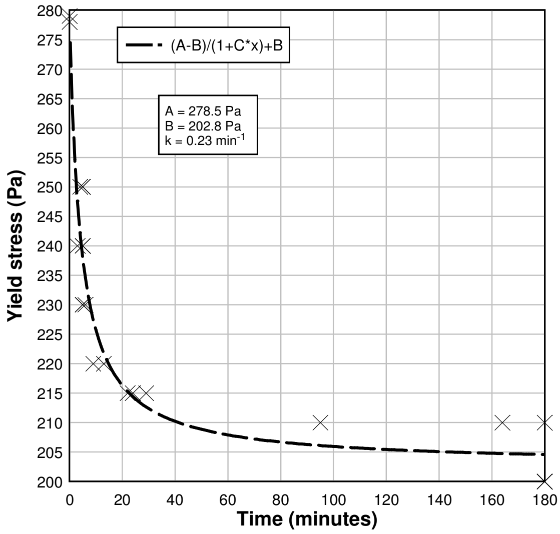

Figure 6. African oil at 50 bar and 28 °C.

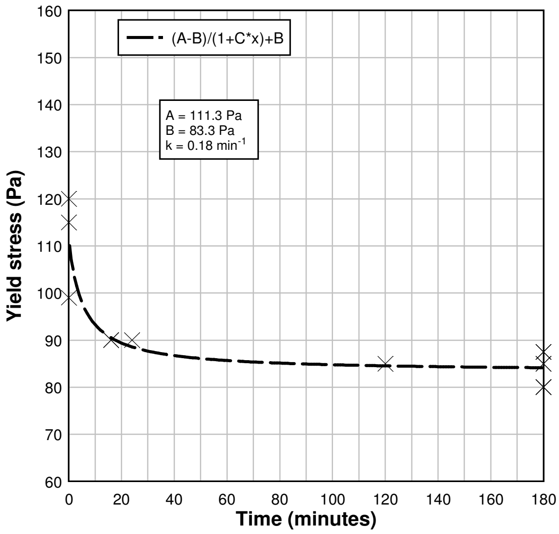

Figure 5. North Sea oil B at 1 bar and 5 °C.

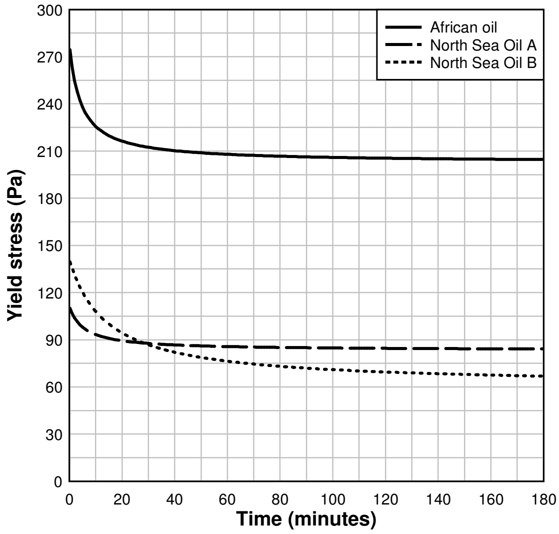

Figure 7. Fluid comparisons.

Table 1. Summary of fluid data.

Fluid	τ_0 (Pa)	τ_∞ (Pa)	k (min^{-1})
North Sea oil A	141.0	61.0	0.07
North Sea oil B	111.3	83.3	0.18
African oil	278.5	202.8	0.23

DISCUSSION

The detailed sample preparation and preconditioning shown in Fig. 1 is a result of much trial and error to obtain test repeatability. Bringing the sample up to 80 °C removes any structure in the sample. The relatively slow cooling allows the internal structure in the sample build, and the resting time of 30 minutes before test start stabilizes the sample. For samples that build a structure slowly, the measured yield stress may depend on this resting time, but this as not been investigated in the present work.

The method has been tested on several fluids that exhibit different behaviour. It is advised that a fluid characterization should be based on a large enough data set in order to obtain a low value of J. In this work the number of data points in each set were 22 for the African oil, 27 for North Sea oil A and 15 for North Sea oil B.

It is required to use a tool like MATLAB to determine the equation constants.

The yield stress versus time data show clearly that the yield stress reduces with time. The same type of behaviour is seen for all the oils tested in this study. The time constant, k, varies between the three oils tested. The two North Sea oils have k-values of 0.07 min^{-1} and 0.18 min^{-1}, respectively, while the African oil has a value of 0.23 min^{-1} (Table 1). This means that North Sea oil A, with lowest k-value, exhibits the slowest yield stress reduction.

There is also a clear difference between the yield stresses at zero time and at infinite time for the oils tested.

CONCLUSIONS

A method for determination of the time dependent yield stress of hydrocarbon liquids has been established, and the method has been tested on two oils from the North Sea and an oil from Africa. All the fluids tested showed a clear reduction of yield stress versus time.

Characterization methods at atmospheric pressure and at elevated pressures have been established.

The method gives values of the yield stress at zero time and at infinite time plus the time constant of the time dependent behaviour. Determination of these parameters is in practise calculated using a MATLAB script.

ACKNOWLEDGMENTS

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